

**REACTIVITY ESTIMATES FOR SELECTED
CONSUMER PRODUCT COMPOUNDS**

Final Report to the

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By

William P. L. Carter

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Center for Environmental Research and Technology
College of Engineering
University of California
Riverside, California 92521

ABSTRACT

An experimental and modeling study was conducted to assess the ground-level atmospheric ozone impacts of several types of consumer product compounds. Environmental chamber experiments were carried out for the representative amines 2-amino-2-methyl-1-propanol (AMP), ethanolamine, isopropyl amine and *t*-butyl amine and also for *d*-limonene. AMP and *t*-butyl amine were found to inhibit ozone formation, but the others enhanced ozone, and most were found to significantly enhance formation of secondary particle matter (PM). Methods to estimate mechanisms for amines that were qualitatively consistent with the chamber data were developed. However, the amine chamber data were not useful for quantitative valuation because the amount of amine available for gas-phase reaction could not be measured, and appeared to be significantly less than the amount injected. Estimates of atmospheric ozone impacts for the amines are also very uncertain because the amount of amines removed by reaction with HNO₃ in the atmosphere cannot be predicted. The chamber data obtained for *d*-limonene were well simulated by the existing *d*-limonene mechanism.

Representations of the atmospheric reactions of for 15 amines and 30 other types of consumer product VOCs were added to the SAPRC-07 mechanism and its MIR and other reactivity scale tabulations, which are included with this report.

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Although this project was funded by the CARB, the contents of this report reflect only the opinions and conclusions of the author. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

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EXECUTIVE SUMMARY

Background

Emissions from consumer products are a non-negligible component of the total emissions of volatile organic compounds (VOCs) into the atmosphere. VOCs emitted into the atmosphere react in sunlight in the presence of oxides of nitrogen (NO_x) emitted from other sources to contribute to the formation of ground-level ozone (O₃), an important air pollution problem in California. Because controls from other VOC sources may not be sufficient to achieve air-quality standards for ozone, the California Air Resources Board (CARB) has been implementing additional controls for VOC emissions from consumer products. In order to achieve the most cost-effective results, the CARB has proposed to utilize controls that take into account differences in ozone impacts, or "reactivity", of the many types of consumer product VOCs that are in use.

Reactivity-based VOC controls have already been implemented in regulations for mobile source (CARB, 1993) and aerosol coatings (CARB, 2000) emissions in California. These are based on use of the Maximum Incremental Reactivity (MIR) scale, which is designed to reflect differences in impacts of VOCs on O₃ formation in environments where O₃ is most sensitive to VOC emissions. However, consumer product emissions include many VOCs for which reactivity values are unknown or highly uncertain, for which the CARB has had to use "upper limit" estimates of ozone impacts of these compounds, based on worst-case considerations of their unknown atmospheric chemistry. This has led to relatively small amounts of some compounds dominating ozone impact estimates of some product categories. This is problematical because the actual ozone impacts of these product categories may be significantly less, and regulations based on upper limit reactivity estimates may lead inappropriate control strategies.

Objectives

The overall objective of this project is to reduce uncertainties of ozone impact quantifications of selected consumer products compounds of interest to the CARB. The project focused primarily on amines, since use of upper limit reactivity estimates for these compounds is problematic for some categories. The amines 2-amino-2-methyl-1-propanol (AMP) and ethanolamine were chosen for experimental study because of their importance in the consumer product inventories, but atmospheric reaction mechanisms and MIR values were also derived for other amines based in part on the results obtained for those representative compounds. Amines were not the only types of compounds in consumer product inventories where reactivity values are needed, so an additional objective of this project was to estimate reactivity values for other compounds for which such values were not previously available. Experiments were also needed to verify existing atmospheric reaction mechanisms and reactivity estimates for *d*-limonene, an important consumer product VOC for which mechanism evaluation data were inadequate.

Methods and Results

Environmental Chamber Experiments

The major effort in this project was to conduct environmental chamber experiments to test estimated mechanisms for the representative amines AMP and ethanolamine, and to test the existing mechanism for *d*-limonene. Experiments using *t*-butyl isopropyl amine were also carried out to further test the general amine mechanisms developed for this project. The chamber experiments were carried out in the UCR EPA environmental chamber that was developed for mechanism evaluation at lower and more atmospherically representative pollutant levels than previously possible, and that was utilized in recent studies of VOCs used in architectural coatings and pesticides. The type of experiments carried out were “incremental reactivity” experiments, which involved determining the effect of adding the solvent to standard reactive organic gas (ROG) surrogate - NO_x experiments designed to simulate the chemical conditions of polluted urban atmospheres. Experiments at two different ROG and NO_x levels were employed to represent different conditions of NO_x availability, to provide a more comprehensive test of the mechanisms that affect reactivity under differing chemical conditions. The total NO_x levels employed were in the 25-30 ppb range, which is designed to be representative of urban areas in California and which are lower than employed in previous reactivity chamber studies.

The chamber experiments were useful for quantitative mechanism evaluation for *d*-limonene and for qualitative evaluation of the mechanisms for the amines. The results indicated that *d*-limonene, ethanolamine and isopropyl amine had relatively high and positive impacts on ozone formation, but also indicated (somewhat unexpectedly) that AMP and *t*-butyl amine were ozone inhibitors. Unfortunately, the data obtained for the amines were not useful for quantitative mechanism evaluation because of uncertainties in the amounts of injected amines that were available for reaction in the gas phase. The amount of amine in the gas-phase could not be measured because of lack of suitable analytical methods for these compounds, and the chamber results could only be fit by assuming that the amount of amine reacting in the gas phase was only 5-60% of the injected amine, with the ratio varying significantly from run to run. On the other hand, the results of the limonene experiments were useful for obtaining high quality data for mechanism evaluation for this compound.

Chemical Mechanism Development and Evaluation

The SAPRC-07 mechanism (Carter, 2007a), which was recently developed under CARB funding and utilized to derive an updated MIR scale for use in California reactivity-based regulations was used as the starting point. New methods were developed to estimate mechanisms for amines, based on available laboratory information and also the results of the experiments for this project. The new estimation methods predicted that amines that lack reactive hydrogen atoms vicinal to the amino groups would be ozone inhibitors, as indicated by the results of the AMP and *t*-butyl amine experiments carried out for this project. On the other hand, amines such as ethanolamine are predicted and confirmed to have positive and relatively high ozone impacts, though not as high as the upper limit estimates that would otherwise be used in CARB regulations. Estimated mechanisms were developed for 11 other amines besides the 4 that were studied, using an approach that was consistent with the chamber data that were obtained. Estimated mechanisms, or methods for estimating atmospheric ozone impacts, were developed for 30 other types of VOCs found in consumer products emission inventories. The existing SAPRC-07 mechanism for *d*-limonene was found to give good simulations of the results of the experiments for this project and was not modified.

An additional consideration in the mechanisms for amines is the fact that they are basic compounds that can react with atmospheric nitric acid (HNO_3) to form amine nitrate salts, which partition into the aerosol phase. The chamber experiments are not sensitive to this reaction because the injected amine was in large excess over the HNO_3 formed in the experiments, but this could be important under atmospheric conditions. However, modeling this under atmospheric conditions is difficult because it requires knowledge of unknown equilibrium constants and also requires better knowledge of sources and sinks of HNO_3 , ammonia, and other amines in the atmosphere, which are unknown and probably highly variable. Model simulations were carried out based on using two extreme assumptions in this regard – one assuming that the amine + HNO_3 reaction had a negligible effect on removing amines from ozone formation reactions, as would occur if the salt equilibrium favored dissociation in the atmosphere, or if there were other significant sinks for HNO_3 in the atmosphere, such as reaction with ammonia or other amines; and the other assuming that the amine + HNO_3 reaction was rapid and irreversible.

Atmospheric Reactivity Calculations

Compounds in consumer products inventories for which ozone impact estimates were added for this project, and their recommended MIR values for regulatory applications, are listed in Table E-1. The values in the "Previous" column were the values given for a few of the amines in previous MIR tabulations provided to the CARB for regulatory applications using the SAPRC-99 (Carter, 2003), and those in the "Upper Limit" column were derived using the upper limit method (Appendix D of Carter, 2000a) that would be the probable default values for regulatory MIR's if better estimates were not available. The values in parentheses are percent changes in the new values relative to the tabulated values shown. It can be seen that in most cases the new values are lower than the previous SAPRC-99 estimates for the few cases where they were available, and in all cases the new values were significantly lower than the upper limit MIR estimates. Uncertainty codes for the current estimated mechanisms are given in the full updated reactivity tabulations included as Appendix C to this report. The uncertainty codes are based on those used in previous versions of the mechanism (Carter, 2000a, 2003, 2007a) and are given in footnote [b] to Table C-1.

It should be noted that the MIR values given for the amines on Table E-1 and Appendix C were calculated assuming that the removal of the amines by reaction with HNO_3 is negligible under atmospheric conditions. If the upper limit estimate for removal by this reaction is assumed, the magnitudes of the ozone impacts are lower by an order of magnitude or more. However, for regulatory purposes, we recommend that values used in the Maximum Incremental Reactivity (MIR) be based on conditions where they would have the maximum ozone impact, and those are the conditions where removal by reaction with HNO_3 is negligible. This is consistent with the general concept of maximum incremental reactivity (Carter, 1994a).

PM Impact Results

Although the primary focus of this project was reducing uncertainties in ozone impact estimates, data were also obtained concerning the relative PM formation potentials for AMP, ethanolamine, and *d*-limonene. All three of these compounds were found to have very high PM formation potentials compared to most of the coatings (Carter et al, 2005b) and pesticide (Carter and Malkina, 2007) VOCs studied previously.

Table E-1. Compounds in consumer products inventories for which ozone impact estimates were added for this project, and recommended MIR values for regulatory applications.

Compound	MIR (gm O ₃ / gm VOC)		
	This Work	Previous	Upper Limit
Methylamine	7.25		10.8 (-33%)
Dimethyl amine	2.65	9.4 (-72%)	14.9 (-82%)
Ethyl amine	5.45	7.8 (-30%)	14.9 (-63%)
Trimethyl amine	5.27	7.1 (-25%)	17.1 (-69%)
Triethyl amine	3.07		16.6 (-81%)
Triethylene diamine	2.77		15.0 (-81%)
Ethanolamine	6.59	6.0 (+11%)	11.0 (-40%)
Dimethylaminoethanol	5.15	4.8 (8%)	15.1 (-66%)
2-Amino-1-butanol	4.79		15.1 (-68%)
2-Amino-2-methyl-1-propanol	-2.68	4.8 (negative)	15.1 (negative)
Diethanol amine	2.22	4.0 (-45%)	12.8 (-83%)
Triethanolamine	3.25	2.8 (+18%)	11.3 (-71%)
Triisopropanolamine	1.99		8.8 (-77%)
Terpinolene	6.14		12.3 (-50%)
Tripropylene glycol	2.07		3.0 (-32%)
Diethylene glycol mono(2-ethylhexyl) ether	1.45		2.7 (-46%)
Tripropylene glycol n-butyl ether	1.55		2.4 (-34%)
Triethyl citrate	0.66		2.9 (-77%)
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	0.33		2.8 (-88%)
Citronellol (3,7-dimethyl-6-octen-1-ol)	5.80		3.8 (53%)
Linalool	5.44		10.8 (-49%)
Geraniol	5.10		9.8 (-48%)
Hexyl cinnamal	2.93		7.8 (-62%)
Hydroxycitronellal	2.54		10.9 (-77%)
Cinnamic aldehyde	4.79		12.7 (-62%)
Amyl cinnamal	3.13		8.3 (-62%)
4-Vinylphenol	1.44		14.0 (-90%)
Methylparaben (4-hydroxy benzoic acid, methyl ester)	1.70		11.0 (-85%)
Propylparaben	1.44		9.3 (-85%)
2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol	1.18		7.6 (-85%)
Beta-phenethyl alcohol	4.49		13.8 (-67%)
Cinnamic alcohol	0.83		12.5 (-93%)
Anethol	0.75		11.3 (-93%)
2-Ethylhexyl benzoate	0.92		7.2 (-87%)
1-Nitropropane	0.20		11.3 (-98%)
Ethyl methyl ketone oxime	1.55		15.4 (-90%)
Lauryl pyrrolidone	0.89		6.6 (-87%)
<i>o</i> -Dichlorobenzene	0.17		11.4 (-99%)
2-Chlorotoluene	2.86		13.3 (-78%)
Methyl nonafluorobutyl ether	0.05		7.2 (-99%)
Methyl nonafluoroisobutyl ether	0.05		7.2 (-99%)
Ethyl nonafluorobutyl ether	0.19		6.4 (-97%)
Ethyl nonafluoroisobutyl ether	0.19		6.4 (-97%)

Discussion and Recommendations

This project made significant progress towards achieving its objectives of decreasing uncertainties and improving estimates of ozone impacts of consumer product compounds of interest to the CARB. Ozone impact estimates and MIR values were derived for a total of 7 amines and 30 other compounds present in consumer products inventories for which estimates were not previously available, ozone impact estimates and MIR values were significantly improved for 8 amines, and data were obtained to support the predictive capabilities of the previously derived mechanism for *d*-limonene. The major contribution of this project concerned the development of improved methods for estimating mechanisms for calculating ozone impact estimates for amines, which were previously represented using highly approximate "placeholder" mechanisms, or for which only upper limit ozone impact estimates were available. As a result of this project, the estimated ozone impacts of amines appropriate for regulatory applications were found to be much lower than the upper limit values would indicate.

However, significant uncertainties still remain concerning the atmospheric reaction mechanisms of the amines. The most important concerns the removal of the amines by reaction with HNO₃, which requires improved values for the equilibrium constants for these reactions, as well as more information about sources and sinks of HNO₃, amines, and ammonia in the atmosphere. However, there are other uncertainties in the amine mechanisms and the available chamber data could not be used to quantitatively evaluate mechanism predictions because of the lack of suitable analytical methods for quantitative analysis of amines in the gas phase. Methods need to be developed to quantitatively inject and monitor these compounds in the gas phase before quantitative data can be obtained to comprehensively evaluate the mechanisms for these compounds.

Mechanisms and reactivity estimates were also derived for a number of other compounds found in consumer product inventories for which estimates were not previously available. However, the CARB staff had also requested reactivity estimates for a total of 63 other compounds for which reactivity estimates are still needed. Of these, 4 are probably of negligible reactivity and 20 are probably non-volatile, leaving 39 compounds for which reactivity estimates are actually needed. In some of these cases the chemical structures could not be determined, but in others the mechanisms are too uncertain to estimate; while for others, estimates could be made if more time and resources were available. Additional work in this area may be appropriate if the missing estimates remain problematic for the CARB.

Although the primary focus of this project was reducing uncertainties in ozone impact estimates, data were also obtained concerning the relative PM formation potentials for the compounds studied. Developing mechanisms for PM impacts was beyond the scope of this project, and it should be emphasized that the results are applicable only for the conditions of these experiments, and relative PM impacts in the atmosphere may be different. However, the data obtained should be useful for testing mechanisms for PM formation of these compounds, and work in this area is needed.

INTRODUCTION

Background

Many different types of volatile organic compounds (VOCs) are emitted into the atmosphere, where they can affect photochemical ozone formation and other measures of air quality. Because VOCs can react in the atmospheres at different rates and with different mechanisms, the different types of VOCs can differ significantly in their effects on air quality. Therefore, VOC control strategies that take these “reactivity” differences into account can potentially achieve ozone reductions and other air quality benefits in a more cost-effective manner than strategies that treat all non-exempt VOCs equally. Reactivity-based control strategies have already been implemented in the California Air Resources Board (CARB) Clean Fuel/Low Emissions Vehicle (CF/LEV) regulations (CARB, 1993), aerosol coatings regulations (CARB, 2000), and are being considered for architectural coatings (CARB 2007) and other stationary source applications. Since California has been successful in implementing reactivity-based regulations as a cost-effective way to reduce ozone, it is reasonable to expect that this approach will be adopted in other jurisdictions as well. For example, the U.S. EPA recently proposed a national rule on aerosol sprays based on reactivity (EPA, 2007).

Implementation of reactivity-based controls requires some means to measure and quantify relative ozone impacts of different VOCs. This is not a simple problem, because the ozone impact of a VOC depends on the environment where the VOC is emitted as well as the nature of the VOC (e.g., see Carter and Atkinson, 1989). The effect of a VOC on ozone formation in a particular environment can be determined from its “incremental reactivity”, which is defined as the amount of additional ozone formed when a small amount of the VOC is added to the environment, divided by the amount added. Although this can be measured in environmental chamber experiments, such experiment cannot be assumed to be the same as incremental reactivities in the atmosphere (Carter and Atkinson, 1989; Carter et al., 1995a). This is because it is not currently practical to duplicate in an experiment all the environmental factors that affect relative reactivities; and, even if it were, the results would only be applicable to a single type of environment. The only practical means to assess atmospheric reactivity, and how it varies among different environments, is to estimate its atmospheric ozone impacts using airshed models. However, such model calculations are no more reliable than the chemical mechanisms upon which they are based. While the initial atmospheric reaction rates for most VOCs are reasonably well known or at least can be estimated, for most VOCs the subsequent reactions of the radicals formed are complex and have uncertainties that can significantly affect predictions of atmospheric impacts. Laboratory studies can reduce these uncertainties, but for most VOCs they will not provide the needed information in the time frame required for current regulatory applications. For this reason, environmental chamber experiments and other experimental measurements of reactivity are necessary to test and verify the predictive capabilities of the chemical mechanisms used to calculate atmospheric reactivities.

The SAPRC-99 chemical mechanism (Carter, 2000a) has been the most widely used mechanism in the United States for calculating relative impacts (reactivities) of VOCs on ozone formation, and is the basis of the MIR ozone reactivity scale used in the current CARB reactivity-based regulations. This mechanism, and its corresponding reactivity scales, have recently been updated to the SAPRC-07 mechanism (Carter, 2007a), and it is expected that the current CARB regulatory reactivity scale will be updated to the SAPRC-07 version in the next update. The SAPRC-99 and SAPRC-07 mechanisms are based on the wide body of available laboratory data, kinetic and mechanistic evaluations, atmospheric chemical theories and estimation methods, and environmental chamber data for the many types of

compounds involved (Carter, 2000a, 2007a and references therein). The most recent SAPRC-07 reactivity tabulation has ozone impact estimates for over 1000 types of compounds. However, the number of compounds that have been experimentally studied is much more limited, and some of these ozone impacts are based on highly uncertain estimated or approximated mechanisms. In addition, there are still many compounds in emissions inventories for which mechanisms have not been derived, and therefore ozone impact estimates are not available.

Consumer products are an important component of the total emissions of VOCs into the atmosphere, which might make a non-negligible contribution to ozone formation. Because of this, the CARB has been implementing additional controls for VOC emissions from consumer products, and is considering use of reactivity-based controls for these source categories. However, the uncertainties in quantification of ozone impacts (reactivity) of many compounds contained in consumer products are a concern. For example, reactivity estimates for several constituents in hairspray and nail care products, particularly amines such as 2-amino-2-methyl-1-propanol (AMP) and ethanolamine, are highly uncertain. Improved reactivity estimates for these and others are needed. For many such compounds the CARB has had to use "upper limit" estimates of ozone impacts of these compounds, based on worst-case considerations of reaction rates and mechanisms (see Appendix D of Carter, 2000a). This has led to relatively small amounts of some compounds dominating ozone impact estimates of some product categories. This is problematical because the actual ozone impacts of these product categories may be significantly less, and regulations based on upper-limit reactivity estimates may lead inappropriate control strategies.

Objectives

The overall objective of this project is to reduce uncertainties of ozone impact quantifications of selected consumer products compounds of interest to the CARB. Specific objectives included carrying out environmental chamber experiments needed to develop or evaluate mechanisms for a few selected representative compounds, derive mechanisms for these and related compounds and other compounds of interest based on the data obtained and other available information and estimates, and use the results to update or enhance the SAPRC-07 mechanism to include representations and ozone impacts for these compounds.

Based on discussions with the CARB staff, it was decided that this project would focus primarily on reducing uncertainties in reactivity estimates for amines, with environmental chamber experiments being carried out using the representative amines AMP and aminoethanol. It was also determined that experiments were needed to reduce uncertainties in ozone impacts for *d*-limonene, an important consumer product VOC for which mechanism evaluation data were inadequate. The CARB staff also requested that the reactivity estimates be made for a number of compounds for which mechanisms reactivity estimates were not available, and to accomplish this it was necessary to derive estimated mechanisms or approximate representations for the atmospheric reactions of these compounds for the purpose of calculating reactivity values.

Overall Approach

This work was carried out at the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside. The chamber experiments were carried out in the UCR EPA chamber, which was developed under EPA funding for more precise mechanism evaluation at lower and more atmospherically representative pollutant levels than previously possible (Carter et al, 1999; Carter, 2002; Carter et al 2005a). Results of earlier experiments carried out in

this chamber, including characterization results that are applicable to this study, are given in previous reports or publications (Carter, 2004; Carter and Malkina, 2005; Carter et al, 2005a,b). The approach employed followed that used in our previous studies of architectural coating (Carter and Malkina, 2005; Carter et al, 2005b) and pesticide (Carter and Malkina, 2007; Carter, 2007b) VOC reactivity.

The primary objective of these experiments with respect to ozone formation is not to directly measure atmospheric ozone reactivity, but to provide data to test the ability of chemical mechanisms used in models to predict their ozone impacts in the atmosphere. If the mechanism can be shown to adequately simulate the relevant impacts of the VOC in well-characterized environmental chamber experiments with a range of chemical conditions representative of the atmosphere, one has increased confidence in the predictive capabilities of the model when applied to atmospheric scenarios. If the mechanism performance in simulating the experiments is less than satisfactory, then the need to improve the mechanism is indicated, and one has decreased confidence in its predictions of atmospheric reactivity.

The most realistic chemical environment in this regard is one where the test compounds or mixtures react in the presence of the other pollutants present in the atmosphere. Therefore, most of the environmental chamber experiments for this and the coatings VOC reactivity programs consisted of measurements of “incremental reactivity” of the subject compounds or solvents under various conditions. These involve two types of irradiations of model photochemical smog mixtures. The first is a “base case” experiment where a mixture of reactive organic gases (ROGs) representing those present in polluted atmospheres (the “ROG surrogate”) is irradiated in the presence of oxides of nitrogen (NO_x) in air. The second is the “test” experiment that consists of duplicating the base case irradiation, except that the VOC whose reactivity is being assessed is added. The differences between the results of these experiments provide a measure of the atmospheric impact of the test compound. These results can be used to test the ability of a chemical mechanism to predict the compound's atmospheric impacts under the chemical conditions of the experiment.

Base case experiments to simulate ambient chemical environments require choice of an appropriate reactive organic gas (ROG) surrogate mixture to represent the reactive organics that are important in affecting ozone formation in the urban atmospheres. For this and the coatings reactivity projects, we continued to use a modified version of the 8-component “full surrogate” that was employed in our previous reactivity studies for this project. This is because, as discussed previously (Carter et al, 1995a), use of this surrogate gives a reasonably good representation of ambient anthropogenic VOC emissions as represented in current models, and use of more detailed mixtures would not give significantly different reactivity results. However, because of experimental problems, for this and many of the experiments in the coatings project, the formaldehyde was removed from the surrogate and the initial concentrations of the other ROG components were increased by 10% to make up for this reactivity change. Model calculations indicate that this surrogate modification should not have significant effects on experimental incremental reactivity results (Carter and Malkina, 2005). Target and average measured compositions of the ROG surrogates for the reactivity experiments for coatings projects are given by Carter and Malkina (2005). The target concentrations used in the experiments for this program were the same.

In order to provide data to test mechanism impacts of the test compounds or mixtures under differing atmospheric conditions, the incremental reactivity experiments are generally carried out using two different standard conditions of NO_x availability relevant to VOC reactivity assessment. Probably the most relevant for California regulatory applications is “maximum incremental reactivity” (MIR) conditions, which are relatively high NO_x conditions where ozone formation is most sensitive to VOC emissions. However, it is also necessary to provide data to test mechanism predictions under lower NO_x

conditions, since different aspects of the mechanisms are important when NO_x is limited. The NO_x levels that define the boundary line between VOC-sensitive, MIR-like conditions and NO_x -limited (and therefore NO_x -sensitive) conditions is that which yields the maximum ozone concentrations for the given level of ROG, or the conditions of the “maximum ozone incremental reactivity” (MOIR) scale. Therefore, experiments with NO_x levels that are approximately half that for MOIR conditions might provide an appropriate test of the mechanism under NO_x -limited conditions. This is referred to as “MOIR/2” conditions in the subsequent discussion. If NO_x levels are reduced significantly below this, the experiment becomes less sensitive to VOC levels and thus less relevant to VOC reactivity assessment.

The conditions of NO_x availability are determined by the ROG/ NO_x ratios in the base case incremental reactivity experiments. In order to completely fix the conditions of these experiments, it is also necessary to specify a desired absolute NO_x level. We sought input from the CARB staff concerning the NO_x levels they would consider to be appropriate to use for reactivity studies in the new chamber (Carter and Malkina, 2005). Based on their input, and model simulations of reactivity characteristics in our chamber, it was determined that the nominal initial concentrations of the MIR base case experiment would consist of ~ 30 ppb NO_x and ~ 0.5 ppmC ROG surrogate, and the MOIR/2 experiment would consist of ~ 25 ppb NO_x and ~ 1 ppmC ROG surrogate (Carter and Malkina, 2005). These were therefore the two standard base cases for all the incremental reactivity experiments discussed in this report.

A number of other control and characterization experiments were also carried out in order to adequately characterize the conditions of the chamber for mechanism evaluation and background particulate matter (PM). These experiments are discussed where applicable in the results and modeling methods sections.

The SAPRC-07 mechanism, as documented by Carter (2007a), was used as the starting point for the mechanism development aspect of the project. The mechanisms for the VOCs studied for this project were added to this mechanism, and these VOCs were added to the list of compounds for which reactivity values are tabulated. The SAPRC-07 documentation and tabulations (Carter, 2007a, available at <http://www.cert.ucr.edu/~carter/SAPRC>) were updated to include the mechanisms and reactivity assignments developed or updated for this project.

EXPERIMENTAL METHODS

Chamber Description

All of the environmental chamber experiments for this project were carried out using the UCR EPA environmental chamber. This chamber was constructed under EPA funding to address the needs for an improved environmental chamber database for mechanism evaluation (Carter et al, 1999, Carter, 2002). The objectives, design, construction, and results of the initial evaluation of this chamber facility are described in more detail elsewhere (Carter et al, 1999, Carter, 2002; Carter, 2004, Carter et al, 2005a). A description of the chamber is also given below.

The UCR EPA chamber consists of two ~85,000-liter Teflon® reactors located inside a 16,000 cubic ft temperature-controlled “clean room” that is continuously flushed with purified air. The clean room design is employed in order to minimize background contaminants into the reactor due to permeation or leaks. Two alternative light sources can be used. The first consists of a 200 KW argon arc lamp with specially designed UV filters that give a UV and visible spectrum similar to sunlight. This light source could not be used for this project because it was not operational during this period. Banks of blacklights are also present to serve as a backup light source for experiments where blacklight irradiation is sufficient, and this was used for the experiments for this project because of availability and because use of blacklights was judged to be sufficient to satisfy the project objectives. The interior of the enclosure is covered with reflective aluminum panels in order to maximize the available light intensity and to attain sufficient light uniformity, which is estimated to be $\pm 10\%$ or better in the portion of the enclosure where the reactors are located (Carter, 2002). A diagram of the enclosure and reactors is shown in Figure 1. The spectrum of the blacklight light source is given by Carter et al (1995b).

The dual reactors are constructed of flexible 2 mil Teflon® film, which is the same material used in the other UCR Teflon chambers used for mechanism evaluation (e.g., Carter et al, 1995b; Carter, 2000a, 2007a, and references therein). A semi-flexible framework design was developed to minimize leakage and simplify the management of large volume reactors. The Teflon film is heat-sealed into separate sheets for the top, bottom, and sides (the latter sealed into a cylindrical shape) that are held together and in place using bottom frames attached to the floor and moveable top frames. The moveable top frame is held to the ceiling by cables that are controlled by motors that raise the top to allow the reactors to expand when filled or lower the top to allow the volume to contract when the reactors are being emptied or flushed. These motors in turn are controlled by pressure sensors that raise or lower the reactors as needed to maintain slight positive pressure. During experiments the top frames are slowly lowered to maintain continuous positive pressure as the reactor volumes decrease due to sampling or leaks. The experiment is terminated if the volume of one of the reactor reaches about 1/3 the maximum value, where the time this took varied depending on the amount of leaks in the reactor, but was greater than the duration of most of the experiments discussed in this report. Since at least some leaks are unavoidable in large Teflon film reactors, the constant positive pressure is important to minimize the introduction of enclosure air into the reactor that may otherwise result.

As indicated in Figure 1, the floor of the reactors has openings for a high volume mixing system for mixing reactants within a reactor and also for exchanging reactants between the reactors to achieve equal concentrations in each. This utilizes four 10” Teflon pipes with Teflon-coated blowers and flanges to either blow air from one side of a reactor to the other, or to move air between each of the two reactors

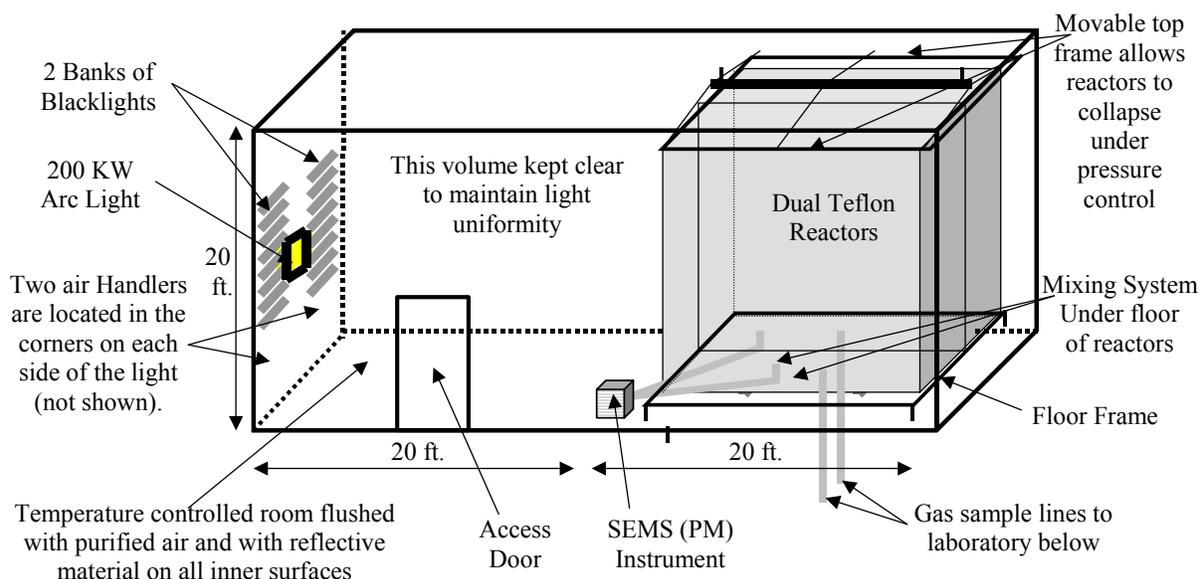


Figure 1. Schematic of the UCR EPA environmental chamber reactors and enclosure.

Teflon-coated air-driven metal valves are used to close off the openings to the mixing system when not in use, and during the irradiation experiments.

An AADCO air purification system that provides dry purified air at flow rates up to 1500 liters min^{-1} is used to supply the air to flush the enclosure and to flush and fill the reactors between experiments. The air is further purified by passing it through cartridges filled with Purafil® and heated Carulite 300® which is a Hopcalite® type catalyst, and also through a filter to remove particulate matter. The measured NO_x , CO, and non-methane organic concentrations in the purified air were found to be less than the detection limits of the instrumentation employed (see Analytical Equipment, below).

The chamber enclosure is located on the second floor of a two-floor laboratory building that was designed and constructed specifically to house this facility (Carter et al, 2002). Most of the analytical instrumentation is located on the ground floor beneath the chamber, with sampling lines leading down as indicated in Figure 1.

Analytical Instrumentation

Table 1 gives a listing of the analytical and characterization instrumentation whose data were utilized for this project. Other instrumentation was available and used for some of these experiments, as discussed by Carter 2002a and Carter et al, 2005a, but the data obtained were not characterized for modeling and thus not used in the mechanism evaluations for this project. The table includes a brief description of the equipment, species monitored, and their approximate sensitivities, where applicable. These are discussed further in the following sections.

Table 1. List of analytical and characterization instrumentation for the UCR EPA chamber.

Type	Model or Description	Species	Sensitivity	Comments
Ozone Analyzer	Dasibi Model 1003-AH. UV absorption analysis. Also, a Monitor Labs Chemiluminescence Ozone Analyzer Model 8410 was used as a backup.	O ₃	2 ppb	Standard monitoring instrument.
NO - NO _y Analyzer	TECO Model 42 C with external converter. Chemiluminescent analysis for NO, NO _y by catalytic conversion.	NO NO _y	1 ppb 1 ppb	Useful for NO and initial NO ₂ monitoring. Converter close-coupled to the reactors so the "NO _y " channel should include HNO ₃ as well as NO ₂ , PANs, organic nitrates, and other species converted to NO by the catalyst.
CO Analyzer	Thermo Environmental Instruments Inc. Model 48 C	CO	50 ppb	Standard monitoring instrument
GC-FID Instruments	Dual HP 6890 Series II GC with dual columns, loop injectors and FID detectors. Controlled by computer interfaced to network.	VOCs	~10 ppbC	30 m x 0.53 mm GS-Alumina column used for the analysis of light hydrocarbons such as ethylene, propylene, <i>n</i> -butane and trans-2-butene and 30 m x 0.53 mm DB-5 column used for the analysis of C ₅₊ alkanes and aromatics, such as toluene and <i>m</i> -xylene. Loop injection is suitable for low to medium volatility VOCs that are not too "sticky" to pass through valves. Two 30 m x 0.32 mm DB-5 column measure C ₅₊ alkanes and aromatics, such as toluene and <i>m</i> -xylene.
PTR-MS	Ionicon Analytik high sensitivity proton transfer reaction mass spectrometer equipped with a quadruple MS. Controlled by computer interface.	VOCs	~5ppt	Used to measure light VOCs such as formaldehyde and some other compounds. Used primarily for formaldehyde for this project.
Gas Calibrator	Model 146C Thermo Environmental Dynamic Gas Calibrator	N/A	N/A	Used for calibration of NO _x and other analyzers. Instrument acquired early in project and under continuous use.
Data Acquisition System	Windows PC with custom LabView software, 16 analog input, 40 I/O, 16 thermo-couple, and 8 RS-232 channels.	N/A	N/A	Used to collect data from most monitoring instruments and control sampling solenoids. In-house LabView software was developed using software developed by Sonoma Technology for ARB for the Central California Air Quality Study as the starting point.

Table 1 (continued)

Type	Model or Description	Species	Sensitivity	Comments
Temperature sensors	Various thermocouples, radiation shielded thermocouple housing	Temperature	~0.1 °C	Primary measurement is thermocouples inside reactor. However, comparison with temperature measurements in the sample line suggests that irradiative heating may bias these data high by ~2.5°C. See text.
Humidity Monitor	General Eastern HYGRO-M1 Dew Point Monitor	Humidity	Dew point range: -40 - 50°C	Instrument performs as expected, but dew point below the performance range for most of the experiments discussed in this report, except for those with added humidity.
QSL Spherical Irradiance Sensor	Biospherical QSL-2100 PAR Irradiance Sensor. Responds to 400-700 nm light.	Spherical Broad-band Light Intensity	Adequate	Provides a measure of absolute intensity and light uniformity that is more directly related to photolysis rates than light intensity on surface. Gives more precise measurement of light intensity trends than NO ₂ actinometry, but is relatively sensitive to small changes in position.
Scanning Mobility Particle Spectrometer (SMPS)	TSI 3080L column, TSI 3077 ⁸⁵ Kr neutralizer, and TSI 3760A CPC. Instrument design, control, and operation similar to that described in Cocker et al. (2001)	Aerosol number and size distributions	Adequate	Provides information on size distribution of aerosols in the 28-730 nm size range, which accounts for most of the aerosol mass formed in our experiments. Data can be used to assess effects of VOCs on secondary PM formation.

Ozone, CO, NO, and NO_y were monitored using commercially available instruments as indicated in Table 1. The instruments were spanned for NO, NO₂, and CO and zeroed prior to most experiments using the gas calibration system indicated in Table 1, and a prepared calibration gas cylinder with known amounts of NO and CO. O₃ and NO₂ spans were conducted by gas phase titration using the calibrator during this period. Span and zero corrections were made to the NO, NO₂, and CO data as appropriate based on the results of these span measurements, and the O₃ spans indicated that the UV absorption instrument was performing within its specifications.

Organic reactants other than the amines were measured by gas chromatography with FID detection as described elsewhere (Carter et al, 1995b); see also Table 1. The surrogate gaseous compounds ethylene, propylene, *n*-butane and trans-2-butene were monitored by using 30 m megabore GS-Alumina column and the loop sampling system. The second signal of the same GC outfitted with FID, loop sampling system and 30 m megabore DB-5 column was used to analyze surrogate liquid components toluene, *n*-octane, and *m*-xylene. The sampling methods employed for injecting the sample with the test compounds on the GC column depended on the volatility or “stickiness” of the compounds.

Both the GC instruments were controlled and their data were analyzed using HPChem software installed on a dedicated PC. The GC's were spanned using the prepared calibration cylinder with known amounts of ethylene, propane, propylene, *n*-butane, *n*-hexane, toluene, *n*-octane and *m*-xylene in ultrapure nitrogen. Analyses of the span mixture were conducted approximately every day an experiment was run, and the results were tracked for consistency.

The surrogate components analyzed by the above system were calibrated by repeated analysis of a standard mixture containing these compounds, and verified by injecting and sampling known amounts of the compound in calibration chamber of known volume. The amounts of gaseous compounds injected were determined by vacuum methods, using an MKS Baratron precision pressure gauge, and bulbs of known volume, determined by weighing when filled with water. The amounts of liquid compounds injected were determined by measuring amounts injected using microliter syringes. The volumes of the calibration chambers were determined by injecting and analyzing compounds whose analyses have been calibrated previously.

d-Limonene was monitored by the GC with the 30 m megabore DB-5 column. The GC was calibrated using the known volume of the reactor and the amount injected for these and previous experimental runs with this compound.

Unfortunately, we were not able to develop a GC or other method to quantitatively analyze the amines in the gas phase. Although they give a response on the GC when sampled using the Tenax cartridge sampling, this was not found to be quantitative or reproducible in practice. Insufficient resources, personnel, or time were available to develop a suitable method for this project, and a suitable analytical method we could use was not found in the literature. Therefore, most amine compound concentrations were determined using the amount injected and the chamber reactors known volume.

Most of the instruments, other than the GCs and aerosol instrument, were interfaced to a PC-based computer data acquisition system under the control of a LabView program written for this purpose. These data, and the GC data from the HP ChemStation computer, were collected over the CE-CERT computer network and merged into Excel files that were used for applying span, zero, and other corrections, and preparation of the data for modeling.

Sampling Methods

Samples for analysis by the continuous monitoring instrument were withdrawn alternately from the two reactors and zero air, under the control of solenoid valves that were in turn controlled by the data acquisition system discussed above. For most experiments the sampling cycle was 5 minutes for each reactor, the zero air, or (for control purpose) the chamber enclosure. The program controlling the sampling sent data to the data acquisition program to indicate which state was being sampled, so the data could be appropriately apportioned when being processed. Data taken less than 3-4 minutes after the sample switched were not used for subsequent data processing. The sampling system employed is described in more detail by Carter (2002).

Samples for GC analysis of surrogate compounds were taken at approximately every 20-minute directly from each of the reactors through the separate sample lines attached to the bottom of the reactors. The GC sample loops were flushed for a desired time with the air from reactors using a pump.

Samples from the PTR-MS were conducted from selected reactors for some of the experiments. The reactors sampled were selected manually, typically sampling for at least an hour before switching sides. The PTR-MS data were used primarily for monitoring formaldehyde in a few of the experiments.

Characterization Methods

Use of chamber data for mechanism evaluation requires that the conditions of the experiments be adequately characterized. This includes measurements of temperature, humidity, and light, and wall

effects characterization. Wall effects characterization is discussed in detail by Carter (2004) and updated by Carter and Malkina (2005) and Carter (2007a), and most of that discussion is applicable to the experiments for this project. The instrumentation used for the other characterization measurements is summarized in Table 1, above, and these measurements are discussed further below.

Temperature was monitored during chamber experiments using calibrated thermocouples attached to thermocouple boards on our computer data acquisition system. The temperature in each of the reactors was continuously measured using relatively fine gauge thermocouples that were located ~1' above the floor of the reactors. These thermocouples were not shielded from the light, though it was expected that irradiative heating would be minimized because of their small size. Experiments where the thermocouple for one of the reactors was relocated to inside the sample line indicated that radiative heating is probably non-negligible, and that a correction needs to be made for this by subtracting ~2.5°C from the readings of the thermocouples in the reactors. This is discussed by Carter (2004).

Light Spectrum and Intensity. The spectrum of the light source in the 300-850 nm region has been measured using a LiCor LI-1800 spectroradiometer, which is periodically calibrated at the factory (e.g., see Carter et al, 2005b). Based on previous extensive measurements the spectrum of the blacklight light was assumed to be constant, and was not measured during the time period of this project. The method used to derive the light intensity using the blacklight light source was based on that discussed by Carter et al (2005b), updated as described by Carter and Malkina (2007). Briefly, the absolute light intensity is measured by carrying out NO₂ actinometry experiments periodically using the quartz tube method of Zafonte et al (1977) modified as discussed by Carter et al (1995b). In most cases the quartz tube was located in front of the reactors. Since this location is closer to the light than the centers of the reactors, the measurement at this location is expected to be biased high, so the primary utility of these data are to assess potential variation of intensity over time. However, several special actinometry experiments were previously conducted where the quartz tube was located inside the reactors, to provide a direct measurement of the NO₂ photolysis rates inside the reactors. The results of these measurements were used to derive a correction factor of 0.698 to derive NO₂ photolysis rates in the reactor from those measured in front of the reactor (Carter et al, 2005b). The trend of in-reactor and corrected in-front-of-reactor actinometry results over blacklight run number (the number of runs conducted using blacklights) were then used to derive an assigned NO₂ photolysis rate as a function of blacklight run number. Results of actinometry measurements carried during the course of this project are given in the "Characterization results" section, below.

Experimental Procedures

The reaction bags were collapsed to the minimum volume by lowering the top frames, and then emptied and refilled at least six times after each experiment, and then were filled with dry purified air on the nights before experiments. Span measurements were generally made on the continuous instruments prior to injecting the reactants for the experiments. The reactants were then injected through Teflon injection lines (that are separate from the sampling lines) leading from the laboratory below to the reactors. The common reactants were injected in both reactors simultaneously, and were mixed by using the reactor-to-reactor exchange blowers and pipes for 10 minutes. The valves to the exchange system were then closed and the other reactants were injected to their respective sides and mixed using the in-reactor mixing blowers and pipes for 1 minute. The contents of the chamber were then monitored for at least 30 minutes prior to irradiation, and samples were taken from each reactor for GC analysis.

Once the initial reactants are injected, stabilized, and sampled, the blacklights are turned on to begin the irradiation. During the irradiation the contents of the reactors are kept at a constant positive pressure by lowering the top frames as needed, under positive pressure control. The reactor volumes therefore decrease during the course of the experiments, in part due to sample withdrawal and in part due

to small leaks in the reactor. A typical irradiation experiment ended after about 6 hours, by which time the reactors are typically down to about half their fully filled volume. Larger leaks are manifested by more rapid decline of reactor volumes, and the run is aborted early if the volume declines to about 1/3 the maximum. This was not the case for most of the experiments discussed in this report. After the irradiation the reactors were emptied and filled six times as indicated above.

The procedures for injecting the various types of reactants were as follows. The NO, and NO₂ were prepared for injection using a vacuum rack. Known pressures of NO, measured with MKS Baratron capacitance manometers, were expanded into Pyrex bulbs with known volumes, which were then filled with nitrogen (for NO) or purified air (for NO₂). In order to maintain constant NO/NO₂ ratios the same two bulbs of specified volume were utilized in most of experiments. The contents of the bulbs were then flushed into the reactor(s) with nitrogen. For experiments with added CO, the CO was purified by passing it through an in-line activated charcoal trap and flushing it into the reactor at a known rate for the amount of time required to obtain the desired concentration. Measured volumes of volatile liquid reactants were injected, using a micro syringe, into a 2 ft long Pyrex injection tube surrounded with heat tape and equipped with one port for the injection of the liquid and other ports to attach bulbs with gas reactants. For injections into both reactors (e.g. the NO_x and base ROG surrogate components in incremental reactivity experiments), one end of the injection tube was attached to the “Y”-shape glass tube (equipped with stopcocks) that was connected to reactors and the other end of injection tube was connected to a nitrogen source. The injections into a single reactor (e.g., for an amine in the reactivity experiments) was similar except the “Y” tube was not used.

The procedures for injection of the hydrocarbon surrogate components were as follows. A cylinder containing *n*-butane, trans-2-butene, propylene and ethylene in nitrogen, was used for injecting the gaseous components of the surrogate. The cylinder was attached to the injection system and a gas stream was introduced into reactors at controlled flow for certain time to obtain desired concentrations. A prepared mixture with the appropriate ratios of toluene, *n*-octane and *m*-xylene was utilized for injection of these surrogate components, using the procedures as discussed above for pure liquid reactants. All the gas and liquid reactants intended to be the same in both reactors were injected at the same time. The injection consisted of opening the stopcocks and flushing the contents of the bulbs and the liquid reactants with nitrogen, with the liquid reactants being heated slightly using heat that surrounded the injection tube. The flushing continued for approximately 10 minutes.

The amines and *d*-limonene were injected, using a microsyringe, into a glass injection tube leading into the reactor to be employed for the compound. The procedure was similar to that used for the liquid hydrocarbon surrogate components. The compounds were flushed into the chamber at least 30 minutes or longer, until there was no material visible in the injection tube. The amines and sample lines leading into the chamber were heated to ~90-100°C.

Materials

The sources of the NO, CO and the various base case surrogate compounds came from various commercial vendors as employed in previous projects at our laboratory. The AMP was obtained from Fluka, the ethanolamine was from Sigma, and the *d*-limonene was from MP Biochemicals. In all cases the stated purities were at least 99%, and no further purification was carried out.

MODELING METHODS

Base Mechanism

The starting point for the chemical mechanism evaluated in this work is the SAPRC-07 mechanism as documented and listed by Carter (2007a). Files and software implementing this chemical mechanism are being prepared and will be available at the SAPRC mechanism web site at <http://www.cert.ucr.edu/~carter/SAPRC>. The changes and additions made to the mechanism as a result of work for this project are discussed later in this section.

As discussed previously (Carter, 2000a,b, 2007a), the SAPRC mechanisms consist of a “base mechanism” that represents the reactions of the inorganic species and common organic products and lumped organic radical model species and “operators”, and separate mechanisms for the initial reactions of the many types other organic compounds that are not in the base mechanism. The compounds, or groups of compounds, that are not included in the base mechanism but for which mechanism assignments have been made, are referred to as detailed model species. These include all the base ROG surrogate constituents and the compounds whose reactions were modeled in this work. These compounds can either be represented explicitly, with separate model species with individual reactions or sets of reactions for each, or using lumped model species similar to those employed in the “fixed parameter” version of SAPRC (Carter, 2000b, 2007a). The latter approach is useful when modeling complex mixtures in ambient simulations or simulations of experiments with complex mixtures, but the other approach, representing each compound explicitly, is more appropriate when evaluating mechanisms for individual compounds or simple mixtures. This is because the purpose of mechanism evaluations against chamber data is to assess the performance of the mechanism itself, not to assess the performance lumping approaches. The latter is most appropriately assessed by comparing simulations of explicit and condensed versions of the same mechanism in ambient simulations.

In view of this, all of the organic constituents of the base ROG surrogate were represented explicitly using separate model species for each compound. In addition, the individual test compounds were also represented explicitly when simulating experiments with those compounds. This gives the least approximate representation of the atmospheric reactions of these compounds within the framework of the SAPRC-07 mechanism. The mechanisms for the individual test compounds are discussed later in this section.

Representation of Chamber Conditions

The procedures used in the model simulations of the environmental chamber experiments for this project were based on those discussed in detail by Carter (2004) and were employed in more recent studies (Carter and Malkina, 2007, and references therein), except as indicated below. Carter (2004) should be consulted for details of the characterization model and chamber effects parameters employed. The temperatures used when modeling were the averages of the temperatures measured in the reactors, corrected as discussed by Carter (2004). The light intensity for the black light experiments varied with time, and the NO₂ photolysis rate for those experiments was derived as discussed in the Characterization Results section, below. The blacklight spectral distribution given by Carter et al (1995b) was found to be appropriate for the blacklights in this chamber and was therefore used when modeling the blacklight runs discussed in this report.

The chamber effects parameters used when modeling the experiments in this chamber were the same as those given by Carter (2004) except for the HONO offgasing parameters, which were derived based on results of characterization runs carried out in conjunction with these experiments. As discussed by Carter (2004), the chamber effects model currently used for this chamber represents both the chamber radical source and background NO_x offgasing by HONO offgasing, whose magnitude is determined by the chamber effects parameter RN-I, which is the ratio of the HONO offgasing rate to the NO₂ photolysis rate. The RN-I parameter that best fits the characterization data tends to vary over time depending on the conditions of the chamber, and the results of the characterization experiments applicable to modeling the experiments discussed in this report, and the assignment of the RN-I values used, are given in the Characterization Results section, below.

The initial reactant concentrations used in the model simulations were based on the measured values except for the amines, for which no quantitative analytical method could be found during the course of this project. In those cases, an upper limit to the initial concentration can be derived from the volume of liquid injected and the volume of the reactors, which were determined in separate experiments where known amounts of materials were injected and analyzed in the gas-phase. Although the reactors are flexible, their initial volumes were very consistent from run to run because of the use of the pressure control system when filling the reactor to its maximum volume prior to the reactant injections (see Chamber Description section, above, and Carter, 2004). However, in the case of the amines, the results of the reactivity experiments indicate that it is probable that not all of the liquid injected was successfully introduced into the gas phase. Therefore, it was necessary to use the initial amine concentrations as an adjustable parameter in the model simulations of the added amine experiments. This is discussed in the Mechanism Evaluation Results section, below.

Mechanisms for Amines

Amines might react in the atmosphere with OH radicals, O₃, NO₃ radicals, and all these possibilities need to be considered when estimating their mechanisms for reactivity assessment. In addition, unlike most other VOCs currently represented in the SAPRC mechanisms, amines are basic and might also be lost to some extent by reaction with HNO₃, forming non-volatile amine salts, potentially reducing their availability for ozone formation. Photolysis is not expected to be important based on available absorption cross-section data for representative amines.

The amines for which mechanisms have been derived for the current project are listed on Table 2, along with rate constants used for their reactions in the model. The mechanisms in terms of SAPRC-07 model species are given in Table A-1 in Appendix A. The derivations of these rate constants and mechanisms are discussed below.

Reaction with OH radicals

Available kinetic information concerning the rate constant for the reactions of amines relevant to those modeled in this study with OH radicals is summarized on Table 2. It is assumed that the reaction proceeds from H-atom abstraction, since there does not appear to be a chemically reasonable alternative mechanism. The rate constants are relatively high compared to H-atom abstractions from alkyl groups. This is also the case for tertiary amines, where abstraction from NH cannot occur, which indicates that the amino group enhances reaction at adjacent groups when abstracting the alpha-hydrogens. On the other hand, the rate constants are also high for reaction of OH with amines, such as AMP, which do not have reactive adjacent groups, which indicates that the reaction at the amino group itself is also relatively rapid. Therefore, both types of reaction need to be taken into account when deriving group additivity estimates.

Table 2. Experimental and estimated rate constants for the reactions of amines included in mechanisms were derived for this project.

Compound	Rate Constant				Diff [d]		
	Measured values [a]		Avg. [b]	Est'd [c]			
	<u>Reaction with OH</u> ($10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)						
Methyl amine	1.73	1	2.20	2	1.97	3.08	36%
Dimethyl amine	6.49	1	6.54	3	6.52	6.51	0%
Ethyl amine	2.38	1	2.77	3	2.58	3.59	28%
Trimethyl amine	3.58	1	6.09	3	4.84	5.01	4%
Isopropylamine						3.78	
t-Butyl amine	1.18	6			1.18	1.79	34%
Triethyl amine						5.57	
Ethanolamine						4.41	
N,N-Dimethylethanolamine (DMAE)	9.00	4	4.70	5	6.85	6.02	-14%
2-Amino-1-butanol						5.32	
2-Amino-2-methyl-1-propanol (AMP)	2.80	5			2.80	2.19	-28%
Diethanol amine						10.1	
Triethanol amine						8.04	
Triisopropanol amine						9.37	
	<u>Reaction with NO₃</u> ($10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)						
Methyl amine						0.96	
Dimethyl amine						2.03	
Ethyl amine						1.16	
Trimethyl amine						1.56	
Isopropylamine						1.21	
t-Butyl amine						0.59	
Triethyl amine						1.71	
Ethanolamine						1.35	
N,N-Dimethylethanolamine (DMAE)						1.80	
2-Amino-1-butanol						1.70	
2-Amino-2-methyl-1-propanol (AMP)						0.59	
Diethanol amine						3.30	
Triethanol amine						2.29	
Triisopropanol amine						2.29	
	<u>Reaction with O₃</u> ($10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)						
Methyl amine	0.007	7			0.007	0.011	52%
Dimethyl amine	1.67	7			1.67	0.64	-61%
Ethyl amine						0.020	
Trimethyl amine	7.84	7			7.84	6.87	-12%
Isopropylamine						0.033	
t-Butyl amine						0	
Triethyl amine						12.10	
Ethanolamine						0.066	
N,N-Dimethylethanolamine (DMAE)	6.76	7			6.76	13.2	95%
2-Amino-1-butanol						0.36	
2-Amino-2-methyl-1-propanol (AMP)						0	
Diethanol amine						3.77	

Table 2 (continued)

Compound	Rate Constant			
	Measured values [a]	Avg. [b]	Est'd [c]	Diff [d]
Triethanol amine			40.2	
Triisopropanol amine			40.2	
<u>Reaction with HNO₃ (10⁻¹¹ cm³ molec⁻¹ s⁻¹)</u>				
All amines – Lower limit assumption			0	
All amines – Upper limit assumption			4	
[a] References for measured rate constants:				
1	Carl and Crowley (1998)	2	Atkinson et al. (1977)	
3	Atkinson et al. (1978)	4	Anderson and Stephens (1988)	
5	Harris and Pitts (1983)	6	Koch et al (1996)	
7	Tuazon et al (1994)			
[b] Average of measured values. Used for deriving best-fit structure-reactivity parameters, and for environmental chamber and/or atmospheric reactivity modeling.				
[c] Estimated rate constant derived from structure-reactivity estimates as discussed in the text. Used for environmental chamber and/or atmospheric reactivity modeling if the entry in the "Used" column is blank				
[d] Difference between average experimental and estimated rate constant, where applicable.				

The kinetic data in Table 2 were used to derive parameters for group additivity estimates for the rate constants for reactions of OH with amines, using the parameters in the SAPRC-99 and -07 mechanism generation systems (Carter, 2000a, 2007a) for reactions at the other positions in the molecules. Table 3 gives the H-abstraction group-additivity parameters used in the SAPRC-07 mechanism generation system, to which reactions at the amino groups have been added. For completeness, the table shows all the H-atom abstraction parameters used in the system, including those for compounds other than amines. Footnotes to the table indicate how these parameters were derived. Table 2 indicates that the group-additivity methods can estimate the rate constants for the amines to within $\pm 26\%$ on the average. Table 2 also gives the estimated OH radical rate constants for the amines represented in the mechanism for which no measured rate constant data are available, which were used in the mechanisms derived for these compounds.

The subsequent reactions of the carbon-centered radicals formed in these reactions can be derived using the mechanism generation system as employed for other compounds, except that estimates need to be made for reactions of α -amino alkoxy radicals, e.g., RCH[O·]-NHR'. Although this is uncertain, to simplify the mechanism generation we assume that decompositions forming N-centered radicals, e.g., RCH[O·]-NHR' \rightarrow RCHO + R'NH·, are not important, and estimate the relative rates of reactions for the competing routes based on estimates for other radicals considered to be similar. The applicable radicals and reactions assumed to dominate when generating mechanisms for amines in the current version of the mechanism are indicated on Table 4. These assumptions are uncertain, though alternative assumptions probably do not yield mechanisms with significantly different reactivities.

The subsequent reactions of the nitrogen-centered radicals formed after H-abstraction from NH₂ or NH groups depends on whether there is an abstractable hydrogen in the α -position to the amine. If there is, then it is assumed that the dominant reaction is abstraction of this hydrogen by O₂, forming HO₂ and the corresponding C=N compound, e.g.,

Table 3. Group additivity parameters used for estimating rate constants for abstraction reactions by OH and NO₃ radicals and by Cl atoms.

Table 3a. Abstraction rate constants assigned to groups

Group	k(300)	OH [a]				NO ₃		Cl	
		A	B	D	Notes [b]	k(300)	Notes	k(300)	Notes
CH ₃	1.39e-13	4.49e-18	2	320	1,2	7.00e-19	9	3.43e-11	13
CH ₂	9.41e-13	4.50e-18	2	-253	1,2	1.50e-17	9	6.77e-11	13
CH	1.94e-12	2.12e-18	2	-696	1,2	8.20e-17	9	4.46e-11	13
OH	1.42e-13	2.10e-18	2	85	1,2	0	10	0	10
CHO	1.56e-11	5.55e-12	0	-311	1,3	2.84e-15 [c]	11	6.64e-11	13
HCO(O)	0				1,4	0	10	0	12
OH(O)	9.99e-13	1.47e-17	2	85	5	0	10	0	10
CH ₃ (Bz) [d]	4.92e-13				6	7.00e-19	12	3.43e-11	12
CH ₂ (Bz) [d]	1.88e-12				7	1.50e-17	12	6.77e-11	12
CH(Bz) [d]	1.33e-12				8	8.20e-17	12	4.46e-11	12
CH ₃ (NH _x) [e]	1.67e-11				22	~6.2e-14	24	[f]	
CH ₂ (NH _x) [e]	1.84e-11				22	~4.4e-14	24	[f]	
CH(NH _x) [e]	2.01e-11				23	~9.9e-14	24	[f]	
NH ₂	1.41e-11				22	~5.2e-14	24	[f]	
NH	3.17e-11				22	~5.7e-14	24	[f]	

[a] Temperature dependences for OH rate constants given by $k(T) = A B^T \exp(-D/T)$, where T is in °K.

[b] Notes for derivations of the group rate constants and substituent correction factors are given below (Note [a] with Table 3b).

[c] The temperature dependence of this group rate constant is given by $1.40e-12 \times \exp(-1860/T)$.

[d] "Bz" refers to any aromatic carbon.

[e] Applicable for x=0,1,2.

[f] Group rate constants for reactions of chlorine with amines were not derived.

Table 3b. Group correction factors for abstraction reactions

Group	Substituent Correction Factor					
	OH		NO ₃		Cl	
	Factor	Note [a]	Factor	Note	Factor	Note
CH ₃	1	1,2,14	1	17	0	14
CH _x (x<3)	1.23	1,2	1.34	11	0.95	13
CH _x (CO)	3.90	1,2	1.34	17	0.95	17
CH _x (CO-O)	1.23	1,2	1.34	17	0.95	17
CH _x (Cl)	0.36	1,2	1.34	17	0.19	19
CH _x (Br)	0.46	1,2	1.34	17	0.95	17
CH _x (F)	0.61	1,2	1.34	17	0.95	17
OH	3.50	1,2	0	18	1.07	13
CHO	0.75	1,2	0.18	11	0.40	13
CO	0.75	1,2	0.89	11	0.04	13
CO(O)	0.31	15	0	12	0.04	17
CO(OH)	0.74	1,2	0	12	0.04	17

Table 3b (continued)

Group	Substituent Correction Factor					
	OH		NO ₃		Cl	
	Factor	Note [a]	Factor	Note	Factor	Note
O	8.40	1,2	0	18	1.07	20
O(CO)	1.60	1,2	0	18	1.07	17
O(HCO)	0.90	1,15	0	18	1.07	17
O(NO ₂)	0.04	1,2	0	18	1.07	17
O(OH)	3.90	5	1	18	1.07	17
NO ₂	0.00	1,2	0	12	n/a	
F	0.09	1,2	0	12	0.01	21
Cl	0.38	1,2	0	12	0.01	13
Br	0.28	1,2	0	12	n/a	
I	0.53	1,2	0	12	n/a	
C=C	1.00	1,2	1	17	0.95	13
ONO ₂	0.04	1,2	0	12	0.12	
Bz	1	14	1	17	2.03	13
NH ₂ , NH, N	1	14	1	14	[b]	

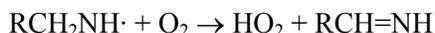
[a] Notes for derivations of the group rate constants and group correction factors are as follows. (Note that the cited references are given by Carter (2007a) and are not in the reference list for this report unless they are relevant for the amines).

- 1 Same as used in SAPRC-99
- 2 Kwok and Atkinson (1995)
- 3 Based on IUPAC (1997) recommendations for acetaldehyde and propionaldehyde
- 4 Reaction at formate group assumed to be negligible based on tabulated formate rate constants.
- 5 Derived to fit IUPAC (2006) recommended rate constant and branching ratio for reaction of OH with methyl hydroperoxide.
- 6 Average of estimated rate constants per methyl group for the alkylbenzenes for which aromatic aldehyde yields have been derived. Reaction at the methyl group is estimated based on the aromatic aldehyde yield and the total rate constant.
- 7 Derived from the difference for the total rate constants for ethylbenzene and toluene, assuming the same rate constant for addition to the aromatic ring and the estimated rate constant at the methyl group in ethylbenzene.
- 8 Derived from the difference for the total rate constants for isopropylbenzene and toluene, and *p*-cymene and *p*-xylene, assuming the same rate constant for addition to the aromatic ring and the estimated rate constants for reactions at the methyl groups in isopropylbenzene and *p*-cymene.
- 9 From Atkinson (1991). Derived from the correlation between NO₃ and OH radical rate constants.
- 10 Assumed to be negligible.
- 11 Derived from the IUPAC (1997) recommended rate constant for acetaldehyde.
- 12 No explicit assignment made. By default, the system uses the same assignment as for standard CH₃, CH₂, or CH groups.
- 13 Derived by Carter (2007a) from measured chlorine + VOC rate constants.
- 14 Assigned.
- 15 From Kwok et al (1996).
- 16 Adjusted to fit OH + ethyl and propyl formate rate constants (Wallington et al, 1988)

Table 3b (continued)

- 17 No assignment made. This is the default value used by the mechanism generation system, and may not be appropriate.
- 18 This is the assignment incorporated into the current system. It may not be appropriate. It is not used as the basis for estimating NO₃ rate constants for any detailed model species.
- 19 Based on chloroacetaldehyde only
- 20 Estimated to be approximately the same as the factor for OH.
- 21 Estimated to be approximately the same as the factor for Cl.
- 22 Derived to give the best fits to the available kinetic data for simple amines and alcohol amines for which kinetic data are available, as indicated in Table 2. In order to fit the data for tertiary amines, it is necessary to assume that OH reacts with an enhanced rate at groups next to the amino group, and in order to fit the data for amines, such as AMP and t-butyl amine, that do not have abstractable hydrogens next to the amino group it is necessary to assume that reaction also occurs at a significant rate at the NH or NH₂ groups.
- 23 No data are available for which to derive group-additivity estimates for this type of group. The group rate constant is estimated by linear interpolation from those used for CH₃(NH_x) and CH₂(NH_x).
- 24 The only kinetic data concerning the reactions of NO₃ radicals with amines is for N-methyl-2-pyrrolidinone (NMP), where a relatively high rate constant of 1.26 x 10⁻¹³ cm³ molec⁻¹ s⁻¹ is measured (Aschmann and Atkinson, 1999). This suggests that this reaction is also rapid for other amines. We assume that this is an H-atom abstraction reaction, forming HNO₃. For lack of other data, use the rate constant for NMP as the basis for estimating the group rate constants for reaction at the -CH₂(N) or CH₃(N) groups. The group rate constants for reactions at other amine groups, including NH and NH₂, are estimated assuming that the ratios of rate constants for reactions at the various groups are the same for the NO₃ reaction as derived for the OH reaction. This is highly uncertain.

[b] Group rate constants for reactions of chlorine with amines were not derived



This is based on kinetic data obtained by Lindley et al (1979) for reactions of (CH₃)₂N· with O₂, NO, and NO₂, where the reaction with O₂, forming HO₂ + CH₃-N=CH₂, is calculated to dominate under atmospheric conditions.

The subsequent reactions of the C=N products formed in these reactions are unknown and therefore this is an additional source of uncertainty in the mechanism. These are expected to be reasonably reactive compounds. For the current mechanism, they are approximately represented by the generic reactive non-aldehyde oxygenated species PROD2. The appropriateness of this representation is highly uncertain.

The above type of reaction cannot occur if the nitrogen-centered radical lacks an abstractable hydrogen in the α-position, as is the case in radicals predicted to be formed in the reactions of t-butyl amine and 2-Amino-2-Methyl-1-Propanol (AMP). In these cases, the only expected reactions of the nitrogen-centered radical is reaction with NO, NO₂, or HO₂, e.g.,

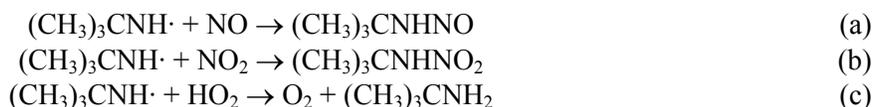


Table 4. Assignments made for alkoxy radical intermediates predicted to be formed in the photooxidation mechanisms of the amines.

Radical	Reaction Assumed to Dominate
$\cdot\text{OCH}_2\text{-NH}_2 + \text{O}_2$	$\text{HCO-NH}_2 + \text{HO}_2\cdot$
$\text{CH}_3\text{-NH-CH}_2\text{O}\cdot + \text{O}_2$	$\text{CH}_3\text{-NH-CHO} + \text{HO}_2\cdot$
$\cdot\text{OCH}_2\text{CH}_2\text{-NH}_2$	$\text{HCHO} + \cdot\text{CH}_2\text{-NH}_2$
$\text{CH}_3\text{CH(O}\cdot\text{)NH}_2 + \text{O}_2$	$\text{CH}_3\text{C(O)NH}_2 + \text{HO}_2\cdot$
$\text{CH}_3\text{-N(CH}_3\text{)CH}_2\text{O}\cdot + \text{O}_2$	$\text{CH}_3\text{-N(CH}_3\text{)CHO} + \text{HO}_2\cdot$
$\text{NH}_2\text{CH(O}\cdot\text{)CH}_2\text{OH}$	$\text{HCO-NH}_2 + \cdot\text{CH}_2\text{OH}$
$\text{CH}_3\text{C(O}\cdot\text{)(CH}_3\text{)NH}_2$	$\text{CH}_3\text{C(O)NH}_2 + \text{CH}_3\cdot$
$\text{CH}_3\text{C(CH}_3\text{)(CH}_2\text{O}\cdot\text{)NH}_2$	$\text{HCHO} + \text{CH}_3\text{C}\cdot\text{(CH}_3\text{)NH}_2$
$\text{CH}_3\text{-N(CH}_2\text{O}\cdot\text{)CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{-N(CH}_2\text{OH)CH}_2\text{CH}\cdot\text{(OH)}$
$\text{CH}_3\text{C(CH}_2\text{O}\cdot\text{)(NH}_2\text{)CH}_2\text{OH} + \text{O}_2$	$\text{CH}_3\text{C(CHO)(NH}_2\text{)CH}_2\text{OH} + \text{HO}_2\cdot$
$\cdot\text{OCH}_2\text{CH}_2\text{CH(NH}_2\text{)CH}_2\text{OH}$	$\text{NH}_2\text{CH(CH}_2\text{CH}_2\text{OH)CH}\cdot\text{(OH)}$
$\text{CH}_3\text{-N(CH}_3\text{)CH(O}\cdot\text{)CH}_2\text{OH}$	$\text{CH}_3\text{-N(CH}_3\text{)CHO} + \cdot\text{CH}_2\text{OH}$
$\text{CH}_3\text{CH(O}\cdot\text{)CH(NH}_2\text{)CH}_2\text{OH}$	$\text{CH}_3\text{CHO} + \text{NH}_2\text{CH}\cdot\text{(CH}_2\text{OH)}$
$\text{CH}_3\text{CH}_2\text{C(O}\cdot\text{)(NH}_2\text{)CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{C(O)NH}_2 + \cdot\text{CH}_2\text{OH}$
$\text{HOCH}_2\text{CH}_2\text{-NH-CH(O}\cdot\text{)CH}_2\text{OH}$	$\text{HCO-NH-CH}_2\text{CH}_2\text{OH} + \cdot\text{CH}_2\text{OH}$
$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}_3\text{)CH}_2\text{CH}_2\text{O}\cdot$	$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}_2\text{OH)CH}\cdot\text{(CH}_3\text{)}$
$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}_3\text{)CH(O}\cdot\text{)CH}_3$	$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}_2\cdot\text{)CH(CH}_3\text{)OH}$
$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}_2\text{O}\cdot\text{)CH(CH}_3\text{)OH}$	$\text{CH}_3\text{CH}\cdot\text{(N(CH}_2\text{CH}_2\text{OH)CH(CH}_3\text{)OH)}$
$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}_2\text{OH)CH(O}\cdot\text{)CH}_3$	$\text{CH}_3\text{CH}_2\text{-N(CH}_2\text{CH}\cdot\text{(OH)CH(CH}_3\text{)OH)}$
$\text{CH}_3\text{CH(O}\cdot\text{)N(CH}_2\text{CH}_2\text{OH)CH(CH}_3\text{)OH}$	$\text{CH}_3\text{CH(OH)N(CH}_2\text{CH}\cdot\text{(OH)CH(CH}_3\text{)OH)}$
$\text{HOCH}_2\text{CH}_2\text{-N(CH}_2\text{CH}_2\text{OH)CH(O}\cdot\text{)CH}_2\text{OH}$	$\text{HCO-N(CH}_2\text{CH}_2\text{OH)CH}_2\text{CH}_2\text{OH} + \cdot\text{CH}_2\text{OH}$
$\text{CH}_3\text{CH(OH)CH}_2\text{-N(CH}_2\text{CH(CH}_3\text{)OH)CH}_2\text{-CH(CH}_2\text{O}\cdot\text{)OH}$	$\text{HCHO} + \text{CH}_3\text{CH(OH)CH}_2\text{-N(CH}_2\text{CH}\cdot\text{(OH)CH}_2\text{CH(CH}_3\text{)OH}$
$\text{CH}_3\text{CH(OH)CH}_2\text{-N(CH}_2\text{CH(CH}_3\text{)OH)-CH(O}\cdot\text{)CH(CH}_3\text{)OH}$	$\text{CH}_3\text{CH(OH)CH}_2\text{-N(CHO)CH}_2\text{CH(CH}_3\text{)OH} + \text{CH}_3\text{CH}\cdot\text{(OH)}$

If NO_x is present, the major reaction is expected to be process (b), forming the nitramine, since the nitrosoamines formed in process (a) are expected to undergo rapid photolysis back to NO and the radical, resulting in no net reaction. Since nitramine formation is a radical terminating process, this mechanism predicts that *t*-butyl amine and AMP would be radical inhibitors, since reaction forming the N-centered radical is estimated to be the major initial reaction. This is consistent with the fact that these compounds are indeed found to be strong ozone and radical inhibitors in environmental chamber experiments, as discussed in the Mechanism Evaluation Results section, below.

For implementation in the mechanism, the model species "NRAD" is used to represent the reactions of the N-centered radicals that lack abstractable hydrogens in the α position. This species is representing as reacting with NO_2 to form a nitramine, with a rate constant estimated by assuming that it is the same as for the reaction of NO_2 with the generic higher acyl peroxy radical species RCO_3 . The nitramine is approximately represented by PROD2 in the current mechanism, though the appropriateness of this representation is also highly uncertain. The reaction with NO , forming the nitrosoamine, is neglected because of the expected rapid photolysis of the nitrosoamine to reverse the reaction. In the absence of NO_x , the NRAD is represented as reacting with HO_2 to re-form the amine, with a rate constant

assumed to be the same as used for the reaction of RCO_3 with HO_2 . Because of the way the mechanism is implemented it is not practical to represent the amine formed in the reaction as the amine itself, so its subsequent reactions are therefore neglected. This is because the two amines represented to form NRAD are inhibitors, so representing them with reactive product model species such as PROD2 is inappropriate.

Table A-1 in Appendix A gives the mechanisms that were derived for the reactions of the OH radicals with amines based on these assumptions and representations.

Reaction with NO_3 Radicals

The only kinetic data concerning the reactions of NO_3 radicals with amines is for N-methyl-2-pyrrolidinone (NMP), where a relatively high rate constant of $1.26 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ was measured (Aschmann and Atkinson, 1999). This suggests that this reaction is also rapid for other amines. We assume that this is an H-atom abstraction reaction, forming HNO_3 . For lack of other data, we use the rate constant for NMP as the basis for estimating the group rate constants for reaction at the $-\text{CH}_2(\text{N})$ or $\text{CH}_3(\text{N})$ groups. The group rate constants for reactions at other amine groups, including NH and NH_2 , are estimated assuming that the ratios of rate constants for reactions at the various groups are the same for the NO_3 reaction as derived for the OH reaction. This is highly uncertain.

These assumptions were used as the basis for deriving group-additivity estimates for H-atom abstraction reactions of NO_3 radicals with amines, as indicated on Table 3, above. For completeness, that table also gives group-additivity parameters for other H-atom abstractions by NO_3 from other groups as implemented in the current mechanism generation system. These were used for deriving rate constants and initial branching ratios for the reactions of NO_3 with all the amines used in the current study. These estimated rate constants are included in Table 2, above.

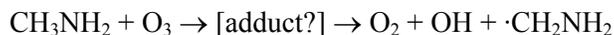
The radicals formed in the H-atom abstraction reactions that are assumed to be formed in the initial $\text{NO}_3 + \text{amine}$ reactions are the same as those formed in the OH system. The representations of those reactions, and of the products formed, have been already discussed above. The mechanisms so derived are given in Table A-1 in Appendix A.

Reactions with Ozone

The limited available kinetic data concerning the reaction of O_3 with amines are given in Table 2, above. The rate constant for methylamine is too low to be important under atmospheric conditions, but the rate constants for the other compounds are sufficiently high that O_3 reaction may be non-negligible, though probably not dominant, under atmospheric conditions. Therefore, the possible reactions of O_3 with amines need to be taken into account when deriving atmospheric mechanisms for these compounds.

Although some product data were obtained in the study of Tuazon et al (1994), the mechanism is uncertain, though the products they observed were similar to those observed or expected from the OH reaction. Murphy et al (2007) studied aerosol-phase products of the reactions of trimethyl amine with O_3 and observed similar aerosol phase products in the O_3 reaction as formed in the NO_x -air photooxidations of the amine, which are expected to be dominated by the OH reaction. If O-addition reactions occur, the adduct formed must eventually decompose to form products similar to those formed in H-abstraction reactions, otherwise different types of products would be observed in O_3 reactions as formed in OH reactions or photooxidations. The relatively high rate constants for the reaction of O_3 with trimethyl amine and DMAE, and the low rate constant for methylamine, suggests that abstraction from N-H bonds is probably not the major process.

Based on these considerations, for rate constant and mechanism estimation purposes we assume that the initial reaction of O₃ with amines is at the group next to the amino group, ultimately resulting in abstraction from α C-H bonds, forming OH radicals and the same types of radicals as formed in the OH reaction, e.g.,



This is consistent with the fact that similar products appear to be formed in the O₃ as the OH reaction, and is also reasonably consistent with the fact that the O₃ + amine rate constant data are well correlated with the estimated rate constant for reaction of OH radicals at the group next to the amino group, with the correlation being better than the correlation of the O₃ rate constant to the total rate constant. This is shown on Figure 2, where it can be seen that the O₃ rate constants are better correlated to the rate constant for OH abstraction from the adjacent group than to the total OH radical rate constant.

The correlation between the estimated rate constants for reaction of OH with the group next to the amino groups and the total O₃ rate constants were used as the basis for estimating the rate constants for reactions of O₃ at these groups, forming OH, O₂, and the corresponding H-abstraction radical. The data for the methylamines and DMAE were fit by

$$K(\text{group}, \text{O}_3) = 10^{-42.97 - \{5.84 k(\text{group}, \text{OH})\}}$$

where k(group) refers to net H-atom abstraction at a group adjacent to the amino group and the rate constants are in cm³ molec⁻¹ s⁻¹. This was used as the basis for estimating both total O₃ rate constants and relative rates of reaction at different positions (secondary or tertiary amines) that have non-equivalent substituents. The O₃ rate constants so derived are given in Table 2, above, where it can be seen that the measured values are predicted within a factor better than 2.

The radicals formed in these O₃ reactions are assumed to be the same as formed when OH abstracts from the C-H bond in the group adjacent to the amino group, and the representations of their

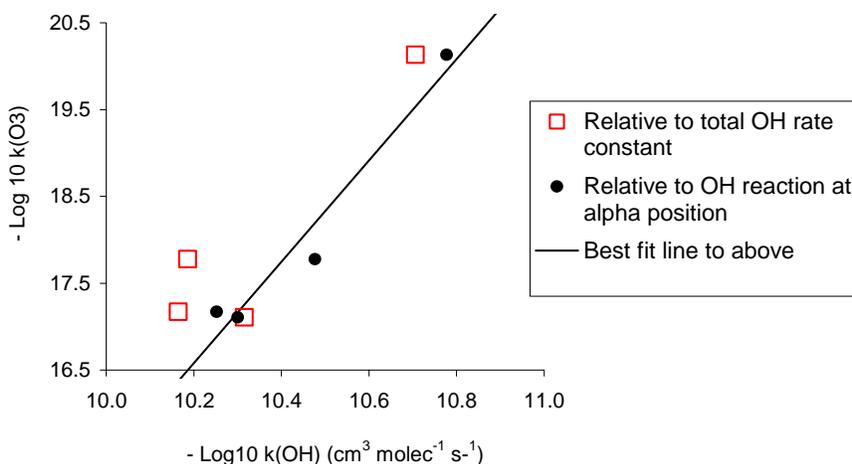


Figure 2. Plots of logs of the rate constants for the reactions of the methylamines and DMAE with O₃ against the logs of the rate constants for reaction of OH radicals at the group next to the amino group and also against the total OH rate constant.

subsequent reactions, and of the products formed, are the same as used for the OH radical reactions, discussed above. The mechanisms so derived are given in Table A-1 in Appendix A.

Reactions with HNO₃

Amines are basic compounds that can react with HNO₃ to form amine salts, which are nonvolatile and partition into the aerosol phase, making the amine unavailable for reaction in the gas phase. However, this reaction is reversible and an equilibrium exists between the salt, and the amine and HNO₃. This means that under sufficiently low amine or HNO₃ concentrations, or if other basic species such as NH₃ are present to compete with the HNO₃, or there are other important loss processes for the amine or HNO₃, then the salt formation may be less important in affecting the availability of the amine to react in the gas phase. The equilibrium constants for amine salt formation are too uncertain to be useful for estimating availability based on theoretical equilibrium considerations (Murphy et al, 2007). Aerosol amine salt formation from reactions of amines with HNO₃ in environmental chamber experiments under simulated atmospheric conditions has been studied by Murphy et al (2007), who found that aerosol amine salt formation occurs rapidly when the gas-phase amine and HNO₃ are present at concentrations of ~100 ppb. However, they also found that the amine salt aerosol formation eventually declined relatively under conditions where the amine can undergo gas-phase reactions, such as when O₃ is added or photooxidation in the presence of NO_x. This suggests that revolatilization may be important under atmospheric conditions, and because of the relatively high gas phase reactivity of the amines, the amine salt formation may not be a permanent sink for the amine under conditions where O₃ formation can occur. In addition, if excess NH₃ is present in the environment, it may compete with the amine for nitrate salt formation, making loss of the amine to salt formation less important.

Model simulations of the environmental chamber experiments carried out for this project were found not to be sensitive to assumptions made concerning the loss of amines by reaction with gas-phase HNO₃. Model calculations assuming rapid (and irreversible) loss of the amine due to reaction with HNO₃ gave essentially the same results in terms of calculations of O₃ and other measured gas-phase species as those assuming no reaction between the amine and HNO₃. This is because the amount of HNO₃ calculated to be formed in the gas-phase reactions of NO_x is small compared to the amount of amine injected. Therefore, the chamber experiments are not useful for assessing whether loss of amines due to this reaction may be important under atmospheric conditions.

On the other hand, as discussed in the Atmospheric Reactivity Results section, below, in the model simulations of the ozone impacts of the amines in the box model, atmospheric scenarios used for calculation of the ozone reactivity scales (Carter, 1994a, 2000a, 2007a) are highly sensitive to assumptions made concerning the loss of the amine due to reaction with HNO₃. The impact in the real atmosphere depends on the magnitudes of HNO₃ sources and sinks, the amounts of other amines or ammonia present to compete with the HNO₃, and the amine salt equilibrium constants, which are unknown. At present, there is insufficient information available to quantify these impacts, or even to assess which of these extremes is most likely to be representative of ozone exceedances in California.

Because of these uncertainties, atmospheric reactivity assessment calculations are carried out assuming either no amine + HNO₃ reaction, or assuming that the reaction is rapid and irreversible. The latter simulations use an amine + HNO₃ rate constant of $4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, which is a high rate constant representative of radical + radical reactions. The product formed is assumed to be unreactive in these upper limit calculations. The actual rate constants are unknown but probably less than this value, which is considered appropriate for upper limit analyses only.

As indicated above, the environmental chamber simulations are not sensitive to assumptions concerning the rate or reversibility of the amine + HNO₃ reaction. However, because the results of the

model simulations of the added amine experiments indicate that not all the injected amine is available for reaction in the gas phase, most of the chamber simulations are based on the assumption that the amine + HNO₃ reaction is rapid and irreversible.

Mechanism for *d*-Limonene

The mechanism used for *d*-limonene in this work is the same as that given with the SAPRC-07 mechanism as documented by Carter (2007a). This was derived using the SAPRC-07 mechanism estimation and generation system, incorporating the measured rate constants for its various atmospheric reactions. The reactions and rate constants are given in Table A-1 in Appendix A, with footnotes to the table indicating the sources of the rate constants used. Because the SAPRC-07 limonene mechanism performed reasonably well in simulating the new limonene experiments carried out for this project, this mechanism was not changed as a result of this work.

Mechanisms for Other VOCs.

The consumer products compounds for which mechanisms and/or ozone reactivity estimates have been added as part of this project are summarized on Table 5. In addition to the amines, discussed above, these include a number of other compounds found in consumer products speciation surveys for which reactivity estimates are needed by the CARB staff. The table indicates how the mechanisms were derived or, for compounds represented using the "lumped molecule approach", the compound or model species assumed to have the same ozone impact on a per-molecule basis. The reactions and rate constants for the compounds that were represented explicitly are given in Table A-1 in Appendix A, and footnotes to the table give more information how the mechanisms and/or rate constants were estimated. Table A-2 summarizes the lumped molecule representations used, for compounds where this is applicable.

The CARB staff also requested ozone impacts for other compounds found in consumer product speciation surveys for which ozone impacts have not yet been derived. These are also listed in Table 5, along with the reasons why we were unable to derive mechanisms or assignments for those compounds.

Atmospheric Reactivity Simulations

Atmospheric reactivity model simulations were carried out to derive MIR and other atmospheric reactivity values for the selected compounds whose ozone impacts were evaluated for this project. The scenarios and methods used were the same as those used when calculating the MIR and other atmospheric ozone reactivity scales, and were described previously (Carter, 1994a,b 2000a, 2007). The base ROG constituents were represented using the lumping procedures incorporated in the condensed version of the SAPRC-07 mechanism (Carter, 2007a), and individual compounds whose reactivities were being assessed were represented explicitly. The mechanisms used for the compounds studied in this project are discussed above and also given in Table A-1 in Appendix A.

Note that the impact of the reactions of amines with HNO₃ under atmospheric conditions is very uncertain, and for that reason the atmospheric reactivity calculations were carried out using only upper and lower limit assumptions in this regard. The effects of assumptions regarding the importance of amine removal are shown in the Atmospheric Reactivity Calculation Results section, below. For the purpose of deriving reactivity scales for regulatory applications, it is probably appropriate to use upper limit estimates of the ozone impacts of these compounds under conditions where they will have their highest impacts. For that reason, the tabulated atmospheric reactivity values given in the Atmospheric Reactivity Calculation Results section were derived based on calculations assuming that loss by reaction with HNO₃ is negligible.

Table 5. List of compounds whose reactivities have been added to the SAPRC-07 reactivity tabulation or whose reactivities have been requested by the CARB.

Compound	CAS No.	Mechanism Derivation Method or Representation
Amines for which mechanisms were derived		
Methylamine	74-89-5	The mechanisms were derived based on work for this project as discussed in this report. Reactions and rate constants as implemented in the SAPRC-07 mechanism are given in Table A-1 in Appendix A. The atmospheric ozone impacts of these compounds depend on the extent to which they are removed by reaction with HNO ₃ , which is highly uncertain. In order to provide an upper limit estimate of the ozone impacts of these compounds under conditions where they will have their highest impacts, the tabulated atmospheric reactivity values were derived based on calculations assuming that loss by reaction with HNO ₃ is negligible. If loss by this process is important, the magnitude of the ozone impact may be more than an order of magnitude lower.
Dimethyl amine	124-40-3	
Ethyl amine	75-04-7	
Trimethyl amine	75-50-3	
Isopropylamine	75-31-0	
t-Butyl amine	75-64-9	
Triethyl amine	121-44-8	
Ethanolamine	141-43-5	
Dimethylaminoethanol	108-01-0	
2-Amino-1-butanol	96-20-8	
2-Amino-2-methyl-1-propanol	124-68-5	
Diethanol amine	111-42-2	
Triethanolamine	102-71-6	
Triisopropanolamine	122-20-3	
Other Compounds whose mechanisms were added		
Tripropylene glycol	24800-44-0	The mechanisms were derived using the SAPRC-07 mechanism generation system without modifications or new explicit assignments. The reactions and rate constants as implemented in SAPRC-07 are listed in Table A-1 in Appendix A.
Diethylene glycol mono(2-ethylhexyl) ether	1559-36-0	
Tripropylene glycol n-butyl ether	55934-93-5	
Triethyl citrate	77-93-0	
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	
Citronellol (3,7-dimethyl-6-octen-1-ol)	106-22-9	
Linalool	78-70-6	
Geraniol	106-24-1	
Hydroxycitronellal	107-75-5	
Terpinolene	586-62-9	
1-Nitropropane	108-03-2	The mechanisms were derived using the SAPRC-07 mechanism generation system without modifications except that the dominant reaction pathways for some radicals had to be assigned based on mechanism generation estimates for similar radicals. The reactions and rate constants as implemented in SAPRC-07 are listed in Table A-1 in Appendix A.
Methyl nonafluorobutyl ether	163702-07-6	
Ethyl nonafluorobutyl ether	163702-05-4	
2-Ethylhexyl benzoate	5444-75-7	Mechanism estimated. The reactions and rate constants as implemented in SAPRC-07 are listed in Table A-1 in Appendix A. Footnotes to the table indicate the estimation methods used.
Ethyl methyl ketone oxime	96-29-7	

Table 5 (continued)

Compound	CAS No.	Mechanism Derivation Method or Representation
Methyl iodide	74-88-4	Mechanism of Carter (2007b) used. The reactions and rate constants as implemented in SAPRC-07 are also listed in Table A-1 in Appendix A. Footnotes to the table give the sources of the rate constants and estimates.
Compounds represented using the "Lumped Molecule" approach (assumed to have the same ozone impact per molecule emitted as another compound or model species)		
Hexyl cinnamal	101-86-0	Assumed to have the same per-molecule reactivity as the lumped c5+ unsaturated carbonyl model species (ISOPROD) used to represent these products in the isoprene mechanism.
Cinnamic aldehyde	104-55-2	
Amyl cinnamal	122-40-7	
4-Vinylphenol	2628-17-3	Assumed to have the same per-molecule reactivity as styrene
Methylparaben (4-Hydroxy benzoic acid, methyl ester)	99-76-3	Assumed to have the same per-molecule reactivity as <i>o</i> -cresol
Propylparaben	94-13-3	Assumed to have the same per-molecule reactivity as benzyl alcohol
2,6-Di-tert-butyl- <i>p</i> -cresol	128-37-0	
Beta-phenethyl alcohol	98-85-1	
Cinnamic alcohol	104-54-1	Assumed to have the same per-molecule reactivity as β -methyl styrene
Anethol	104-46-1	Assumed to have the same per-molecule reactivity as triethyl amine
Triethylene diamine	280-57-9	
Lauryl pyrrolidone	2687-96-9	
<i>o</i> -Dichlorobenzene	95-50-1	Assumed to have the same per-molecule reactivity as <i>p</i> -dichlorobenzene
2-Chlorotoluene	95-49-8	Assumed to have the same per-molecule reactivity as toluene
Methyl nonafluoroisobutyl ether	163702-08-7	Assumed to have the same per-molecule reactivity as the corresponding nonafluorobutyl ether.
Ethyl nonafluoroisobutyl ether	163702-06-5	
Compounds requested by the CARB staff for which mechanisms were not derived because the compounds are estimated to have very low ozone impacts.		
HCFC-225ca	422-56-0	
HCFC-225cb	507-55-1	
HFC 43-10mee	138495-42-8	
HFC-245fa	460-73-1	

Table 5 (continued)

Compound	CAS No.	Mechanism Derivation Method or Representation
Compounds requested by the CARB staff for which mechanisms were not derived because there was insufficient time and resources available in the project to derive estimated mechanisms. (It may be possible to develop estimated mechanisms for these compounds, but reactivity estimates would be highly uncertain)		
Acetamide MEA (N-acetyl monoethanolamine)	142-26-7	
Benzyl benzoate	120-51-4	
Benzyl salicylate	118-58-1	
Butylphenyl methylpropional (Lilac-synthetic fragrance)	80-54-6	
Compounds requested by the CARB staff for which mechanisms were not derived because their mechanisms are too uncertain to estimate		
Acetic acid benzyl ester	140-11-4	
Benzophenone-3	131-57-7	
Benzophenone-4	4065-45-6	
Benzyl nicotinate	94-44-0	
Beta-myrcene	123-35-3	
Biotin (Vitamin H or B7)	58-85-5	
Butetamate (Buteth-3)	14007-64-8	
Butylparaben	94-26-8	
Coumarin	91-64-5	
Ethylparaben	120-47-8	
Eugenol	97-53-0	
Isobutylparaben	4247-02-3	
Isoeugenol	97-54-1	
L-Cysteine (2-amino-3-sulfanylpropanoic acid)	52-90-4	
Musk ketone	81-14-1	
Musk xylene	81-15-2	
Niacinamide (Vitamin B3)	98-92-0	
Pantothenic acid (Vitamin B5)	79-83-4	
Phenyl trimethicone (Methyl phenyl polysiloxane)	2116-84-9	
Vanillin	121-33-5	
Compounds requested by the CARB staff that are probably sufficiently low in volatility that they may not have significant ozone impacts. They probably should not be included in VOC emissions inventories.		
Adenosine triphosphate	56-65-5	
Alpha Olefin sulfonate	68439-57-6	
Ammonium benzoate	1863-63-4	
Ascorbic acid (Vitamin C)	50-81-7	
Di-2-ethylhexyl sebacate	122-62-3	
Di- <i>n</i> -butyltin dilaurate	77-58-7	

Table 5 (continued)

Compound	CAS No.	Mechanism Derivation Method or Representation
Dioctyl Sodium Sulfosuccinate	577-11-7	
Ethylene diamine tetraacetic acid	60-00-4	
Ethylhexyl salicylate (octyl salicylate)	118-60-5	
Lauramide DEA	120-40-1	
Mixed fatty acid methyl esters, C16 - C18	67762-38-3	
Myristic acid (C14 fatty acid)	544-63-8	
Octyl methoxycinnamate	5466-77-3	
Oleic acid	112-80-1	
Palmitic acid (C16 fatty acid)	57-10-3	
Pyridoxine hydrochloride (Vitamin B6)	58-56-0	
Sodium benzoate (Benzoic acid, sodium salt)	532-32-1	
Sodium lauroyl sarcosinate (sodium salt (8CI))	137-16-6	
Sodium PCA (monosodium salt)	28874-51-3	
Stearic acid	57-11-4	
Compounds or mixtures requested by the CARB staff for which we were unable to determine the chemical composition or structure.		
Cedarwood (Cedrus Atlantica) Oil	68990-83-0	
Chlorinated paraffin solvent	63449-39-8	
4,4-(Oxydi-2,1-ethanediyl) bismorpholine	6425-39-4	
Cocamide DEA	68603-42-9	
Diethyltoluenediamine (DETDA)	68479-98-1	
Dimethyl lauramine isostearate	70729-87-2	
HFC-365mfc	406-58-6	
Lauryl lactate	6283-92-7	
MEA borate; monoethanolamine borate	68130-12-1	
MIPA borate; monoisopropanolamine borate	68003-13-4	
Panthenyl ethyl ether (N-(3-Ethoxypropyl)-2,4-dihydroxy-3,3-dimethylbutyramide)	667-83-4	
Soy methyl esters		
Trimethylolpropane trioleate	68002-79-9	
Trimethylolpropane trioleate polyol ester	57675-44-2	

RESULTS AND DISCUSSION

Summary of Experiments and Characterization Results

A chronological listing of the environmental chamber experiments carried out for this project is given in Table B-1 in Appendix B. These included experiments with the test compounds of interest for this study and appropriate characterization and control experiments needed for the data to be useful for mechanism evaluation. The results of the mechanism evaluation experiments are discussed in the Mechanism Evaluation Results section, below. The characterization results are discussed in the remainder of this section.

The results of the individual characterization experiments that are relevant to the experiments for this project are summarized in the “Results” column of Table B-1. The initial characterization experiments relevant this chamber are described in detail by Carter (2004) or by Carter and Malkina (2005) or Carter et al (2005b), and thus need not be discussed further here. Characterization results specific to this project are discussed below.

Blacklight Characterization

Because of problems with the arc light source during the period of this project, all of the experiments for this project were carried out using the blacklight light source. Methods for characterizing the intensity of the blacklight light source were discussed by Carter et al (2005b), though some revisions were made as a result of subsequent measurements. As with the arc light source, NO₂ actinometry measurements were made using the quartz tube method of Zafonte et al (1977), modified as discussed by Carter et al (1995b), with the quartz tube both inside the reactors and also in front of the reactors. As discussed by Carter et al (2005b), the results of these measurements, and other measures of light intensity, indicated a steady decline in light intensity with time, with the results being best correlated with the “blacklight run count”, which is the number of experiments carried out in the chamber using the blacklights, and is thus an indicator of the ageing of the lights due to use. A plot of the results of the in- and out-of-reactor actinometry measurements against run count for UCR EPA experiments carried out using the blacklight light source is shown on Figure 3.

The actinometry measurements made in front of the reactor as shown on Figure 3 are corrected by a factor of 0.698 to give an estimate of the corresponding light intensity inside the reactor. As discussed by Carter et al (2005b), this was derived from near-simultaneous actinometry measurements made both inside and in front of the reactor. Both measurements show similar declines in intensity with time, though the measurements in front of the reactor are more comprehensive because of the larger number of measurements and the larger period of time for which measurements were made.

The actinometry measurements using the blacklight lights source are reasonably well fit by the following empirical expression, where k_1 is the NO₂ photolysis rate in min⁻¹:

$$k_1 = 0.0958 \times [1 + \exp(-\text{Blacklight Run Count} \times 0.003914)] \quad (I)$$

The parameters in Equation (I) were derived to minimize sum-of-squares errors in predictions of both the in-reactor actinometry measurements and the in-front-of-reactor measurements corrected by a factor of 0.698. This equation was used to derive the NO₂ photolysis rates used when modeling the blacklight experiments modeled for this project. Figure 3 indicates the range of blacklight run counts that is applicable to the experiments for this project.

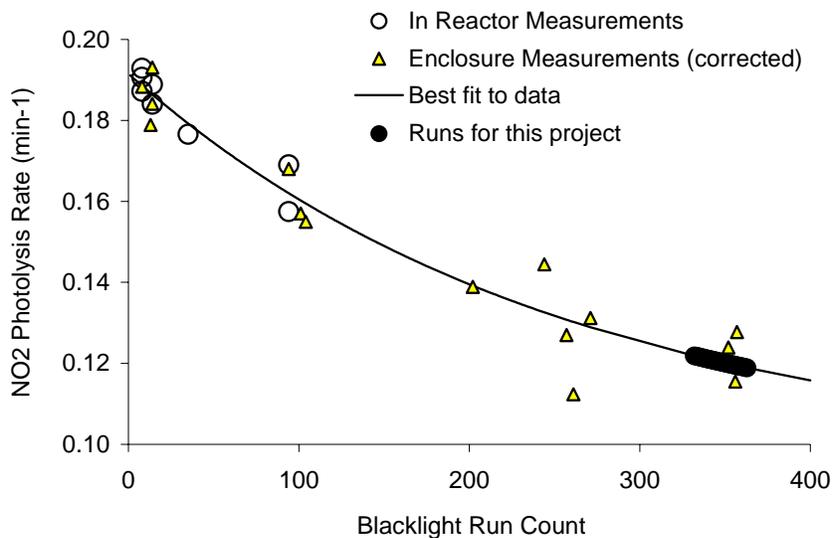


Figure 3. Plots of light intensity data used to assign NO₂ photolysis rates for the blacklight light source.

The spectrum of the blacklights in this chamber has been measured periodically and continues to be essentially the same as the spectrum recommended by Carter et al (1995b) for modeling blacklight chamber runs.

Chamber Effects Characterization

Except as discussed below, the characterization results for the more recent experiments for this project are consistent with those discussed by Carter et al (2005b) and Carter and Malkina (2005, 2007), and the same characterization parameters were used for modeling. The most important chamber effect, and the only chamber effect parameter that was changed when modeling the experiments for this project, concerns the apparent HONO offgasing, which is believed to be responsible for both the chamber radical source and NO_x offgasing effects (Carter, 2004). This is represented in the chamber effects model by the parameter RN-I, which is the HONO offgasing rate used in the simulations divided by the light intensity as measured by the NO₂ photolysis rate. Figure 4 shows the HONO offgasing parameters that best fit the radical or NO_x - sensitive characterization experiments carried out in the UCR EPA during the period of the last three sets of reactors. Note that the experiments carried out for this project start at run EPA777, so the applicable characterization data for this project is for the last set of reactors shown on the figure.

For the runs carried out for this project, which were all in the newest set of reactors installed after run 683, the RN-I value used for both reactors was 15 ppt, the average of the measured values for the applicable characterization runs. The values assigned for modeling the runs in the last three sets of reactors are indicated on Figure 4.

Side equivalency test experiments, in which the same mixture is irradiated in both reactors, are carried out periodically as controls for the incremental reactivity experiments. Generally good side equivalency is observed for the gas-phase results, though sometimes one reactor is more favorable for particle formation than the other (Carter et al, 2005b). The results of the side equivalency test

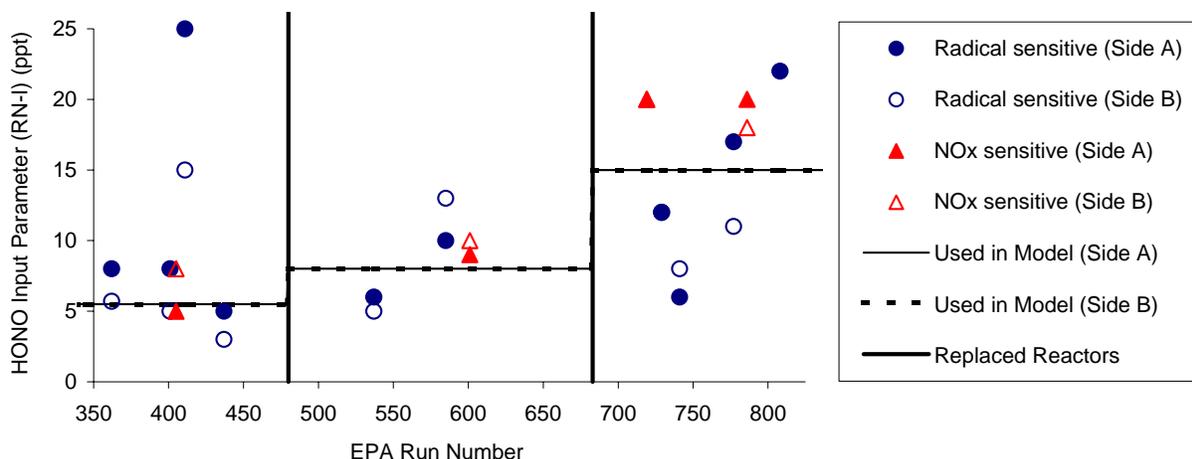


Figure 4. Plots of best fit HONO offgassing parameters against UCR EPA run number.

experiment carried out during this project were similar, and are discussed below in conjunction with the incremental reactivity experiments with the added test compounds.

Background PM Characterization

Although the primary objective of this project was to obtain data on ozone impacts, particulate matter (PM) volume number measurements were made in conjunction with the experiments that were carried out. The results of the initial PM characterization experiments in this chamber were discussed by Carter et al (2005a,b). The most useful PM background characterization experiments are pure air irradiations, where small but measurable PM formation is generally observed. This is apparently due to reaction of OH radicals with some PM precursor, since no PM formation is observed in CO - air or NO_x - air irradiations, where the presence of the added CO or NO_x tend to suppress the OH radical levels. Because of this, pure air irradiations continue to be carried out for the purpose of characterizing background PM levels, including experiments around the time of the mechanism evaluation experiments for this project.

Plots of the 5-hour PM volume levels measured in this chamber since the time that routine PM measurements began are shown on Figure 5. (Data from runs with 5-hour PM volume of greater than 1.5 µg/m³, which includes some early runs in the first set of reactors; and run EPA796 carried out during this program, which appears to be anomalously contaminated, are not shown.) As discussed by Carter et al (2005a,b), for the first two sets of reactors the background PM level was consistently higher in Side A than in Side B, with the background in Side B being quite low. However, for the third set of reactors, the PM levels were essentially the same on both sides, at about the low range of the level of Side A in the previous sets of reactors. For the fourth set of reactors, those used for the runs for this project, the background PM levels were lower, being comparable to those found on Side B in the first two reactors, though the PM levels were somewhat lower on Side B than on Side A. This background PM level is small compared to that formed in the incremental experiments with the added test compounds, and thus should not significantly alter conclusions of this study concerning relative PM impacts of the various compounds that were studied.

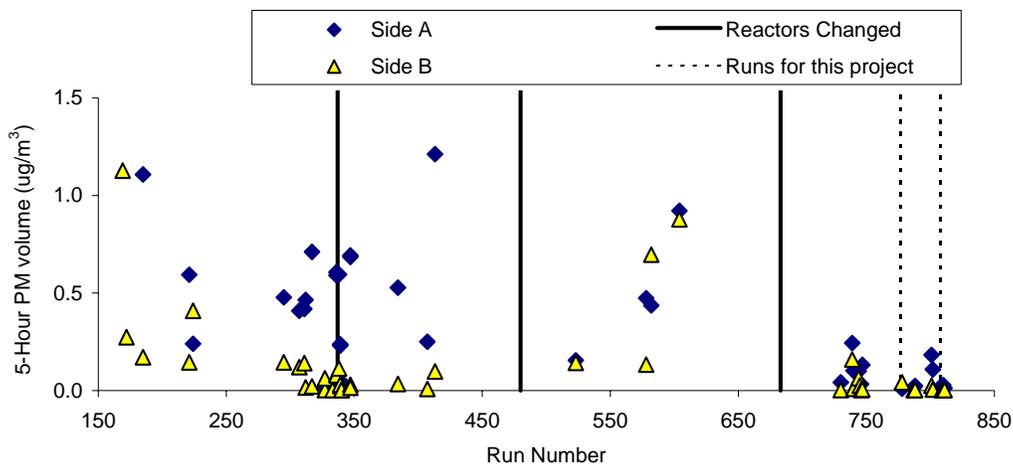


Figure 5. Plots of 5-hour PM volume measurements in pure air experiments the EPA chamber against EPA run number.

Gas-Phase Mechanism Evaluation Results

Table 6 lists the initial concentrations and selected gas-phase results for the incremental reactivity experiments carried out for this project. For comparison, the results of the side equivalency test experiment, which had no added reactants, are also shown. The measures of gas-phase reactivity used to evaluate the mechanisms in the incremental reactivity experiments are the effects of the test compound or solvent on $\Delta([\text{O}_3]-[\text{NO}])$, or $([\text{O}_3]_t-[\text{NO}]_t)-([\text{O}_3]_0-[\text{NO}]_0)$, and IntOH, the integrated OH radical levels. As discussed elsewhere (e.g., Johnson, 1983; Carter and Atkinson, 1987; Carter and Lurmann, 1991, Carter et al, 1993), $\Delta([\text{O}_3]-[\text{NO}])$ gives a direct measure of the amount of conversion of NO to NO₂ by peroxy radicals formed in the photooxidation reactions, which is the process that is directly responsible for ozone formation in the atmosphere. This gives a useful measure of factors affecting O₃ reactivity even early in the experiments where O₃ formation is suppressed by the unreacted NO. Although this is the primary measure of the effect of the VOC on O₃ formation, the effect on radical levels is also a useful measure for mechanism evaluation, because radical levels affect how rapidly all VOCs present, including the base ROG components, react to form ozone.

The integrated OH radical levels are not measured directly, but can be derived from the amounts of consumption of reactive VOCs that react only with OH radical levels. In particular,

$$\text{IntOH}_t = \frac{\ln([\text{tracer}]_0/[\text{tracer}]_t) - Dt}{k\text{OH}^{\text{tracer}}} \quad (\text{II})$$

where $[\text{tracer}]_0$ and $[\text{tracer}]_t$ are the initial and time t concentrations of the compound used as the OH tracer, $k\text{OH}^{\text{tracer}}$ is its OH rate constant, and D is the dilution rate in the experiments. The latter is small in our chamber and is neglected in our analysis. For these experiments, the base ROG surrogate component *m*-xylene is the most reactive compound in the experiment that reacts only with OH radicals, and was therefore used as the OH tracer to derive the IntOH data. The *m*-xylene OH radical rate constant used in this analysis was $2.36 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Atkinson, 1989).

Table 6. Summary of initial concentrations and selected gas-phase results of the incremental reactivity experiments.

Run	Test Side	Type [a]	Test VOC Added (ppb) [b]		Base Run Initial Concentrations		Hours Light [c]	Final O ₃ (ppb)		D([O ₃]-[NO]) Change (ppb)		IntOH Change (ppt-min)
			Calc	Adj	NO _x (ppb)	ROG (ppmC)		Test	Base	2 Hr	Final	
Side Equivalency Test												
785	A	MIR	-		29	0.55	6	81	79	-2	2	2
AMP (calculated and adjusted amounts added)												
799	A	MIR	64	20	28	0.56	5	32	64	-19	-35	-17
782	A	MIR	525	30	29	0.60	5	16	61	-21	-51	-24
781	A	MIR	536	25	29	0.50	5	14	48	-18	-42	-23
792	A	MOIR/2	52	10	16	1.05	5	64	69	-31	-5	-6
789	B	MOIR/2	53	25	25	1.15	5	72	104	-47	-32	-15
783	A	MOIR/2	105	35	25	1.21	5	67	100	-53	-33	-12
784	A	MOIR/2	105	40	25	1.08	5	59	100	-57	-40	-15
Ethanolamine (calculated and adjusted amounts added)												
780	A	MIR	100	70	33	0.50	3	71	24	42	50	1
790	A	MIR	101	5	30	0.58	6	81	81	-1	-1	0
791	A	MOIR/2	53	15	25	1.16	5	90	100	1	-11	-5
798	A	MOIR/2	101	20	29	1.34	5	92	96	4	-7	-1
805	A	MOIR/2	250	50	24	1.09	5	81	95	9	-16	-10
Isopropyl amine (calculated and adjusted amounts added)												
807	A	MOIR/2	252	100	22	1.18	6	106	97	34	9	-10
<i>t</i> -Butyl amine (calculated and adjusted amounts added)												
806	A	MOIR/2	251	140	22	1.09	5	13	95	-62	-86	-21
<i>d</i> -Limonene (measured amounts added)												
797	A	MIR	26		25	0.60	5	77	65	22	11	-10
793	A	MIR	35		29	0.58	5	99	62	46	36	-5
804	A	MOIR/2	23		19	1.08	6	83	89	10	-6	-4

[a] Codes for types of base case experiments for the incremental reactivity experiments are as follows: "MIR": ~30 ppb NO_x and ~0.55 ppmC ROG surrogate; "MOIR/2": ~25 ppb NO_x and ~1.1 ppmC ROG surrogate.

[b] For the amines, the initial concentrations calculated from the amount of liquid injected are given in the "Calc" column, and the initial concentrations that gave the best fit of model simulations to the data are given in the "Adj" column. For *d*-limonene, the measured initial concentrations, which are consistent with the calculated amounts injected, are given.

[c] Hours of irradiation for which O₃ and Δ([O₃]-[NO]) data are available.

A series of *d*-limonene - NO_x experiments were also carried out for the purpose of providing additional mechanism evaluation data for that compound. The results of those experiments are discussed in conjunction of the mechanism evaluation results for those compounds.

Amines

The amines whose ozone impacts were experimentally studied for this project consisted primarily of 2-amino-2-methyl-1-propanol (AMP) and aminoethanol, though one experiment each was carried out for *t*-butyl amine and isopropyl amine. The first two were studied because they are important in consumer products inventories, while the latter two were studied to provide additional data to evaluate the general mechanism estimation approach. Conditions and selected gas-phase results of the incremental reactivity experiments are shown on Table 6 and experimental and calculated concentration-time plots for selected species are shown on Figure 6 and Figure 8 for AMP and on Figure 7 and Figure 9 for the other amines.

It was immediately apparent that AMP is a strong inhibitor of the gas-phase reactions, since its addition caused a significant slowing of O₃ formation, NO oxidation and integrated OH radical levels in all experiments. This was also observed with *t*-butyl amine, but not for aminoethanol and isopropyl amine, both of which tended to enhance rates of NO oxidation and O₃ formation (at least initially) in most experiments. The strong inhibition characteristics of AMP was not expected based on the initially estimated mechanisms that assumed that reactions at the amino group were unimportant, but is consistent with the mechanism derived in this work, as described above. The inhibiting characteristics of AMP and *t*-butyl amine are attributed to the fact that these compounds lack abstractable hydrogens in the position next to the amino group, which means that they have no significant radical propagation pathways available following the reactions of OH radicals with the amino group.

The estimated amine mechanisms developed in this work were qualitatively consistent with the results of the reactivity experiments, in that they predicted that AMP and *t*-butyl amine were strong inhibitors; while the other two had a generally positive effect on initial O₃ formation and NO oxidation rates, and relatively small effects on integrated OH levels.

However, quantitative mechanism evaluation using the amine experiments was complicated by the fact that we were unable to develop a useful quantitative gas-phase analysis method for amines for this project, so the amounts of amines injected into the gas phase in these experiments could not be determined experimentally, and was therefore uncertain. The amount of compound in the gas phase can be estimated from the measured amount of liquid injected, assuming complete injection of all the material, and loss of the materials on the wall. This approach has been successfully employed in experiments with complex hydrocarbon mixtures such as petroleum distillates used in coatings (Carter and Malkina, 2005) and kerosene (Carter and Malkina, 2007). But if this is assumed in the case of the amines, then, as shown on Figure 6 and Figure 7, the model significantly overpredicts the effects of the amines on NO oxidation and O₃ formation in essentially all the amine experiments, both in a negative sense for AMP and *t*-butyl amine, and in a positive sense for aminoethanol and isopropyl amine. Although the possibility that this is due to mechanism problems cannot be completely ruled out, the much more likely explanation is that only a fraction of the injected amine is making it to the gas phase in the experiments, the remainder being lost either to the walls of the reactors or to the injection lines. PM formation during injection is probably not playing an important role, since as discussed below no significant PM formation occurred in the added amine experiments until the irradiation began.

In order to obtain at least approximately satisfactory fits of model simulations to the chamber data, it is necessary to adjust the initial gas-phase amine concentration for each added amine experiment. The best fit concentrations are summarized on Table 6, and the results of the model calculations using

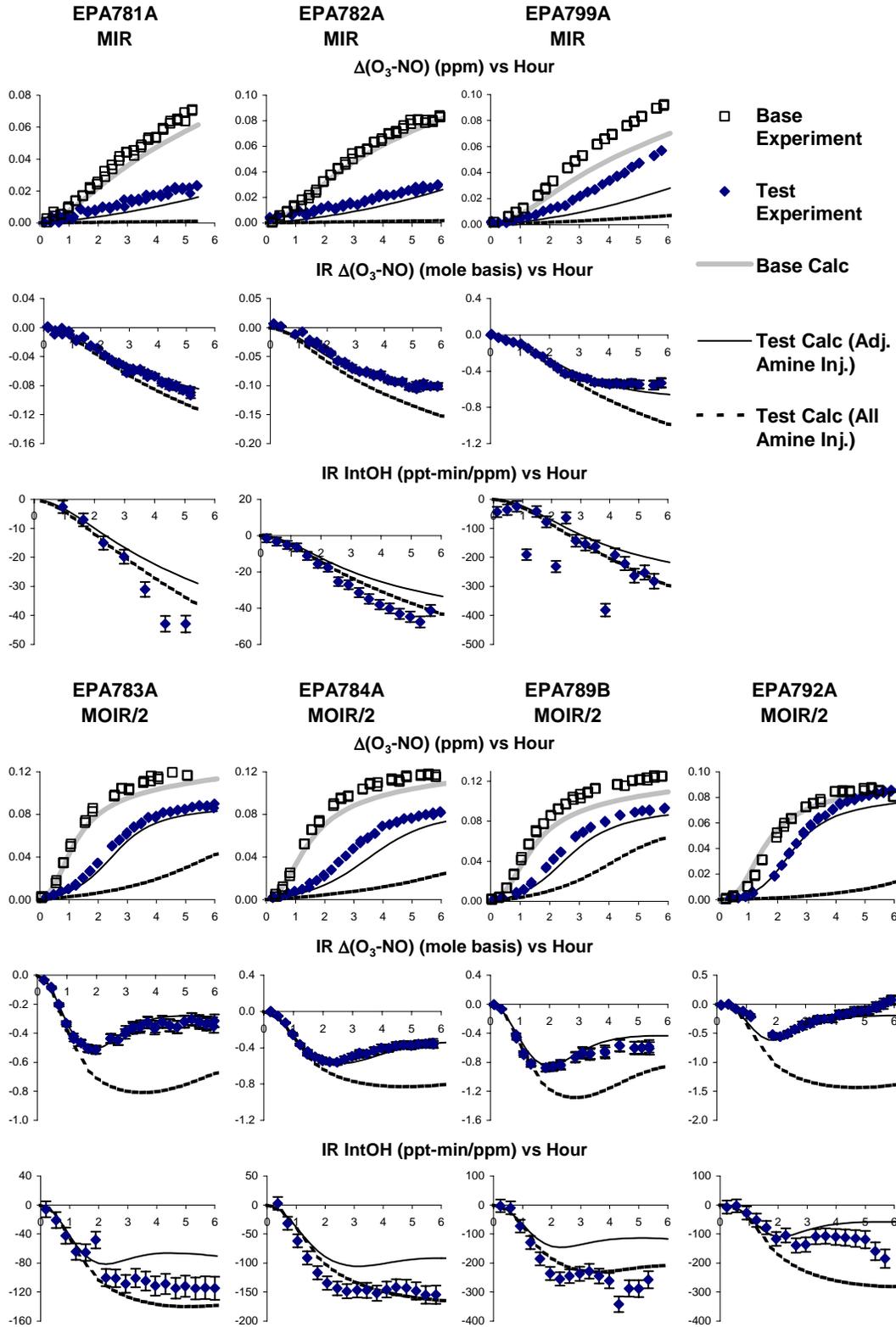


Figure 6. Plots of selected experimental and calculated incremental reactivity results for AMP.

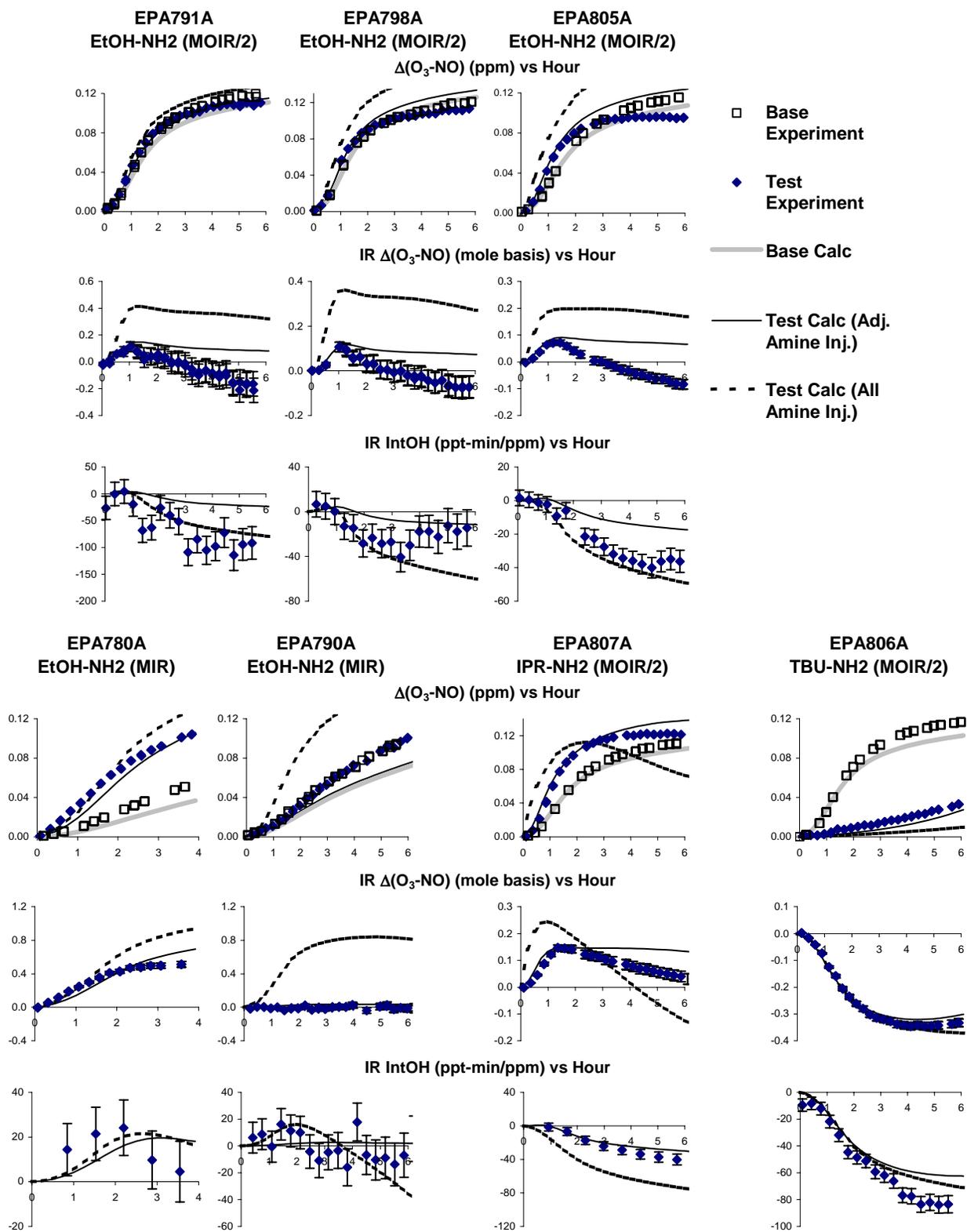


Figure 7. Plots of selected experimental and calculated incremental reactivity results for aminoethanol, isopropyl amine, and t-butyl amine.

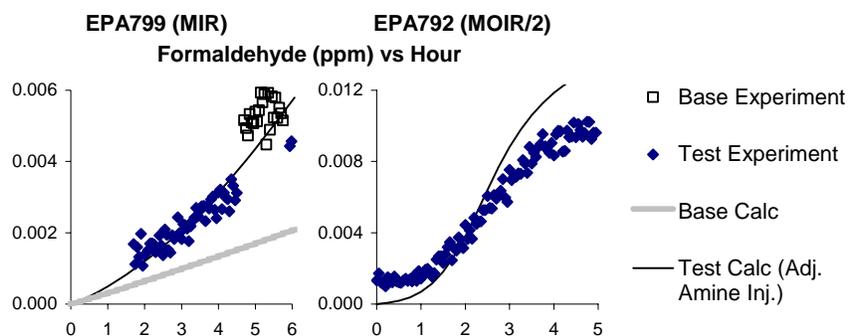


Figure 8. Plots of experimental and selected calculated data for formaldehyde when measured in AMP experiments.

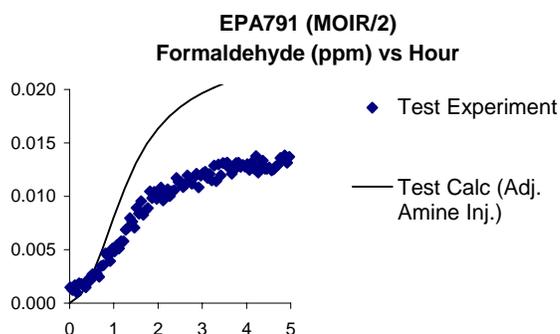


Figure 9. Plots of experimental and selected calculated data for formaldehyde in the ethanolamine experiment with useable formaldehyde data.

these adjusted initial concentrations are shown on Figure 6 through Figure 9. Plots of the best fit initial concentrations against the initial concentrations calculated from the amount of liquid injected are shown on Figure 10. The apparent amount of amine in the gas phase ranged from 5% to ~60% of the amount injected, with the least squares fit ratio being 26%. The fact that there is no systematic trend for this fraction based on the compound, amount injected, or type of experiment suggests that this apparent incomplete injection is due to experimental variability, and not due to systematic problems with the mechanisms used in the model simulations. The higher apparent fractions injected for *t*-butyl and isopropyl amine compared to AMP and aminoethanol can be attributed to the expectation that the latter two compounds would be more "sticky" because they have hydroxyl as well as amino groups, which the former two compounds lack.

In any case, the fact that the initial reactant concentrations had to be treated as an adjustable parameter in the model simulations in order to obtain even approximately satisfactory fits of the model simulations to the data indicates that these data are not very good quantitative tests of the mechanism. The only conclusion that can be drawn is that the experiments are *qualitatively* consistent, or at least not inconsistent, with model predictions.

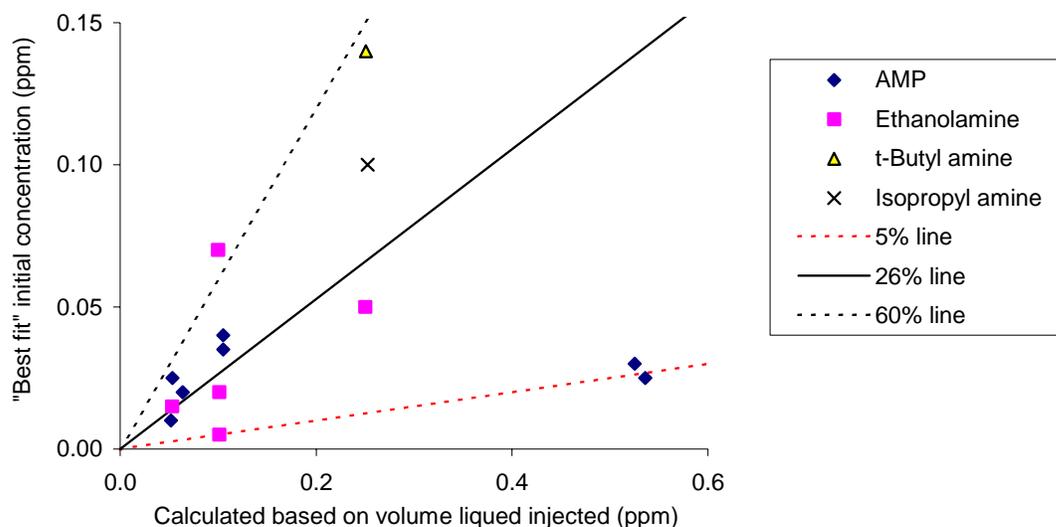


Figure 10. Plots of initial amine concentrations that gave best fits to results of model simulations to concentrations calculated from the amount of liquid amine injected.

Figure 6 shows that if the initial AMP concentrations are adjusted, then the model simulates the $\Delta([\text{O}_3]-[\text{NO}])$ and IntOH incremental reactivity results reasonably well. The good fits to the $\Delta([\text{O}_3]-[\text{NO}])$ at the initial states of the experiments can be attributed to the adjustment, but the $\Delta([\text{O}_3]-[\text{NO}])$ data at the later stages of the experiments, and the IntOH data are also fit reasonably well. Similarly good simulations are also obtained for the *t*-butyl amine experiments as well, as shown on Figure 7.

For ethanolamine, Figure 7 shows that when the initial amine concentration is adjusted so the model simulates the initial $\Delta([\text{O}_3]-[\text{NO}])$ levels, the simulations of the $\Delta([\text{O}_3]-[\text{NO}])$ later in the experiment and of the IntOH data are reasonably satisfactory in the MIR experiments, but the simulations are not quite as good in the more NO_x -limited MOIR/2 runs. In those runs, the added amine causes a slight reduction in O_3 yields at the end of the experiment, while the model predicts the impact is positive, and also the model tends to underpredict the IntOH reactivity. A similar result is observed for the $\Delta([\text{O}_3]-[\text{NO}])$ data for the isopropyl amine experiment, though in that case the IntOH reactivity data are reasonably well simulated. The tendency for these amines to reduce peak O_3 in NO_x -limited experiments suggests that their reactions, or more likely the reactions of their oxidation products, have NO_x sinks that are not adequately represented in the current mechanism. This may be due to the highly approximate representation of C=N products predicted to be formed from the reactions of amines with α C-H bonds.

This discrepancy in the predictions of the effects of ethanolamine and isopropyl amine on peak O_3 levels suggests that the current mechanism may underpredict the O_3 impacts of these compounds, and other non-inhibiting amines, under NO_x -limited conditions. However, this should not necessarily result in biases in predictions of O_3 impacts in the MIR scale, which are based on conditions when NO_x is in excess and are therefore generally insensitive to NO_x sinks in the mechanisms for the compounds.

Figure 8 and Figure 9 show experimental and calculated formaldehyde results for the few added amine experiments where formaldehyde measurement data were available. Note that the PTR-MS has not yet been quantitatively calibrated for formaldehyde and the response is based on theoretical considerations which have some uncertainties. Generally the results are consistent with model predictions

that the impacts of AMP and aminoethanol on formaldehyde formation are relatively small. However, the formaldehyde data in run EPA799 suggests that the model may be somewhat overpredicting the effect of AMP on formaldehyde formation. In that experiment, the formaldehyde levels observed in the added amine reactor was slightly lower than that in the base case reactor, while the model predicted a slight positive effect of AMP on the amine formation. However, the AMP mechanism (shown in Table A-1 in Appendix A) does not have formaldehyde as a direct product in any AMP reaction, so the slight formaldehyde overprediction is probably due to the approximate representation used for the reactive products.

As discussed above, an uncertainty exists concerning the importance of amine salt formation from the amine + HNO₃ reaction in removing the amines from availability for gas-phase reaction. To check its importance in the environmental chamber simulations, the added amine runs were modeled both by assuming that this reaction is negligible, and by using the upper limit rate constant for the reaction and assuming it is irreversible. The only significant change caused by using the upper limit rate constant and irreversible removal is that the resulting calculation predicted that all the HNO₃ forms the salt. The changes in final calculated $\Delta([\text{O}_3]-[\text{NO}])$ and IntOH caused by making alternative assumptions concerning amine salt formation were less than 3% for all the added amine experiments. This is because the amine present was in large excess over the calculated amount of HNO₃ formed in the experiments, and the model assumes that, other than possible amine salt formation, the gas-phase HNO₃ is unreactive.

***d*-Limonene**

The conditions and selected results of the incremental reactivity experiments with *d*-limonene are shown on Table 6, and plots of selected experimental and calculated data are shown on Figure 11. The model gives reasonably good simulations of $\Delta([\text{O}_3]-[\text{NO}])$, IntOH, and *d*-limonene results of runs EPA793 and EPA804. The simulation of EPA797 is not quite as good, with the model predicting the approximate impact on $\Delta([\text{O}_3]-[\text{NO}])$ but at a later time in the experiment, predicting a later time for most of the limonene consumption, and a somewhat lower magnitude of $\Delta([\text{O}_3]-[\text{NO}])$ impact. However, these discrepancies can be attributed to the mechanism's underpredictions of the rate of $\Delta([\text{O}_3]-[\text{NO}])$ formation, as tends to be the case for the simulations of surrogate experiments at lower ROG/NO_x levels (Carter, 2007a). If this is taken into account, the simulation of the effects of the *d*-limonene addition can be considered to be reasonably satisfactory.

In addition to incremental reactivity experiments, several *d*-limonene - NO_x experiments, without other added reactants, were also carried out for mechanism evaluation as part of this project. Limonene - NO_x experiments were also carried out previously at higher concentrations in a smaller chamber (Carter et al, 1995b), and these results are also used for mechanism evaluation in this work. The conditions and selected results of these and the previous experiments are summarized on Table 7, and experimental and calculated results for selected gas-phase species are shown on Figure 12 and Figure 13.

Figure 12 shows that the model gave very good simulations of the results of the *d*-limonene - NO_x experiments carried out for this program, and generally good simulations of the experiments carried out previously, except perhaps for ETC451. The model predictions of the formaldehyde levels were reasonably consistent with the PTR-MS data in the one new experiment with such data, especially considering the uncertainty in the calibration of this instrument. The model consistently underpredicted the formaldehyde in the earlier *d*-limonene - NO_x experiments, though as discussed by Carter et al (1995b), the formaldehyde instrument used at the time tended to be unreliable and subject to biases. Despite the uncertainty in the calibration, the more recent PTR-MS formaldehyde data probably should be given the greater weight.

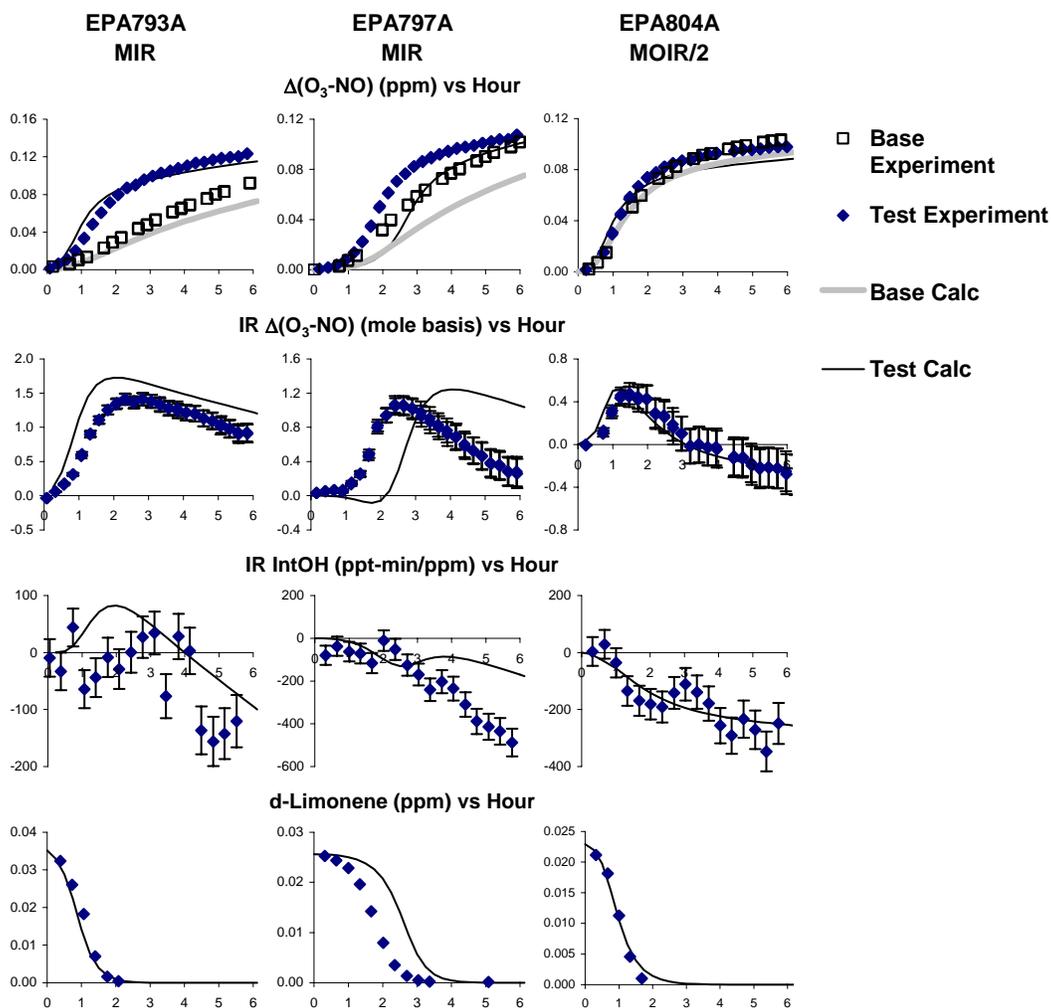


Figure 11. Plots of selected experimental and calculated incremental reactivity results for *d*-limonene.

In view of the generally satisfactory performance of the existing *d*-limonene mechanism in simulating the current and previous chamber data, no modifications were made to the mechanism for that compound as part of this project.

PM Impact Results

The PM volume measurement data taken during the incremental reactivity experiments for this program are shown on Figure 14, and selected PM results from these experiments, and also the side equivalency test experiment, are summarized on Table 8. In addition, the maximum PM volume levels in the *d*-limonene - NO_x experiments carried out for this project are included in Table 7, above.

These results show that, with the possible exception of *t*-butyl amine, all the compounds studied for this project have large, positive impacts on PM formation under simulated atmospheric conditions.

Table 7. Summary of conditions and selected results of the *d*-limonene NO_x experiments.

Run	Initial Conc (ppm)		Ozone (ppb)		Max PM (µg/m ³)
	Limonene	NO _x	2 Hr.	5 Hr	
Previous Experiments [a]					
ETC425	0.30	0.25	279	387	
ETC450	0.27	0.24	295	410	
ETC451	0.26	0.57	22	117	
ETC452	0.27	0.16	317	374	
Experiments for this project					
EPA794B	0.15	0.096	140	168	289
EPA795A	0.32	0.139	144	176	681
EPA795B	0.15	0.107	131	167	227

[a] See Carter et al (1995b) for a discussion of the conditions and modeling methods for these experiments, which were carried out in the ETC chamber, which consists of a ~4000-liter collapsible Teflon bag with a blacklight light source with a light intensity corresponding to an NO₂ photolysis rate of 0.35 min⁻¹. These runs were modeled using the chamber effects model for the ETC runs as given by Carter et al (1995b) except with a HONO input parameter, RN-I of 40 ppt. No PM data were taken during these experiments.

Note that for the amines, the PM levels at the beginning of the experiments are relatively low (see Figure 14), indicating that the amine itself is not significantly partitioning into the aerosol phase, and aerosol formation does not contribute significantly to the discrepancy between the amount of amines injected and the apparent amount of amine reacting in the gas phase. The PM formation must be due to either amine salt formation from reaction with the HNO₃ formed in the gas-phase reactions, or condensation or heterogeneous reactions of oxidation products, or (most likely) both.

For the purpose of comparing PM impacts of different compounds, it is useful to derive a "PM Incremental Reactivity", which is defined as the mass of PM formed (derived from the PM volume assuming the PM has the density of water) divided by the mass of VOC initially present in the experiments. This normalizes for differences in amounts of VOC injected in the different experiments. In the case of the amines, the "initially present" amount in this context was taken as the calculated amount injected, since even if all the amount injected did not participate in the gas phase reaction it may possibly have contributed somehow to PM formation. These PM incremental reactivity values derived from the 5-hour PM volume values measured for the various experiments are given in Table 8, and the averages of these values for the different compounds are summarized on Table 9.

For comparison with other VOCs, Table 9 also gives the average 5-hour PM incremental reactivities obtained from studies of other compounds and mixtures in this chamber in these types of incremental reactivity experiments. These include coatings VOCs studied by Carter et al (2005b) and pesticide VOCs studied by Carter and Malkina (2007). The compounds are listed in order of increasing PM incremental reactivity.

Table 9 shows that except for *t*-butyl amine, which had a moderately low relative PM impact in the one experiment with this compound, the compounds studied for this project are among the highest in

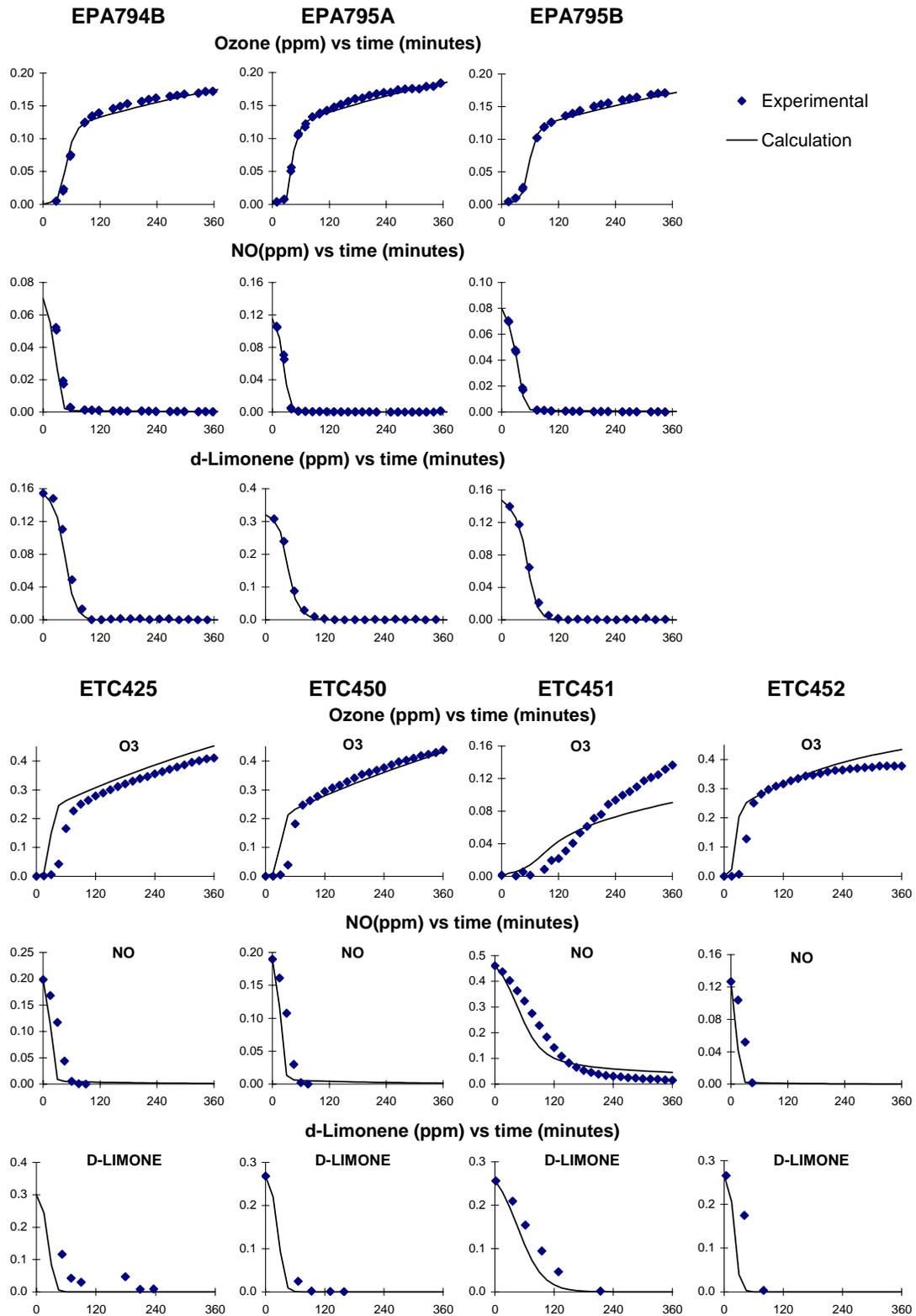


Figure 12. Plots of selected experimental and calculated data for the d-limonene experiments carried out for this program (EPA runs) and previously (ETC runs).

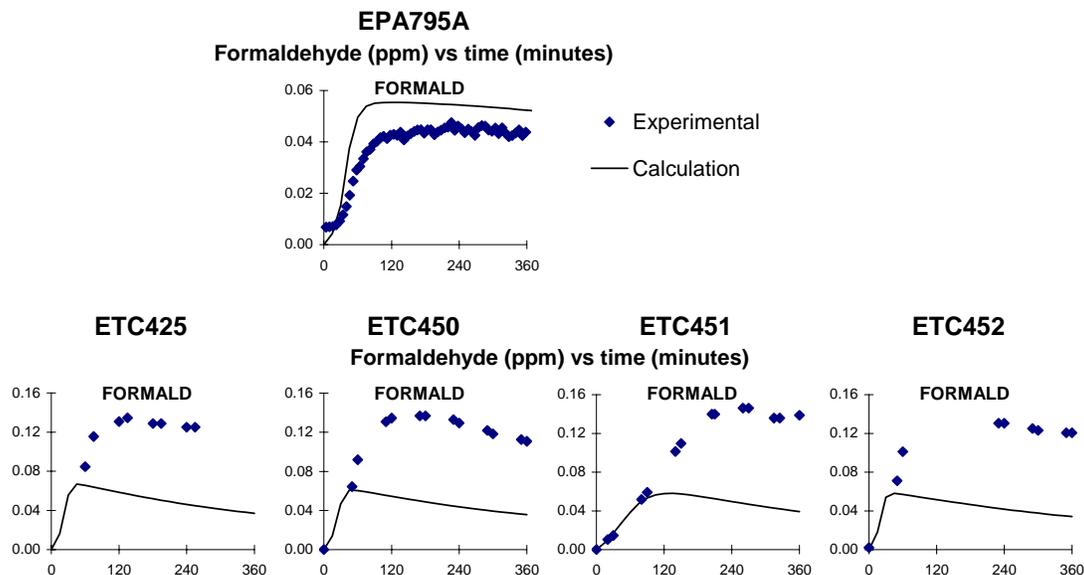


Figure 13. Plot of experimental and calculated formaldehyde data for the *d*-limonene - NO_x experiments where formaldehyde data are available.

terms of PM formation potential of the compounds studied. The highest PM formation was from *d*-limonene and ethanolamine, which were essentially the same to within the experimental variability. The inhibiting amines (AMP and *t*-butyl amine) were the least reactive of the amines studied, presumably in part because they inhibited the overall photooxidation processes, including the rate at which they reacted, and were calculated not to react to completion in these experiments. These may have higher relative PM formation potentials under more photochemically reactive conditions.

It should be noted that the relative PM formation potentials summarized in Table 9 are applicable only for the conditions of these experiments, and the magnitudes, and even the ordering, of the incremental reactivities may be different in atmospheric conditions. The ultimate utility of these data will be to provide tests for model predictions of PM formation from these compounds, once mechanisms for this purpose have been developed. However, developing mechanisms for predicting quantitative PM impacts of these compounds was beyond the scope of this program.

Atmospheric Reactivity Calculations

The atmospheric incremental reactivities calculated for the amines and other compounds added to the SAPRC-07 mechanism for this project are given on Table 10. Table C-1 in Appendix C gives the complete tabulation of VOCs and reactivity values for the SAPRC-07 mechanism, with values for these compounds studied for this project added or updated. Table C-1 also gives codes indicating generally how these VOCs are represented in the mechanism, the availability of rate constant and experimental data for the compounds or mixtures, and uncertainty codes for the mechanisms and atmospheric reactivity estimates. The reactivity values and codes Table C-1 replace those given in the initial SAPRC-07 documentation, dated August 31, 2007 for the compounds studied in this project. [The values for the other compounds are unchanged, except that methyl iodide, studied by Carter (2007b), has also been added.]

Table 8. Selected results of PM number and volume measurements made during the incremental reactivity experiments carried out for this project.

Run	Test Side	Type [a]	Test Cmpd added (ppb) [b]	5-Hour PM Number ($10^3/m^3$)		5-Hour PM Vol. ($\mu g/m^3$)		5 Hr. PM Vol. Incr'l Rct'y [c]	
				Test	Base	Test	Base		
Side Equivalency Test									
785	A	MIR	-	2	2	3.1	0.0	-	
AMP									
799	A	MIR	64	6	3	12.9	0.1	55	
782	A	MIR	525	16	4	1.3	0.1	1	
781	A	MIR	536	17	0	1.6	0.0	1	
792	A	MOIR/2	52	13	11	20.0	0.7	103	
789	B	MOIR/2	53	6	14	26.4	0.7	133	
783	A	MOIR/2	105	12	3	26.5	2.6	63	
784	A	MOIR/2	105	9	13	23.3	0.7	59	
Ethanolamine									
780	A	MIR	100	No 5 hour data - short run					
790	A	MIR	101	7	2	38.4	0.1	153	
791	A	MOIR/2	53	15	11	47.5	0.6	356	
798	A	MOIR/2	101	12	8	62.9	0.6	248	
805	A	MOIR/2	250	23	4	95.7	0.3	154	
Isopropyl amine									
807	A	MOIR/2	252	8	9	47.6	0.4	78	
<i>t</i> -Butyl amine									
806	A	MOIR/2	251	5	9	5.6	0.6	7	
<i>d</i> -Limonene									
797	A	MIR	26	9	7	36.8	0.5	256	
793	A	MIR	35	12	1	34.5	0.1	177	
804	A	MOIR/2	23	14	6	28.8	0.2	225	

[a] See footnotes to Table 6.

[b] For amines this is the calculated initial concentration based on the volume of liquid amine injected. Note that if the amount injected that gave the best fits of the model simulations to the ozone reactivity data were used then the PM volume incremental reactivity would be higher.

[c] PM volume incremental reactivity is in units of μg PM formed per milligram of VOC added. Calculated as the 5-hour PM volume on the test side minus the PM volume in the base case experiments, divided by the amount of mg/m^3 test compound added.

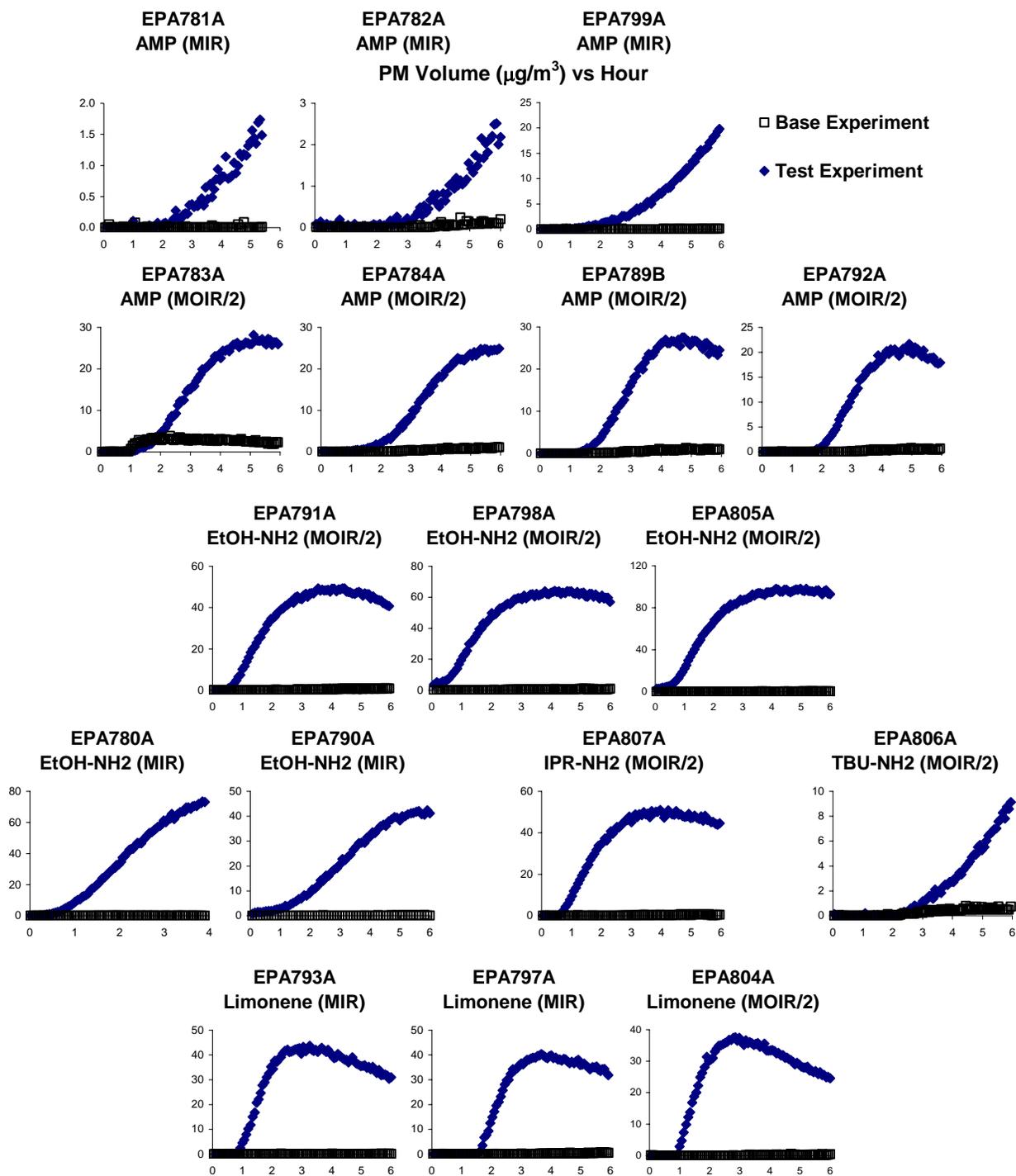


Figure 14. Plots of PM volume data from all of the incremental reactivity experiments carried out for this project.

Table 9. Summary of average 5-hour PM volume incremental reactivities of VOCs studied in incremental reactivity experiments in the UCR EPA chamber.

Compound or Mixture	Average 5-Hour PM IR [a]	Project [b]
1,2-Dichloropropenes	Low	Pesticide
Propylene glycol	Low	Coatings
Ethylene glycol	Low	Coatings
Texanol isomers	Low	Coatings
Synthetic isoparaffinic mixture (ASTM-3C1)	Low	Coatings
Carbon disulfide	6±1	Pesticide
<i>t</i> -Butyl amine	~7	This work
Petroleum distillates (coatings study)	8±3	Coatings
S-ethyl dipropylthiocarbamate (EPTC)	11±3	Pesticide
Methyl isothiocyanate	11±5	Pesticide
2-(2-Butoxyethoxy)-ethanol	34±11	Coatings
Kerosene	41±9	Pesticide
2-Amino-2-methyl-1-propanol	59±49	This work
Isopropyl amine	~78	This work
Benzyl alcohol	92±7	Coatings
<i>d</i> -Limonene	219±40	This work
Ethanolamine	228±97	This work

[a] PM volume incremental reactivity is in units of μg PM formed per milligram of VOC added. Calculated as the 5-hour PM volume on the test side minus the PM volume in the base case experiments, divided by the amount of mg/m^3 test compound added. "Low" means the PM volume in the added test compound experiment was either lower or not significantly different than in the base case experiment. If no standard deviation is given then useful data are available for only a single experiment, and the value must be considered to be uncertain by at least $\pm 50\%$.

[b] Project for which this compound was studied; consult the project report for details: "Coatings": data from Carter et al (2005b); "Pesticide": data from Carter and Malkina (2007); "This work": see Table 8.

The online SAPRC-07 mechanism documentation and reactivity scales available at <http://www.cert.ucr.edu/~carter/SAPRC> have been updated accordingly.

As discussed above, there is a significant uncertainty as to how to represent the possible loss of amines due to reaction with HNO_3 to form the amine salts in the atmospheric ozone impact simulations. Figure 15 shows plots of amine reactivities calculated assuming that this reaction is fast and irreversible, against those calculated assuming that the reaction is unimportant. It can be seen that, unlike the simulations of the chamber experiment, alternative assumptions in this regard have a significant impact on the O_3 reactivity results, with the magnitudes of the ozone impacts of the amines generally being at least an order of magnitude lower if the reaction is assumed to be fast and irreversible. For some of the lower reactivity amines, the low NO_x reactivities (reactivities in some base case and EBIR scenarios) go from positive to negative, which is probably due to the removal of NO_x sources in the mechanism due to the reactions of HNO_3 . The difference between these and the chamber simulations comes from the fact that in the chamber simulations, the amine is in large excess, while in these atmospheric reactivity

Table 10. Calculated atmospheric reactivity values for amines and other compounds added to the atmospheric reactivity tabulations.

Compound	CAS No.	Reactivity (gm O ₃ / gm VOC)			
		MIR	MOIR	EBIR	Avg Base
<u>Amines [a]</u>					
Methylamine	74-89-5	7.25	4.04	2.60	3.57±1.09
Dimethyl amine	124-40-3	2.65	1.84	1.33	1.61±0.56
Ethyl amine	75-04-7	5.45	2.97	1.91	2.63±0.80
Trimethyl amine	75-50-3	5.27	2.75	1.81	2.48±0.74
Isopropylamine	75-31-0	6.97	3.26	2.06	2.97±0.96
<i>t</i> -Butyl amine	75-64-9	-3.26	-1.06	-0.44	-0.99±0.70
Triethyl amine	121-44-8	3.07	1.48	0.91	1.31±0.44
Triethylene diamine	280-57-9	2.77	1.33	0.82	1.18±0.40
Ethanolamine	141-43-5	6.59	2.99	1.85	2.72±0.92
Dimethylaminoethanol	108-01-0	5.15	2.21	1.40	2.05±0.69
2-Amino-1-butanol	96-20-8	4.79	2.14	1.31	1.95±0.67
2-Amino-2-methyl-1-propanol	124-68-5	-2.68	-0.80	-0.30	-0.76±0.62
Diethanol amine	111-42-2	2.22	1.08	0.70	0.98±0.32
Triethanolamine	102-71-6	3.25	1.37	0.81	1.25±0.46
Triisopropanolamine	122-20-3	1.99	0.96	0.60	0.86±0.29
<u>Other Compounds</u>					
Terpinolene	586-62-9	6.14	2.21	1.17	2.09±1.08
Tripropylene glycol	24800-44-0	2.07	1.04	0.64	0.92±0.31
Diethylene glycol mono(2-ethylhexyl) ether	1559-36-0	1.45	0.75	0.42	0.64±0.24
Tripropylene glycol <i>n</i> -butyl ether	55934-93-5	1.55	0.75	0.43	0.65±0.24
Triethyl citrate	77-93-0	0.66	0.31	0.16	0.26±0.11
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	0.33	0.20	0.06	0.14±0.09
Citronellol (3,7-dimethyl-6-octen-1-ol)	106-22-9	5.80	2.05	1.12	1.94±0.96
Linalool	78-70-6	5.44	1.96	1.09	1.85±0.90
Geraniol	106-24-1	5.10	1.88	1.06	1.78±0.85
Hexyl cinnamal	101-86-0	2.93	1.08	0.64	1.03±0.41
Hydroxycitronellal	107-75-5	2.54	1.02	0.61	0.94±0.34
Cinnamic aldehyde	104-55-2	4.79	1.77	1.05	1.68±0.68
Amyl cinnamal	122-40-7	3.13	1.16	0.69	1.10±0.44
4-Vinylphenol	2628-17-3	1.44	0.16	-0.41	-0.01±0.45
Methylparaben (4-hydroxy-benzoic acid, methyl ester)	99-76-3	1.70	0.10	-0.55	-0.04±0.54
Propylparaben	94-13-3	1.44	0.08	-0.47	-0.03±0.45
2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol	128-37-0	1.18	0.07	-0.38	-0.02±0.37
Beta-phenethyl alcohol	98-85-1	4.49	1.57	0.76	1.44±0.72
Cinnamic alcohol	104-54-1	0.83	0.10	-0.29	-0.03±0.27
Anethol	104-46-1	0.75	0.09	-0.26	-0.03±0.24
2-Ethylhexyl benzoate	5444-75-7	0.92	0.42	0.18	0.34±0.17
1-Nitropropane	108-03-2	0.20	0.15	0.11	0.13±0.03
Ethyl methyl ketone oxime	96-29-7	1.55	1.32	1.45	1.40±0.30
Lauryl pyrrolidone	2687-96-9	0.89	0.45	0.27	0.40±0.14

Table 10 (continued)

Compound	CAS No.	Reactivity (gm O ₃ / gm VOC)			
		MIR	MOIR	EBIR	Avg Base
<i>o</i> -Dichlorobenzene	95-50-1	0.17	0.02	-0.04	0.01±0.05
2-Chlorotoluene	95-49-8	2.86	1.00	0.40	0.88±0.50
Methyl nonafluorobutyl ether	163702-07-6	0.05	0.04	0.03	0.04±0.01
Methyl nonafluoroisobutyl ether	163702-08-7	0.05	0.04	0.03	0.04±0.01
Ethyl nonafluorobutyl ether	163702-05-4	0.19	0.12	0.08	0.11±0.03
Ethyl nonafluoroisobutyl ether	163702-06-5	0.19	0.12	0.08	0.11±0.03

[a] Reactivities calculated assuming no loss of amine by reaction with HNO₃. See Figure 15 for results of calculations assuming rapid and irreversible loss of amines by reaction with HNO₃.

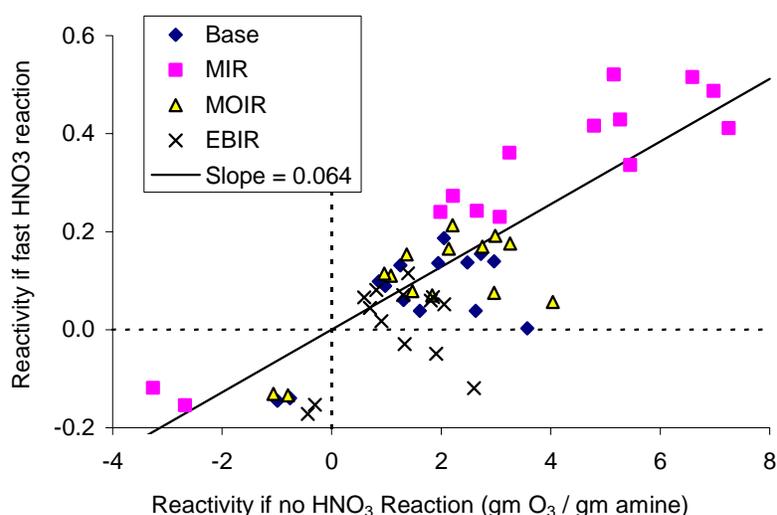


Figure 15. Plots of incremental reactivities of amines for the various types of atmospheric reactivity scenarios calculated assuming rapid and irreversible loss by reaction with HNO₃ against incremental reactivities calculated assuming no reaction with HNO₃.

scenarios, where the incremental effects of small VOC additions are being calculated, the HNO₃ is in excess and consumes most of the amine if the amine salt reaction is assumed to be fast and irreversible.

For regulatory purposes, we recommend that the amine reactivities in the maximum incremental reactivity (MIR) scale be calculated based on assuming no significant loss of amines by reaction with HNO₃, as may occur in environments where there are significant other sinks for HNO₃, such as reaction with ammonia, other amines, or heterogeneous loss processes, or if the equilibrium favors dissociation of the amine salt in the environment under consideration. This would represent the impact of the amines under conditions where they would have the maximum ozone impact, which is consistent with the general concept of maximum incremental reactivity (Carter, 1994a). Therefore, the amine reactivity values given in Table 10 and Table C-1 are based on assuming no loss of the amine by reaction with HNO₃. Footnotes

for the amines in Table C-1 indicate that the tabulated values should be considered upper limits in magnitude.

Table 11 gives the previous estimates of MIR or upper limit MIR values for the amines as a result of this work. The values in the middle column were from the most recent update of the SAPRC-99 tabulation given by Carter (2003) and are based on calculations using highly approximate "placeholder" mechanisms as discussed by Carter (2000a). For most amines for which reactivity values were available in the previous tabulations the new MIR's are somewhat lower, and in the case of AMP the previous estimate was positive, while the current mechanism (and chamber data) indicate it is an ozone inhibitor. For most amines, the reactivity values used for regulatory purposes were the upper limit values derived using the method given in Appendix D of the SAPRC-99 documentation, which are also shown on Table 11. It can be seen that these upper limit values are significantly higher than the current estimates, in most cases by more than a factor of two. Therefore, ozone impacts estimates for most amines have declined as a result of this work.

Table 11. Change in MIR values assigned to amines as a result of this work.

Compound	MIR (gm O ₃ / gm VOC) [a]		
	This work	SAPRC-99 [b]	Upper Limit [c]
Methylamine	7.25		10.8 (-33%)
Dimethyl amine	2.65	9.4 (-72%)	14.9 (-82%)
Ethyl amine	5.45	7.8 (-30%)	14.9 (-63%)
Trimethyl amine	5.27	7.1 (-25%)	17.1 (-69%)
Isopropylamine	6.97		17.1 (-59%)
<i>t</i> -Butyl amine	-3.26		18.4 (negative)
Triethyl amine	3.07		16.6 (-81%)
Triethylene diamine	2.77		15.0 (-81%)
Ethanolamine	6.59	6.0 (+11%)	11.0 (-40%)
Dimethylaminoethanol	5.15	4.8 (8%)	15.1 (-66%)
2-Amino-1-butanol	4.79		15.1 (-68%)
2-Amino-2-methyl-1-propanol (AMP)	-2.68	4.8 (negative)	15.1 (negative)
Diethanol amine	2.22	4.0 (-45%)	12.8 (-83%)
Triethanolamine	3.25	2.8 (+18%)	11.3 (-71%)
Triisopropanolamine	1.99		8.8 (-77%)

[a] Value in parentheses is change relative to the tabulated value as a result of this work.

[b] From tabulation of Carter (2003)

[c] Upper limit MIR calculated using the procedure of Appendix D in the SAPRC-99 documentation (Carter, 2000a).

DISCUSSION AND CONCLUSIONS

This project made significant progress towards achieving its objectives of decreasing uncertainties and improving estimates of ozone impacts of consumer product compounds of interest to the CARB. Ozone impact estimates and MIR values were derived for a total of 7 amines and 30 other compounds present in consumer products inventories for which estimates were not previously available, ozone impact estimates and MIR values for 8 amines were significantly improved, and data were obtained to support the predictive capabilities of the previously derived mechanism for *d*-limonene. The major contribution of this project concerned the development of improved methods for estimating mechanisms for calculating ozone impact estimates for amines, which were previously represented using highly approximate "placeholder" mechanisms, or for which only upper limit ozone impact estimates were available. As a result of this project, the estimated ozone impacts of amines appropriate for regulatory applications are much lower than the upper limit values used previously.

One unexpected result of this project is that certain types of amines, those that lack abstractable hydrogens adjacent to the amino groups, were found to have negative impacts on ozone formation, contrary to previous estimates. The most important example of this is AMP, which was one of the priority consumer product compounds chosen for study in this project. This inhibition is explainable by the current estimated mechanisms, and supported by the environmental chamber experiments with AMP and *t*-butyl amine, another example compound of this type. The chamber experiments with aminoethanol and isopropyl amine support the predictions of the current mechanisms that these compounds have positive impacts on ozone formation, though their impacts are lower than previous upper limit estimates.

On the other hand, this project was not totally successful in reducing uncertainties in mechanisms and ozone impact estimates of amines to the level obtained for other compounds that have been studied previously. Although the experiments carried out for this project were useful in testing mechanisms in a qualitative sense, particularly for determining when compounds are inhibitors as opposed to having positive impacts of ozone formation, they were not particularly useful for *quantitative* mechanism evaluation. This is because amines are extremely "sticky" compounds that are difficult to reliably inject or monitor in the gas phase, and attempts to develop methods to quantitatively monitor these compounds in the gas phase were unsuccessful. The results of the experiments could not be satisfactorily simulated using reasonable mechanisms unless it is assumed that only a fraction of the injected amines are available for reaction in the gas phase, and the amount of amine reacting in the gas phase had to be treated as an adjustable parameter. Because this adjustment could mask errors in the mechanism, this means that the data obtained cannot fully test the mechanism. Methods need to be developed to quantitatively inject and monitor these compounds in the gas phase before quantitative data can be obtained to comprehensively evaluate the mechanisms for these compounds.

On the other hand, the data obtained were sufficient to evaluate the predictive capabilities of the mechanisms concerning general reactivity trends, and for the most part the data did not indicate systematic problems with the estimated mechanisms. The one exception is that the estimated mechanisms did not correctly predict the tendency of the positively reactive amines (aminoethanol and isopropyl amine) to cause a slight decrease in O₃ formation under NO_x-limited conditions. This is attributable to uncertainties and approximations in the mechanism concerning the representation of reactive products, such as compounds with C=N bonds, in the model. This aspect of the amine mechanisms needs to be improved, though how to improve model performance in this respect is presently unclear. However, this ozone overprediction bias under NO_x-limited conditions should not significantly affect predictions of MIR values, which reflect ozone impacts under conditions when NO_x is in excess.

An even more significant problem concerning quantitative predictions of ozone impacts of amines concerns its possible removal by reaction with HNO₃, forming non-volatile amine salts. HNO₃ is an important NO_x sink species formed under conditions where O₃ formation occurs, so its reactions need to be taken into account. Amines are basic compounds and are known to rapidly form amine nitrate salts, which partition into the aerosol phase, when injected into environmental chambers in the presence of HNO₃ under atmospheric conditions (Murphy et al, 2007). However, these will also dissociate back to the amines and HNO₃, and evidence for this dissociation is also observed, though the equilibrium constants are highly uncertain (Murphy et al, 2007). If this process is not important in affecting results of the chamber experiments carried out for this work because the injected amine is in large excess over the HNO₃ formed in the photooxidation reactions, it is calculated to be extremely important under atmospheric conditions. In particular, if the reactions of HNO₃ with amines are rapid and irreversible, then the magnitudes of the incremental reactivity values for these compounds are calculated to be an order of magnitude or more less than is the case if the reaction is assumed to be negligible.

It is extremely uncertain how to represent the amine + HNO₃ reaction in the atmospheric reactivity scenarios because its importance is highly sensitive to atmospheric sources and sinks for ammonia, other amines and HNO₃, which have highly variable levels that are in most cases unknown. For regulatory purposes, we recommend that values used for Maximum Incremental Reactivity (MIR) be based on conditions where they would have the maximum ozone impact, which is consistent with the general concept of maximum incremental reactivity (Carter, 1994a). For this reason, the tabulated MIR and other reactivity values are based on assuming that the reaction with HNO₃ is negligible. However, the magnitudes of their actual impacts will probably be less than these under real atmospheric conditions. If it is desired to derive reactivity values for amines that are more representative to their atmospheric impacts, then appropriate methods to represent sources and sinks for basic pollutants (HNO₃, ammonia, amines, etc.), need to be derived for use in atmospheric reactivity scenarios. This requires a major research effort that is beyond the scope of this project.

In addition to amines, data were also obtained to better evaluate ozone impact mechanisms for *d*-limonene, an important compound in consumer products emissions. In the case of *d*-limonene, mechanism evaluation experiments were limited to limonene - NO_x experiments carried out with relatively high reactant concentrations, and the predictive capabilities of the mechanism had not been tested under conditions more representative of the atmosphere. The new experiments carried out for this project addressed the need for better data to evaluate the mechanism for this important compound, but since the mechanism performed well in simulating these data, no need to change the mechanism was indicated.

Mechanisms and reactivity estimates were also derived for 30 other compounds found in consumer product inventories for which estimates were not previously available. However the CARB staff had also requested reactivity estimates for a total of 63 other compounds for which reactivity estimates are still needed. Of these, 4 are probably of negligible reactivity and 20 are probably non-volatile, leaving 39 compounds for which reactivity estimates are actually needed. In some of these cases the chemical structures could not be determined but in others the mechanisms are too uncertain to estimate, while for other estimates could be made if more time and resources were available. Additional work in this area may be appropriate if the missing estimates remain problematic for the CARB.

Although the primary focus of this project was reducing uncertainties in ozone impact estimates, data were also obtained concerning the relative PM formation potentials for AMP, ethanamine, and *d*-limonene. All three of these compounds were found to have very high PM formation potentials compared to most of the coatings VOCs (Carter et al, 2005b) and pesticide VOCs (Carter and Malkina, 2007) studied previously. The data obtained should be useful for testing mechanisms for PM formation of these compounds, and work in this area is needed.

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APPENDIX A. MECHANISM LISTING

Table A-1. Reactions and rate constants used for amines, *d*-limonene, and the new compounds added to the mechanism for this project.

Compound	Reaction Rate [a]		Reactions
	Expression	Ref	
Methylamine	1.97e-11	1	ME-AMINE + OH = #.458 HO2 + #.542 RO2C + #.458 PROD2 + #.542 xHO2 + #.542 xPROD2 + #.542 yROOH + XN + #-5 XC
	7.40e-21	2	ME-AMINE + O3 = OH + RO2C + xHO2 + xPROD2 + yROOH + #-5 XC + XN
	9.60e-14	e1	ME-AMINE + NO3 = HNO3 + #.458 HO2 + #.542 RO2C + #.458 PROD2 + #.542 xHO2 + #.542 xPROD2 + #.542 yROOH + #-5 XC + XN
	4.00e-11	e2	ME-AMINE + HNO3 = XC + XN
Dimethyl Amine	6.52e-11	1	DM-AMINE + OH = #.243 HO2 + #.514 RO2C + #.243 PROD2 + #.514 xHO2 + #.514 xPROD2 + #.514 yROOH + XN + #-2.542 XC
	1.67e-18	2	DM-AMINE + O3 = OH + RO2C + xHO2 + xPROD2 + yROOH + #-4 XC + XN
	2.03e-13	e1	DM-AMINE + NO3 = HNO3 + #.244 HO2 + #.512 RO2C + #.244 PROD2 + #.512 xHO2 + #.512 xPROD2 + #.512 yROOH + #-2.537 XC + XN
Ethyl Amine	4.00e-11	e2	DM-AMINE + HNO3 = #2 XC + XN
	2.58e-11	1	ET-AMINE + OH = #.485 HO2 + #.515 RO2C + #.485 PROD2 + #.515 xHO2 + #.515 xPROD2 + #.515 yROOH + XN + #-4 XC
	1.98e-20	e3	ET-AMINE + O3 = OH + RO2C + xHO2 + xPROD2 + yROOH + #-4 XC + XN
	1.16e-13	e1	ET-AMINE + NO3 = HNO3 + #.508 HO2 + #.492 RO2C + #.508 PROD2 + #.492 xHO2 + #.492 xPROD2 + #.492 yROOH + #-4 XC + XN
Trimethyl Amine	4.00e-11	e2	ET-AMINE + HNO3 = #2 XC + XN
	4.84e-11	1	TM-AMINE + OH = RO2C + xHO2 + xPROD2 + yROOH + XN + #-3 XC
	7.84e-18	2	TM-AMINE + O3 = OH + RO2C + xHO2 + xPROD2 + yROOH + #-3 XC + XN
isopropylamine	1.56e-13	e1	TM-AMINE + NO3 = HNO3 + RO2C + xHO2 + xPROD2 + yROOH + #-3 XC + XN
	4.00e-11	e2	TM-AMINE + HNO3 = #3 XC + XN
	3.78e-11	e4	IPR-AMIN + OH = #.463 HO2 + #.537 RO2C + #.463 PROD2 + #.537 xMEO2 + #.537 xPROD2 + #.537 yROOH + XN + #-3.537 XC
	3.32e-20	e3	IPR-AMIN + O3 = OH + RO2C + xMEO2 + xPROD2 + yROOH + #-4 XC + XN
	1.21e-13	e1	IPR-AMIN + NO3 = HNO3 + #.487 HO2 + #.513 RO2C + #.487 PROD2 + #.513 xMEO2 + #.513 xPROD2 + #.513 yROOH + #-3.513 XC + XN
4.00e-11	e2	IPR-AMIN + HNO3 = #3 XC + XN	

Table A-1 (continued)

Compound	Reaction Rate [a]		Reactions
	Expression	Ref	
<i>t</i> -butyl amine	1.18e-11	3	TBU-AMIN + OH = #.971 NRAD + #.055 RO2C + #.001 RO2XC + #.001 zRNO3 + #.028 xMEO2 + #.028 xHCHO + #.028 xPROD2 + #.029 yROOH + #.029 XN + #-.113 XC
	5.88e-14	e1	TBU-AMIN + NO3 = HNO3 + NRAD
	Same as rxn BR28 (Neglected)	e5	NRAD + NO2 = PROD2 + #2 XN + #-2 XC
	Same as rxn BR31	e6	NRAD + NO = nitrosoamine
Triethyl Amine	4.00e-11	e7	NRAD + HO2 = #4 XC + XN
	5.57e-11	e2	TBU-AMIN + HNO3 = #4 XC + XN
	1.21e-17	e4	TE-AMINE + OH = #2.297 RO2C + #.311 RO2XC + #.311 zRNO3 + #.689 xHO2 + #.689 xRCHO + yR6OOH + XN + #2.066 XC
	1.71e-13	e3	TE-AMINE + O3 = OH + #2.297 RO2C + #.311 RO2XC + #.311 zRNO3 + #.689 xHO2 + #.689 xRCHO + yROOH + #2.066 XC + XN
Ethanolamine	4.00e-11	e1	TE-AMINE + NO3 = HNO3 + #2.297 RO2C + #.311 RO2XC + #.311 zRNO3 + #.689 xHO2 + #.689 xRCHO + yR6OOH + #2.066 XC + XN
	4.41e-11	e2	TE-AMINE + HNO3 = #6 XC + XN
	6.58e-20	e4	ETOH-NH2 + OH = #.486 HO2 + #.514 RO2C + #.091 RCHO + #.394 PROD2 + #.514 xHO2 + #.514 xHCHO + #.514 xPROD2 + #.514 yROOH + XN + #-4.24 XC
	1.35e-13	e3	ETOH-NH2 + O3 = OH + RO2C + xHO2 + xHCHO + xPROD2 + yROOH + #-5 XC + XN
Dimethylaminoethanol	4.00e-11	e1	ETOH-NH2 + NO3 = HNO3 + #.436 HO2 + #.564 RO2C + #.436 PROD2 + #.564 xHO2 + #.564 xHCHO + #.564 xPROD2 + #.564 yROOH + #-4.564 XC + XN
	6.85e-11	e2	ETOH-NH2 + HNO3 = #2 XC + XN
	6.76e-18	4	DMAE + OH = #.067 HO2 + #.896 RO2C + #.037 RO2XC + #.037 zRNO3 + #.067 RCHO + #.896 xHO2 + #.362 xHCHO + #.535 xRCHO + #.362 xPROD2 + #.933 yROOH + XN + #-557 XC
	1.80e-13	2	DMAE + O3 = OH + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + #.961 xHO2 + #.384 xHCHO + #.576 xRCHO + #.384 xPROD2 + yROOH + #-0.655 XC + XN
2-amino-1-butanol	4.00e-11	e1	DMAE + NO3 = HNO3 + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + #.961 xHO2 + #.406 xHCHO + #.554 xRCHO + #.406 xPROD2 + yROOH + #-743 XC + XN
	5.32e-11	e2	DMAE + HNO3 = #4 XC + XN
	3.65e-19	e4	2A1C4OH + OH = #.404 HO2 + #.594 RO2C + #.024 RO2XC + #.024 zRNO3 + #.076 RCHO + #.328 PROD2 + #.573 xHO2 + #.573 xHCHO + #.021 xCCHO + #.573 xPROD2 + #.596 yROOH + XN + #-2.387 XC
	1.70e-13	e3	2A1C4OH + O3 = OH + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + #.961 xHO2 + #.961 xHCHO + #.961 xPROD2 + yROOH + #-2.961 XC + XN
	4.00e-11	e1	2A1C4OH + NO3 = HNO3 + #.347 HO2 + #.628 RO2C + #.026 RO2XC + #.026 zRNO3 + #.347 PROD2 + #.628 xHO2 + #.628 xHCHO + #.628 xPROD2 + #.653 yROOH + #-2.628 XC + XN
	4.00e-11	e2	2A1C4OH + HNO3 = #4 XC + XN

Table A-1 (continued)

Compound	Reaction Rate [a]		Reactions
	Expression	Ref	
2-Amino-2-Methyl-1-Propanol	2.80e-11	5	AMP + OH = #.185 HO2 + #.799 NRAD + #.015 RO2C + #.001 RO2XC + #.001 zRNO3 + #.185 RCHO + #.015 xHO2 + #.015 xRCHO + #.016 yROOH + #.201 XN + #.199 XC
	5.88e-14	e1	AMP + NO3 = HNO3 + NRAD
	Same as rxn BR28 (Neglected)	e5	NRAD + NO2 = PROD2 + #2 XN + #-2 XC
Diethanol Amine	4.00e-11	e6	NRAD + NO = nitrosoamine
	1.01e-10	e2	NRAD + HO2 = #4 XC + XN
	3.77e-18	e4	AMP + HNO3 = #4 XC + XN
Triethanolamine	1.01e-10	e4	ETOH2-NH + OH = #.316 HO2 + #.43 RO2C + #.018 RO2XC + #.018 zRNO3 + #.08 RCHO + #.236 PROD2 + #.43 xHO2 + #.43 xHCHO + #.43 xPROD2 + #.448 yROOH + XN + #-774 XC
	3.77e-18	e3	ETOH2-NH + O3 = OH + #.961 RO2C + #.039 RO2XC + #.039 zRNO3 + #.961 xHO2 + #.961 xHCHO + #.961 xPROD2 + yROOH + #-2.961 XC + XN
	3.30e-13	e1	ETOH2-NH + NO3 = HNO3 + #.269 HO2 + #.444 RO2C + #.018 RO2XC + #.018 zRNO3 + #.269 PROD2 + #.444 xHO2 + #.444 xHCHO + #.444 xPROD2 + #.463 yROOH + #-832 XC + XN
Triisopropanol amine	4.00e-11	e2	ETOH2-NH + HNO3 = #4 XC + XN
	8.04e-11	e4	ETOH3-N + OH = #.151 HO2 + #.766 RO2C + #.083 RO2XC + #.083 zRNO3 + #.151 RCHO + #.766 xHO2 + #.766 xHCHO + #.766 xPROD2 + #.849 yR6OOH + XN + #-314 XC
	4.02e-17	e3	ETOH3-N + O3 = OH + #.902 RO2C + #.098 RO2XC + #.098 zRNO3 + #.902 xHO2 + #.902 xHCHO + #.902 xPROD2 + yROOH + #-0.902 XC + XN
triisopropanol amine	2.29e-13	e1	ETOH3-N + NO3 = HNO3 + #.902 RO2C + #.098 RO2XC + #.098 zRNO3 + #.902 xHO2 + #.902 xHCHO + #.902 xPROD2 + yR6OOH + #-902 XC + XN
	4.00e-11	e2	ETOH3-N + HNO3 = #6 XC + XN
	9.37e-11	e4	IC3OH3-N + OH = #.268 HO2 + #.581 RO2C + #.151 RO2XC + #.151 zRNO3 + #.268 PROD2 + #.581 xHO2 + #.581 xCCHO + #.581 xPROD2 + #.732 yR6OOH + XN + #1.838 XC
triisopropanol amine	4.02e-17	e3	IC3OH3-N + O3 = OH + #.794 RO2C + #.206 RO2XC + #.206 zRNO3 + #.794 xHO2 + #.794 xCCHO + #.794 xPROD2 + yROOH + #1.413 XC + XN
	2.29e-13	e1	IC3OH3-N + NO3 = HNO3 + #.794 RO2C + #.206 RO2XC + #.206 zRNO3 + #.794 xHO2 + #.794 xCCHO + #.794 xPROD2 + yR6OOH + #1.413 XC + XN
	4.00e-11	e2	IC3OH3-N + HNO3 = #9 XC + XN

Table A-1 (continued)

Compound	Reaction Rate [a]		Reactions
	Expression	Ref	
<i>d</i> -Limonene	4.28e-11 x exp(-0.797)/RT	6	D-LIMONE + OH = #.972 RO2C + #.17 RO2XC + #.17 zRNO3 + #.827 xHO2 + #.003 xRCO3 + #.288 xHCHO + #.539 xRCHO + #.053 xMEK + #.287 xPROD2 + #.019 xMVK + #.012 xIPRD + yR6OOH + #5.001 XC
	2.95e-15 x exp(1.556)/RT	6	D-LIMONE + O3 = #.729 OH + #.009 HO2 + #.619 RO2C + #.177 RO2XC + #.177 zRNO3 + #.029 CO + #.017 CO2 + #.263 PROD2 + #.021 xHO2 + #.482 xMECO3 + #.058 xRCO3 + #.089 xHCHO + #.5 xRCHO + #.015 xMACR + #.007 xIPRD + #.738 yR6OOH + #4.497 XC
	1.22e-11	6	D-LIMONE + NO3 = #1.11 RO2C + #.296 RO2XC + #.296 zRNO3 + #.626 xNO2 + #.076 xHO2 + #.002 xRCO3 + #.078 xHCHO + #.009 xCCHO + #.641 xRCHO + #.039 xMACR + #.009 xMVK + #.028 xIPRD + #.069 xRNO3 + yR6OOH + #5.452 XC + #.304 XN
	7.20e-11	7	D-LIMONE + O3P = PROD2 + #4 XC
Terpinolene	1.96e-10	e8	TRPNOLEN + OH = #.77 RO2C + #.23 RO2XC + #.23 zRNO3 + #.77 xHO2 + #.348 xRCHO + #.422 xACET + #.422 xPROD2 + yROOH + #3.78 XC
	1.02e-15	e8	TRPNOLEN + O3 = #.908 OH + #.003 HO2 + #.872 RO2C + #.113 RO2XC + #.113 zRNO3 + #.01 CO + #.006 CO2 + #.33 ACET + #.419 PROD2 + #.056 xHO2 + #.501 xMECO3 + #.241 xRCO3 + #.35 xHCHO + #.171 xRCHO + #.055 xAFG3 + #.001 xIPRD + #.911 yROOH + #2.825 XC
	6.66e-11	e8	TRPNOLEN + NO3 = #1.22 RO2C + #.343 RO2XC + #.343 zRNO3 + #.486 xNO2 + #.17 xHO2 + #.007 xHCHO + #.091 xRCHO + #.394 xACET + #.394 xPROD2 + #.123 xMVK + #.046 xIPRD + #.171 xRNO3 + yROOH + #2.368 XC + #.343 XN
tripropylene glycol	1.63e-10 6.59e-11	e8 e8	TRPNOLEN + O3P = PROD2 + #4 XC TPR-GLCL + OH = #.255 HO2 + #.938 RO2C + #.165 RO2XC + #.165 zRNO3 + #.255 PROD2 + #.519 xHO2 + #.061 xMEO2 + #.023 xHCHO + #.264 xCCHO + #.92 xPROD2 + #.745 yR6OOH + #.347 XC
diethylene glycol mono(2-ethylhexyl) ether	5.16e-11	e8	DG2EHE + OH = #.079 HO2 + #1.357 RO2C + #.36 RO2XC + #.36 zRNO3 + #.079 RCHO + #.562 xHO2 + #.155 xHCHO + #.03 xCCHO + #.092 xRCHO + #.003 xMEK + #.941 xPROD2 + #.921 yR6OOH + #3.457 XC
tripropylene glycol <i>n</i> -butyl ether	9.54e-11	e8	TGLBE + OH = #.042 HO2 + #1.441 RO2C + #.336 RO2XC + #.336 zRNO3 + #.042 RCHO + #.492 xHO2 + #.13 xMEO2 + #.172 xHCHO + #.031 xCCHO + #.091 xRCHO + #.327 xMEK + #.834 xPROD2 + #.013 xHCOOH + #.958 yR6OOH + #3.895 XC
triethyl citrate	5.91e-12	e8	TETCITRA + OH = #.026 RCO3 + #.727 RO2C + #.248 RO2XC + #.248 zRNO3 + #.026 MEK + #.001 BACL + #.182 xHO2 + #.544 xMECO3 + #.065 xRCHO + #.027 xMEK + #.183 xPROD2 + #.09 xMGLY + #.09 xBACL + #.361 xRCOOH + #.974 yROOH + #6.125 XC
2,2,4-trimethyl-1,3-pentanediol diisobutyrate	1.15e-11	e8	TXIB + OH = #1.976 RO2C + #.53 RO2XC + #.53 zRNO3 + #.443 xHO2 + #.006 xMEO2 + #.022 xRCO3 + #.186 xCO + #.071 xHCHO + #.011 xCCHO + #.026 xRCHO + #.659 xACET + #.842 xMEK + #.004 xPROD2 + #.001 xBACL + #.199 xRCOOH + yROOH + #6.427 XC

Table A-1 (continued)

Compound	Reaction Rate [a]		Reactions
	Expression	Ref	
Citronellol (3,7-dimethy-6-octen-1-ol)	9.87e-11	e8	CITRNLLOL + OH = #.041 HO2 + #.792 RO2C + #.226 RO2XC + #.226 zRNO3 + #.041 RCHO + #.727 xHO2 + #.006 xMEO2 + #.043 xHCHO + #.004 xCCHO + #.7 xRCHO + #.687 xACET + #.027 xPROD2 + #.005 xMACR + #.006 xMVK + #.009 xIPRD + #.959 yR6OOH + #4.05 XC
	3.48e-16	e8	CITRNLLOL + O3 = #.728 OH + #.009 HO2 + #.765 RO2C + #.007 RO2XC + #.007 zRNO3 + #.029 CO + #.017 CO2 + #.7 RCHO + #.3 ACET + #.263 PROD2 + #.031 xHO2 + #.7 xMECO3 + #.703 xHCHO + #.001 xCCHO + #.03 xRCHO + #.737 yR6OOH + #3.141 XC
	9.37e-12	e8	CITRNLLOL + NO3 = #1.337 RO2C + #.389 RO2XC + #.389 zRNO3 + #.084 xNO2 + #.527 xHO2 + #.018 xHCHO + #.013 xCCHO + #.084 xRCHO + #.084 xACET + #.016 xPROD2 + #.528 xRNO3 + yR6OOH + #3.854 XC + #.388 XN
Linalool	3.71e-11	e8	CITRNLLOL + O3P = PROD2 + #4 XC
	1.22e-10	e8	LINALLOOL + OH = #.775 RO2C + #.232 RO2XC + #.232 zRNO3 + #.768 xHO2 + #.064 xHCHO + #.131 xCCHO + #.637 xRCHO + #.558 xACET + #.137 xPROD2 + #.009 xMVK + yR6OOH + #3.841 XC
	3.58e-16	e8	LINALLOOL + O3 = #.712 OH + #.013 HO2 + #.737 RO2C + #.006 RO2XC + #.006 zRNO3 + #.036 CO + #.019 CO2 + #.014 HCHO + #.694 RCHO + #.292 ACET + #.269 PROD2 + #.005 HCOOH + #.03 xHO2 + #.68 xMECO3 + #.704 xHCHO + #.006 xRCHO + #.024 xMVK + #.717 yR6OOH + #3.136 XC
Geraniol	9.38e-12	e8	LINALLOOL + NO3 = #1.298 RO2C + #.388 RO2XC + #.388 zRNO3 + #.084 xNO2 + #.528 xHO2 + #.084 xRCHO + #.084 xACET + #.528 xMVK + #.528 xRNO3 + yR6OOH + #1.887 XC + #.388 XN
	6.60e-11	e8	LINALLOOL + O3P = PROD2 + #4 XC
	1.80e-10	e8	GERANIOL + OH = #.003 HO2 + #.791 RO2C + #.231 RO2XC + #.231 zRNO3 + #.761 xHO2 + #.005 xMEO2 + #.014 xHCHO + #.378 xCCHO + #.378 xRCHO + #.378 xACET + #.378 xPROD2 + #.003 xMACR + #.005 xMVK + #.013 xIPRD + #.997 yR6OOH + #3.205 XC
Geraniol	6.96e-16	e8	GERANIOL + O3 = #.728 OH + #.028 HO2 + #.672 RO2C + #.064 RO2XC + #.064 zRNO3 + #.029 CO + #.017 CO2 + #.019 HCHO + #.35 CCHO + #.35 RCHO + #.15 ACET + #.004 MEK + #.281 PROD2 + #.128 RCOOH + #.015 xHO2 + #.608 xMECO3 + #.031 xRCO3 + #.413 xHCHO + #.258 xRCHO + #.014 xMACR + #.001 xIPRD + #.719 yR6OOH + #2.708 XC
	1.87e-11	e8	GERANIOL + NO3 = #1.096 RO2C + #.319 RO2XC + #.319 zRNO3 + #.419 xNO2 + #.254 xHO2 + #.008 xMEO2 + #.242 xHCHO + #.37 xCCHO + #.055 xRCHO + #.055 xACET + #.364 xPROD2 + #.006 xMACR + #.008 xMVK + #.018 xIPRD + #.266 xRNO3 + yR6OOH + #2.841 XC + #.315 XN
	1.35e-10	e8	GERANIOL + O3P = PROD2 + #4 XC

Table A-1 (continued)

Compound	Reaction Rate [a]		Reactions
	Expression	Ref	
Hydroxycitronellal	2.80e-11	e8	HYCITRLL + OH = #.696 RCO3 + #.366 RO2C + #.103 RO2XC + #.103 zRNO3 + #.181 xHO2 + #.02 xRCO3 + #.012 xCO + #.02 xHCHO + #.005 xCCHO + #.183 xRCHO + #.098 xACET + #.002 xPROD2 + #.015 xMGLY + #.304 yR6OOH + #6.294 XC
	Phot set= C2CHO	e9	HYCITRLL + HV = HO2 + #1.43 RO2C + #.372 RO2XC + #.372 zRNO3 + CO + #.628 xHO2 + #.006 xHCHO + #.622 xRCHO + #.006 xPROD2 + yR6OOH + #4.86 XC
2-ethylhexyl benzoate	1.37e-11	e10	2EHXBOAT + OH = #.067 OH + #.039 HO2 + #1.286 RO2C + #.352 RO2XC + #.352 zRNO3 + #.039 CRES + #.067 AFG3 + #.539 xHO2 + #.045 xGLY + #.029 MGLY + #.382 xPROD2 + #.003 xRCO3 + #.101 xRCHO + #.037 xAFG1 + #.037 xAFG2 + #.801 yR6OOH + #.094 yRAOOH + #8.998 XC
1-nitropropane	1.33e-12	e8	C3-NO2 + OH = #.955 RO2C + #.045 RO2XC + #.045 zRNO3 + #.955 xHO2 + #.129 xRCHO + yROOH + XN + #2.346 XC
ethyl methyl ketone oxime	1.25e-12	e11	EMKO + OH = #.04 {RO2XC + zRNO3} + #.96 {RO2C + xHO2 + xPROD2} + #2 XC + XN
	3.89e-12	e12	EMKO + OH = HO2 + EMKO-NO
methyl nonafluoro butyl ether	1.15e-12	e8	MEONC4F9 + OH = #.935 RO2C + #.065 RO2XC + #.065 zRNO3 + #.935 xHO2 + #.935 NROG + yROOH + #3.675 XC
ethyl nonafluoro butyl ether	7.97e-12	e8	ETONC4F9 + OH = #.902 RO2C + #.098 RO2XC + #.098 zRNO3 + #.902 xHO2 + #.019 xRCHO + #.883 NROG + yROOH + #4.473 XC

[a] Rate constants are in units of $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$. If a temperature dependence is used, it is given by $k(T) = A \exp(-E_a/RT)$, where T is the temperature in degrees k and $R = 0.0019872$. For photolysis reactions, the "Phot set" is the set of absorption cross sections and wavelength-dependent quantum yields (if any) given in Table A-3 of the SAPRC-07 documentation report (Carter, 2007a), and "qy" is the wavelength-independent quantum yield, if applicable. "Same k as Rxn xxx" indicates that the rate constant is the same as a reaction in the base mechanism as listed in Table A-2 of the SAPRC-07 documentation report, where "xxx" is the reaction label. References for measured rate constants or photolysis data are as follows:

- 1 Average of values tabulated by Carl and Crowley (1998).
- 2 Rate constant from Tuazon et al (1994)
- 3 Koch et al (1996)
- 4 Average of values of Harris and Pitts (1983) and Anderson and Stephens (1988), as tabulated by Atkinson (1989).
- 5 Harris and Pitts (1983)
- 6 As recommended or tabulated by Atkinson and Arey (2003)
- 7 As recommended or tabulated by Calvert et al (2002)

Methods used to estimate rate constants or photolysis rates are as follows:

- e1 Estimated based on the $\text{NO}_3 + \text{NMP}$ rate constant and assuming ratios of rate constants for reactions of NO_3 at various types of amine groups is the same as those estimated for the reactions of OH with those groups. Reaction assumed to occur only from NH or NH_2 or from C-H bonds on carbons bonded to the amino group.
- e2 This represents the removal of amines available for gas-phase reaction by reacting with HNO_3 to form the amine salt that is removed from the system. The rate constant shown is an estimated upper limit. The upper limit rate constant is arbitrarily estimated based on typical rate constants for radical + NO_x reactions, which is sufficiently large that this would dominate over other gas-phase reactions if gas-phase HNO_3 were available. Because of the uncertainty and variability of

Table A-1 (continued)

- availability of HNO_3 in atmospheric scenarios, the atmospheric reactivity calculations are carried out both with these amine + HNO_3 reactions with the upper limit rate constant, and assuming that this reaction is negligible (or rapidly reversed). However, it is recommended that the reactivity values used for amines for regulatory applications be based on the assumption that net loss of the amine by this reaction is negligible. This will provide a reasonable upper limit on the magnitude of the amines' impacts on O_3 under conditions where they will have their maximum impact.
- e3 Estimated from the estimated rate of reaction of OH at the alpha position, and correlations between this and the measured O_3 rate constants of Tuazon et al (1994) for the methylamines and DMAE.
 - e4 Derived from structure-reactivity methods, where group rate constants for reactions at HN, NH_2 , at groups adjacent to the amino group were derived based on rate constants for the simple amines for which rate constant data are available.
 - e5 This represents the reactions of N-centered radicals that lack alpha hydrogens with NO_2 to form nitramines. Rate constant assumed to be the same as used for lumped higher acylperoxy (RCO_3) + NO_2 . The nitramines are very approximately represented by PROD2. The appropriateness of this representation is uncertain.
 - e6 The formation of nitrosoamines is neglected because these products are rapidly decomposed by photolysis under conditions where ozone formation occurs.
 - e7 This represents the reactions of N-centered radicals that lack alpha hydrogens with HO_2 to form O_2 and re-form the amine. The rate constant assumed to be the same as used for lumped higher acylperoxy (RCO_3) + HO_2 . The amines that form these radicals are generally inhibitors, so representing them with reactive model species is inappropriate. Therefore, they are represented as being inert.
 - e8 Estimated using the group-additivity estimation assignments implemented in the current mechanism generation system. See Carter (2000a) and the discussion of the mechanism generation system in this report.
 - e9 Assumed to have the same photolysis rate as propionaldehyde (model species RCHO).
 - e10 Rate constant for reaction at the aromatic ring estimated to be the same as the total rate constant for acetophenone (Atkinson, 1989), assuming that ring addition is the major reaction for that compound. The rate constant for reaction at groups off the aromatic ring based on those estimated for 2-ethyl hexyl acetate, since reaction at the acetate group is estimated to be negligible for that compound.
 - e11 The rate constant for addition of OH to the C=N double bond is estimated by the rate constant for OH + isobutene x the average of the ratio of the rate constants for $\text{CH}_2=\text{NOH}$ / Ethene and $\text{CH}_3\text{CH}=\text{NOH}$ / Propene, with abstractions from the methyl group subtracted off. The $\text{CH}_2=\text{NOH}$ and $\text{CH}_3\text{CH}=\text{NOH}$ rate constants are from the tabulation of Atkinson (1989).
 - e12 The rate constants for addition to the methyl groups were estimated using the structure-reactivity methods incorporated in the mechanism generation system.

Table A-2. New lumped molecule representations used for atmospheric reactivity estimates of compounds added to the reactivity tabulations for this project.

Compound	Represented by (on molar basis)
Hexyl cinnamal	lumped c5+ unsaturated carbonyl species (isoprene product)
Cinnamic aldehyde	lumped c5+ unsaturated carbonyl species
Amyl cinnamal	lumped c5+ unsaturated carbonyl species
4-vinylphenol	styrene
methylparaben (4-Hydroxybenzoic acid, methyl ester)	<i>o</i> -cresol
propylparaben	<i>o</i> -cresol
2,6-di-tert-butyl- <i>p</i> -cresol	<i>o</i> -cresol
beta-phenethyl alcohol	benzyl alcohol
Cinnamic alcohol	β -methyl styrene
anethol	β -methyl styrene
triethylene diamine	triethyl amine
lauryl pyrrolidone	<i>n</i> -methyl-2-pyrrolidone
<i>o</i> -dichlorobenzene	<i>p</i> -dichlorobenzene
2-chlorotoluene	toluene
methyl nonafluoroisobutyl ether	methyl nonafluorobutyl ether
ethyl nonafluoroisobutyl ether	ethyl nonafluorobutyl ether

APPENDIX B. CHAMBER EXPERIMENT LISTING

Table B-1. Summary chamber experiments relevant to this project.

Run	Date	Type [b]	Purpose and Conditions	Results
777	6/26	CO - NO _x Irradiation	Characterize chamber radical source. ~25 ppb NO _x and 50 ppm CO injected into both sides.	Data indicated that chamber radical source in the normal range. Somewhat higher radical source in Side A. See Figure 4.
778	6/27	Pure Air Irradiation	Background characterization. No injections.	4 ppb O ₃ formed after 5 hours on both sides. PM levels low on both sides but somewhat higher on Side A
779	6/28	MIR surrogate + ethanolamine (both sides)	Intended to be incremental reactivity experiment to evaluate ethanolamine mechanism, but ~100 ppb ethanolamine injected into both sides, so no base case experiment was carried out.	Results were similar to subsequent MIR surrogate experiments with similar levels of ethanolamine. Run not used for mechanism evaluation because of lack of base case data.
780	6/29	MIR surrogate + ethanolamine	Incremental reactivity experiment to evaluate ethanolamine mechanism. ~100 ppb ethanolamine injected into Side A.	Run ended early because of experimental problems. Results shown on Table 6 and Figure 7.
781	7/3	MIR surrogate + AMP	Incremental reactivity experiment to evaluate AMP mechanism. 0.5 ppm AMP injected into Side A.	Essentially no ozone formed on added AMP side. Measurement data are uncertain because of sampling problem, but data looked reasonable after an estimated correction was made. Results shown on Table 6, Table 8, and Figure 6.
782	7/5	MIR surrogate + AMP	Repeat previous experiment because results were not as expected.	Results similar to previous experiment. Measurement data are uncertain because of sampling problem, but data looked reasonable after an estimated correction was made Results shown on Table 6, Table 8 and Figure 6.
783	7/6	MOIR/2 surrogate + AMP	Incremental reactivity experiment to evaluate AMP mechanism. ~100 ppb AMP injected into Side A.	Results shown on Table 6, Table 8 and Figure 6.
784	7/9	MOIR/2 surrogate + AMP	Repeat previous experiment	Results shown on Table 6, Table 8 and Figure 6.

Table B-1 (continued)

Run	Date	Type [b]	Purpose and Conditions	Results
785	7/10	MIR surrogate side equivalency test	Test for side equivalency in reactivity experiments. Standard base case MIR surrogate - NO _x run on both sides.	Reasonably good side equivalency seen. Results summarized on Table 6 and Table 8.
786	7/11	CO - air irradiation	Characterize background NO _x offgasing. 50 ppm CO injected into both sides	Data indicated that the NO _x offgasing rates were in the normal range Somewhat higher NO _x offgasing in Side A. See Figure 4.
787	7/12	Pure Air Irradiation	Background characterization. No injections.	3 ppb O ₃ formed after 5 hours on both sides. PM levels low on both sides but somewhat higher on Side A
788	7/13	Pure Air Irradiation	Background characterization. No injections.	Results similar to previous run. 4 ppb O ₃ formed after 5 hours on both sides. PM levels low on both sides but somewhat higher on Side A
789	7/16	MOIR/2 surrogate + AMP	Incremental reactivity experiment to evaluate AMP mechanism. ~50 ppb AMP injected into Side B.	Results shown on Table 6, Table 8 and Figure 6.
790	7/17	MIR surrogate + ethanolamine	Incremental reactivity experiment to evaluate ethanolamine mechanism. ~100 ppb ethanolamine injected into Side A.	Effect of ethanolamine on gas-phase results was unexpectedly small, but effect on PM was large. Results shown on Table 6, Table 8 and Figure 7.
791	7/18	MOIR/2 surrogate + ethanolamine	Incremental reactivity experiment to evaluate ethanolamine mechanism. ~50 ppb ethanolamine injected into Side A.	Effect of ethanolamine on gas-phase results was unexpectedly small, but effect on PM was large. Results shown on Table 6, Table 8 and Figure 7.
792	7/19	MOIR/2 surrogate + AMP	Incremental reactivity experiment to evaluate AMP mechanism. ~50 ppb AMP injected into Side A.	Results shown on Table 6, Table 8 and Figure 6.
793	7/24	MIR surrogate + <i>d</i> -Limonene	Incremental reactivity experiment to evaluate <i>d</i> -limonene mechanism. 35 ppb <i>d</i> -limonene injected into Side A.	Results shown on Table 6, Table 8 and Figure 11.
794	7/25	<i>d</i> -Limonene - NO _x Irradiation	Evaluate <i>d</i> -limonene mechanism in the absence of other reactants. See Table 7.	Data on Side A not useable because of instrument and sampling problem. Results for Side B shown on Table 7 and Figure 12
795	7/26	<i>d</i> -Limonene - NO _x Irradiation	Evaluate <i>d</i> -limonene mechanism in the absence of other reactants. See Table 7.	Results shown on Table 7 and Figure 12

Table B-1 (continued)

Run	Date	Type [b]	Purpose and Conditions	Results
796	7/27	Pure Air Irradiation	Background characterization. No injections.	Unusually high O ₃ and PM formation on both sides, with higher levels on Side A. Chamber apparently contaminated, though reason is unknown. 5-Hour O ₃ was 20 and 11 ppb on Sides A and B, respectively.
797	7/30	MIR surrogate + d-Limonene	Incremental reactivity experiment to evaluate d-limonene mechanism. 26 ppb d-limonene injected into Side A.	Results shown on Table 6, Table 8 and Figure 11.
798	8/1	MOIR/2 surrogate + ethanolamine	Incremental reactivity experiment to evaluate ethanolamine mechanism. ~100 ppb ethanolamine injected into Side A.	Effect on O ₃ formation was relatively small. Results shown on Table 6, Table 8 and Figure 11.
799	8/3	MIR surrogate + AMP	Evaluate AMP mechanism with lower added AMP levels. ~60 ppb AMP injected into Side A.	Results shown on Table 6, Table 8 and Figure 6.
801	8/7	Pure Air Irradiation	Background characterization. No injections.	5-Hour O ₃ was 7 and 3 ppb on Sides A and B, respectively. PM levels low on both sides but somewhat higher on Side A.
802	8/8	Pure Air Irradiation	Background characterization. No injections.	Results similar to previous run. 5-Hour O ₃ was 5 and 2 ppb on Sides A and B, respectively. PM levels low on both sides but somewhat higher on Side A.
804	8/13	MOIR/2 surrogate + d-limonene	Incremental reactivity experiment to evaluate d-limonene mechanism. 25 ppb d-limonene injected into Side A.	Results shown on Table 6, Table 8 and Figure 11.
805	8/14	MOIR/2 surrogate + ethanolamine	Incremental reactivity experiment to evaluate ethanolamine mechanism. ~250 ppb ethanolamine injected into Side A.	Results shown on Table 6, Table 8 and Figure 7.
806	8/15	MOIR/2 surrogate + <i>t</i> -butyl amine	Incremental reactivity experiment to evaluate <i>t</i> -butyl amine mechanism. ~250 ppb <i>t</i> -butyl amine injected into Side A.	<i>t</i> -Butyl amine caused significant inhibition of gas-phase reactivity. Results shown on Table 6, Table 8 and Figure 7.
807	8/16	MOIR/2 surrogate + isopropyl amine	Incremental reactivity experiment to evaluate isopropyl amine mechanism. ~250 ppb isopropyl amine injected into Side A.	Isopropyl amine enhanced rate of O ₃ formation. Results shown on Table 6, Table 8 and Figure 7.

Table B-1 (continued)

Run	Date	Type [b]	Purpose and Conditions	Results
808	8/17	CO - NO _x Irradiation	Characterize chamber radical source. ~25 ppb NO _x and 60 ppm CO injected into both sides.	Data indicated that radical source rate was in normal range for Side A. No useable data for Side B because of sampling problems. See Figure 4.
809	8/18	Pure Air Irradiation	Background characterization. No injections.	5-Hour O ₃ was 6 and 2 ppb on Sides A and B, respectively. PM levels low on both sides but somewhat higher on Side A.

[a] “Surrogate” refers to the 8-component “Full Surrogate” as used in previous environmental chamber incremental reactivity studies in our laboratories, except that formaldehyde was removed and the other ROG components were increased by 10% to yield approximately the same reactivity as discussed by Carter and Malkina (2005). The designation “MIR Surrogate” refers to experiments with 0.55 ppmC base case surrogate and 30 ppb NO_x. The designation “MOIR/2 Surrogate” refers to experiments with 1.1 ppmC base case surrogate and 25 ppb NO_x.

APPENDIX C. UPDATED VOC AND ATMOSPHERIC REACTIVITY LISTING

Table C-1. Listing of VOCs for which atmospheric ozone impact estimates are available, their representation in the model, and their calculated atmospheric reactivity values in various reactivity scales. This tabulation is current as of December 20, 2007.

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)			
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR
carbon monoxide	630-08-0	28.01	Exp	1	2	0	1	0.052	0.038	0.029	0.035±0.007
methane	74-82-8	16.04	Exp	1		0	6	0.014	0.008	0.006	0.008±0.002
ethane	74-84-0	30.07	Exp	1	3	0	1	0.26	0.183	0.132	0.163±0.043
propane	74-98-6	44.10	Exp	1	3	0	1	0.46	0.32	0.23	0.28±0.07
n-butane	106-97-8	58.12	Exp	1	2	0	1	1.08	0.71	0.48	0.62±0.17
n-pentane	109-66-0	72.15	Exp	1		0	6	1.22	0.80	0.51	0.69±0.21
n-hexane	110-54-3	86.18	Exp	1	3	0	2	1.14	0.76	0.44	0.63±0.21
n-heptane	142-82-5	100.20	Exp	1		0	6	0.97	0.64	0.33	0.51±0.20
n-octane	111-65-9	114.23	Exp	1	1	0	2	0.80	0.53	0.23	0.40±0.19
n-nonane	111-84-2	128.26	Exp	1		0,+	6b	0.68	0.45	0.171	0.32±0.18
n-decane	124-18-5	142.28	Exp	1		0,+	6b	0.59	0.39	0.129	0.27±0.17
n-undecane	1120-21-4	156.31	Exp	1		0,+	6b	0.52	0.35	0.104	0.23±0.15
n-dodecane	112-40-3	170.33	Exp	1	2	0,+	3b	0.47	0.32	0.088	0.21±0.15
n-tridecane	629-50-5	184.36	Exp	1		0,+	6b	0.45	0.30	0.083	0.198±0.140
n-tetradecane	629-59-4	198.39	Exp	1	2	0,+	3b	0.43	0.29	0.084	0.194±0.136
n-pentadecane	629-62-9	212.41	Exp	1	4	0,+	3b	0.42	0.28	0.085	0.189±0.130
n-c16	544-76-3	226.44	AdjP	1	3	0,+	3b	0.36	0.25	0.051	0.156±0.136
n-c17	629-78-7	240.47	LM			0,+	7b	0.34	0.24	0.048	0.147±0.128
n-c18	593-45-3	254.49	LM			0,+	7b	0.32	0.23	0.045	0.138±0.121
n-c19	629-92-5	268.52	LM			0,+	7b	0.31	0.21	0.043	0.131±0.115
n-c20	112-95-8	282.55	LM			0,+	7b	0.29	0.20	0.041	0.125±0.109
n-c21	629-94-7	296.57	LM			0,+	7b	0.28	0.194	0.039	0.119±0.104
n-c22	629-97-0	310.60	LM			0,+	7b	0.27	0.186	0.037	0.113±0.099
isobutane	75-28-5	58.12	Exp	1	3	0	2	1.18	0.70	0.48	0.63±0.16
branched c5 alkanes		72.15	LM			0	8	1.36	0.88	0.61	0.78±0.20
neopentane	463-82-1	72.15	Exp	1		0	6	0.65	0.38	0.26	0.34±0.09
iso-pentane	78-78-4	72.15	Exp	1		0	6	1.36	0.88	0.61	0.78±0.20
branched c6 alkanes		86.18	LM			0	8	1.22	0.77	0.51	0.67±0.19
2,2-dimethyl butane	75-83-2	86.18	Exp	1		0	6	1.11	0.67	0.43	0.59±0.17
2,3-dimethyl butane	79-29-8	86.18	Exp	1		0	6	0.90	0.61	0.41	0.53±0.13
2-methyl pentane	107-83-5	86.18	Exp	1		0	6	1.40	0.84	0.52	0.72±0.23
3-methylpentane	96-14-0	86.18	Exp	1		0	6	1.69	1.04	0.68	0.91±0.26
branched c7 alkanes		100.20	LM			0	8	1.38	0.81	0.47	0.68±0.23
2,2,3-trimethyl butane	464-06-2	100.20	Exp	1		0	6	1.05	0.62	0.39	0.54±0.15
2,2-dimethyl pentane	590-35-2	100.20	Exp	1		0	6	1.04	0.63	0.38	0.53±0.17
2,3-dimethyl pentane	565-59-3	100.20	Exp			0	7	1.25	0.77	0.48	0.66±0.20
2,4-dimethyl pentane	108-08-7	100.20	Exp	1		0	6	1.46	0.84	0.51	0.72±0.23
2-methyl hexane	591-76-4	100.20	AdjP			0	7	1.09	0.68	0.37	0.55±0.20
3,3-dimethyl pentane	562-49-2	100.20	Exp			0	7	1.12	0.70	0.45	0.61±0.18
3-methyl hexane	589-34-4	100.20	Exp			0	7	1.50	0.88	0.51	0.74±0.26
3-ethylpentane	617-78-7	100.20	Exp			0	7	1.78	1.03	0.64	0.89±0.28

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
branched c8 alkanes		114.23	LM				0	8	1.33	0.77	0.40	0.63±0.25
2,2,3,3-tetramethyl butane	594-82-1	114.23	Exp	1			0	6	0.30	0.183	0.101	0.151±0.053
2,2,4-trimethyl pentane	540-84-1	114.23	Exp	1	3		0	2	1.20	0.67	0.41	0.58±0.18
2,2-dimethyl hexane	590-73-8	114.23	Exp	1			0	6	0.94	0.55	0.29	0.45±0.17
2,3,4-trimethyl pentane	565-75-3	114.23	Exp	1			0	6	0.95	0.60	0.35	0.50±0.16
2,3-dimethyl hexane	584-94-1	114.23	Exp				0	7	1.09	0.67	0.37	0.55±0.20
2,4-dimethyl hexane	589-43-5	114.23	Exp				0	7	1.61	0.90	0.48	0.74±0.28
2,5-dimethyl hexane	592-13-2	114.23	Exp				0	7	1.35	0.78	0.42	0.64±0.24
2-methyl heptane	592-27-8	114.23	Exp				0	7	0.97	0.61	0.29	0.48±0.20
3-methyl heptane	589-81-1	114.23	Exp				0	7	1.12	0.70	0.35	0.55±0.22
4-methyl heptane	589-53-7	114.23	Exp				0	7	1.14	0.68	0.34	0.54±0.22
2,3,3-trimethylpentane	560-21-4	114.23	Exp				0	7	0.95	0.60	0.37	0.51±0.15
3,3-dimethylhexane	563-16-6	114.23	Exp				0	7	1.15	0.68	0.38	0.57±0.20
2,2,3-trimethyl-pentane	564-02-3	114.23	Exp				0	7	1.15	0.66	0.39	0.56±0.18
3,4-dimethylhexane	583-48-2	114.23	Exp				0	7	1.40	0.83	0.48	0.70±0.24
3-ethyl 2-methyl pentane	609-26-7	114.23	Exp				0	7	1.24	0.72	0.41	0.61±0.21
branched c9 alkanes		128.26	LM				0	8b	1.03	0.61	0.27	0.47±0.22
2,2,5-trimethyl hexane	3522-94-9	128.26	Exp				0	7b	1.05	0.59	0.31	0.49±0.19
2,3,5-trimethyl hexane	1069-53-0	128.26	AdjP	1			0	6b	1.12	0.66	0.34	0.54±0.21
2,4-dimethyl heptane	2213-23-2	128.26	Exp				0	7b	1.27	0.71	0.33	0.56±0.25
2-methyl octane	3221-61-2	128.26	Exp	1			0,+	6b	0.73	0.47	0.183	0.34±0.18
3,3-diethyl pentane	1067-20-5	128.26	Exp	1			0,+	6b	1.13	0.68	0.39	0.57±0.20
3,5-dimethyl heptane	926-82-9	128.26	Exp				0	7b	1.42	0.83	0.41	0.66±0.28
4-ethyl heptane	2216-32-2	128.26	Exp				0	7b	1.11	0.65	0.31	0.51±0.23
4-methyl octane	2216-34-4	128.26	Exp	1			0,+	6b	0.85	0.53	0.23	0.40±0.20
2,4,4-trimethylhexane	16747-30-1	128.26	Exp				0	7b	1.25	0.70	0.37	0.58±0.22
3,3-dimethylheptane	4032-86-4	128.26	Exp				0	7b	1.04	0.62	0.32	0.50±0.20
4,4-dimethylheptane	1068-19-5	128.26	Exp				0	7b	1.18	0.65	0.33	0.53±0.22
2,2-dimethylheptane	1071-26-7	128.26	Exp				0	7b	0.92	0.53	0.26	0.42±0.18
2,2,4-trimethylhexane	16747-26-5	128.26	Exp				0	7b	1.17	0.64	0.31	0.52±0.21
2,6-dimethylheptane	1072-05-5	128.26	Exp				0	7b	0.94	0.55	0.25	0.43±0.20
2,3-dimethylheptane	3074-71-3	128.26	Exp				0	7b	0.98	0.61	0.30	0.48±0.20
2,5-dimethylheptane	2216-30-0	128.26	Exp				0	7b	1.23	0.73	0.36	0.58±0.24
3-methyloctane	2216-33-3	128.26	Exp				0	7b	0.88	0.55	0.24	0.42±0.20
3,4-dimethylheptane	922-28-1	128.26	Exp				0	7b	1.13	0.69	0.35	0.55±0.22
3-ethylheptane	15869-80-4	128.26	Exp				0	7b	0.99	0.60	0.27	0.46±0.21
branched c10 alkanes		142.28	LM				0	8b	0.83	0.50	0.20	0.37±0.19
2,4,6-trimethyl heptane	2613-61-8	142.28	Exp				0	7b	1.18	0.64	0.28	0.50±0.24
2,4-dimethyl octane	4032-94-4	142.28	Exp				0	7b	0.92	0.54	0.22	0.41±0.21
2,6-dimethyl octane	2051-30-1	142.28	Exp	1	2		0,+	2b	0.98	0.56	0.25	0.43±0.21
2-methyl nonane	871-83-0	142.28	Exp	1	2		0,+	2b	0.63	0.41	0.135	0.28±0.18
3,4-diethyl hexane	19398-77-7	142.28	Exp	1	2		0,+	2b	0.81	0.49	0.24	0.38±0.16
3-methyl nonane	5911-04-6	142.28	Exp				0	7b	0.66	0.42	0.145	0.30±0.18
4-methyl nonane	17301-94-9	142.28	Exp				0	7b	0.76	0.47	0.181	0.34±0.19
4-propyl heptane	3178-29-8	142.28	Exp				0	7b	0.91	0.54	0.23	0.41±0.20
2,4,4-trimethylheptane		142.28	Exp				0	7b	1.22	0.65	0.31	0.53±0.23
2,5,5-trimethylheptane		142.28	Exp				0	7b	1.15	0.65	0.33	0.53±0.21
3,3-dimethyloctane	4110-44-5	142.28	Exp				0	7b	1.00	0.58	0.28	0.46±0.20
4,4-dimethyloctane	15869-95-1	142.28	Exp				0	7b	1.04	0.59	0.28	0.47±0.21

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
			Rep	k a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2,2-dimethyloctane	15869-87-1	142.28	Exp			0	7b	0.76	0.44	0.185	0.33±0.16
2,2,4-trimethylheptane	14720-74-2	142.28	Exp			0	7b	1.08	0.58	0.26	0.46±0.21
2,2,5-trimethylheptane		142.28	Exp			0	7b	1.17	0.65	0.34	0.54±0.21
2,3,6-trimethylheptane	4032-93-3	142.28	AdjP			0	7b	0.80	0.50	0.21	0.37±0.18
2,3-dimethyloctane	7146-60-3	142.28	Exp			0	7b	0.76	0.48	0.20	0.36±0.18
2,5-dimethyloctane		142.28	Exp			0	7b	0.92	0.55	0.22	0.41±0.21
2-methyl-3-ethylheptane	14676-29-0	142.28	Exp			0	7b	0.89	0.54	0.24	0.41±0.20
4-ethyloctane	15869-86-0	142.28	AdjP			0	7b	0.68	0.44	0.131	0.30±0.20
branched c11 alkanes		156.31	LM			0	8b	0.63	0.40	0.130	0.28±0.17
2,3,4,6-tetramethyl heptane	61868-54-0	156.31	Exp			0	7b	1.00	0.59	0.27	0.46±0.21
2,6-dimethyl nonane	17302-28-2	156.31	Exp			0	7b	0.69	0.42	0.149	0.30±0.17
3,5-diethyl heptane	61869-02-1	156.31	Exp			0	7b	0.99	0.58	0.23	0.43±0.23
3-methyl decane	13151-34-3	156.31	Exp			0	7b	0.55	0.36	0.106	0.24±0.16
4-methyl decane	2847-72-5	156.31	Exp			0	7b	0.59	0.38	0.118	0.26±0.17
branched c12 alkanes		170.33	LM			0	8b	0.54	0.35	0.077	0.22±0.17
2,3,5,7-tetramethyl octane	62199-32-0	170.33	Exp			0	7b	0.81	0.47	0.174	0.34±0.19
2,6-diethyl octane	62183-94-2	170.33	Exp			0	7b	0.86	0.51	0.22	0.39±0.19
3,6-dimethyl decane	17312-53-7	170.33	AdjP			0	7b	0.59	0.38	0.089	0.24±0.18
3-methyl undecane	1002-43-3	170.33	Exp			0	7b	0.50	0.33	0.091	0.22±0.15
5-methyl undecane	1632-70-8	170.33	AdjP			0	7b	0.46	0.31	0.040	0.179±0.169
branched c13 alkanes		184.36	LM			0	8b	0.51	0.33	0.084	0.21±0.16
2,3,6-trimethyl 4-isopropyl heptane		184.36	Exp			0	7b	0.83	0.48	0.20	0.36±0.19
2,4,6,8-tetramethyl nonane	14638-54-1	184.36	AdjP			0	7b	0.66	0.38	0.105	0.26±0.18
3,6-dimethyl undecane	17301-28-9	184.36	Exp			0	7b	0.60	0.37	0.119	0.26±0.16
3,7-diethyl nonane		184.36	Exp			0	7b	0.79	0.45	0.176	0.34±0.18
3-methyl dodecane	17312-57-1	184.36	Exp			0	7b	0.46	0.31	0.082	0.20±0.14
5-methyl dodecane	17453-93-9	184.36	AdjP			0	7b	0.38	0.26	0.017	0.143±0.157
branched c14 alkanes		198.39	LM			0	8b	0.47	0.30	0.077	0.197±0.146
2,4,5,6,8-pentamethyl nonane		198.39	Exp			0	7b	0.84	0.51	0.20	0.37±0.20
2-methyl 3,5-diisopropyl heptane		198.39	AdjP			0	7b	0.47	0.30	0.066	0.189±0.150
3,7-dimethyl dodecane	82144-67-0	198.39	Exp			0	7b	0.54	0.34	0.107	0.23±0.15
3,8-diethyl decane	6224-52-8	198.39	AdjP			0	7b	0.50	0.33	0.076	0.21±0.16
3-methyl tridecane	6418-41-3	198.39	Exp			0	7b	0.43	0.29	0.077	0.188±0.137
6-methyl tridecane	13287-21-3	198.39	AdjP			0	7b	0.37	0.25	0.019	0.139±0.152
branched c15 alkanes		212.41	LM			0	8b	0.42	0.28	0.067	0.179±0.138
2,6,8-trimethyl 4-isopropyl nonane		212.41	Exp			0	7b	0.54	0.33	0.099	0.23±0.15
3,7-dimethyl tridecane		212.41	Exp			0	7b	0.47	0.30	0.091	0.20±0.14
3,9-diethyl undecane	13286-72-1	212.41	Exp			0	7b	0.43	0.29	0.078	0.188±0.138
3-methyl tetradecane	18435-22-8	212.41	Exp			0	7b	0.40	0.27	0.074	0.178±0.130
6-methyl tetradecane	26730-16-5	212.41	AdjP			0	7b	0.34	0.24	0.015	0.127±0.144
branched c16 alkanes		226.44	LM			0	8b	0.40	0.26	0.074	0.174±0.127
2,7-dimethyl 3,5-diisopropyl heptane		226.44	AdjP			0	7b	0.44	0.28	0.057	0.176±0.148
3-methyl pentadecane	2882-96-4	226.44	Exp			0	7b	0.38	0.26	0.072	0.170±0.124
4,8-dimethyl tetradecane	175032-36-7	226.44	Exp			0	7b	0.41	0.27	0.076	0.180±0.130

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]				Reactivity (gm O ₃ / gm VOC)					
			Rep	k	a	Expt Bias	Unc	MIR	MOIR	EBIR	Base	
7-methyl pentadecane	6165-40-8	226.44	Exp				0	7b	0.38	0.26	0.071	0.168±0.124
branched c17 alkanes		240.47	LM				0	8b	0.37	0.25	0.069	0.164±0.120
branched c18 alkanes		254.49	LM				0	8b	0.35	0.24	0.066	0.155±0.113
branched c19 alkanes		268.52	LM				0	8b	0.33	0.22	0.062	0.147±0.107
branched c20 alkanes		282.55	LM				0	8b	0.32	0.21	0.059	0.140±0.102
branched c21 alkanes		296.57	LM				0	8b	0.30	0.20	0.056	0.133±0.097
branched c22 alkanes		310.60	LM				0	8b	0.29	0.193	0.054	0.127±0.093
cyclopropane	75-19-4	42.08	Exp	1			0	6	0.081	0.056	0.039	0.049±0.014
cyclobutane	287-23-0	56.11	Exp	1			0	6	1.11	0.72	0.48	0.63±0.21
cyclopentane	287-92-3	70.13	AdjP	1			0	6	2.24	1.31	0.82	1.14±0.35
c6 cycloalkanes		84.16	LM				0	8	1.14	0.73	0.41	0.60±0.21
cyclohexane	110-82-7	84.16	AdjP	1	2		0	2	1.14	0.73	0.41	0.60±0.21
isopropyl cyclopropane	3638-35-5	84.16	Exp	1			0	6	1.14	0.74	0.49	0.65±0.18
methylcyclopentane	96-37-7	84.16	AdjP				0	7	2.05	1.14	0.66	0.97±0.34
1,1-dimethylcyclopentane	1638-26-2	98.19	AdjP				0	7	0.99	0.58	0.29	0.47±0.19
1,2-dimethylcyclopentane	2452-99-5	98.19	AdjP				0	7	1.86	1.00	0.54	0.84±0.32
c7 cycloalkanes		98.19	LM				0	7	1.56	0.90	0.46	0.72±0.29
1,3-dimethyl cyclopentane	2453-00-1	98.19	AdjP				0	7	1.81	0.97	0.51	0.80±0.31
cycloheptane	291-64-5	98.19	AdjP	1			0	6	1.80	1.00	0.53	0.82±0.33
ethyl cyclopentane	1640-89-7	98.19	AdjP				0	7	1.87	1.03	0.55	0.85±0.33
methylcyclohexane	108-87-2	98.19	AdjP	1			0	6	1.56	0.90	0.46	0.72±0.29
c8 bicycloalkanes		110.20	LM				0	8	1.39	0.80	0.41	0.65±0.26
1,1,2-trimethylcyclopentane	4259-00-1	112.21	Exp				0	7	1.02	0.58	0.27	0.46±0.20
1,1,3-trimethylcyclopentane	4516-69-2	112.21	Exp				0	7	0.92	0.53	0.23	0.41±0.19
1,1-dimethyl cyclohexane	590-66-9	112.21	Exp				0	7	1.12	0.65	0.31	0.51±0.22
1,2,3-trimethylcyclopentane		112.21	Exp				0	7	1.50	0.83	0.42	0.67±0.28
1,2,4-trimethylcyclopentane		112.21	Exp				0	7	1.42	0.76	0.36	0.61±0.26
1-methyl-3-ethylcyclopentane		112.21	AdjP				0	7	1.51	0.82	0.39	0.66±0.29
1,2-dimethylcyclohexane	583-57-3	112.21	AdjP				0	7	1.27	0.77	0.35	0.59±0.27
1,4-dimethylcyclohexane	589-90-2	112.21	AdjP				0	7	1.48	0.81	0.37	0.64±0.29
c8 cycloalkanes		112.21	LM				0	8	1.35	0.78	0.38	0.62±0.26
1,3-dimethyl cyclohexane	591-21-9	112.21	AdjP				0	7	1.39	0.76	0.34	0.59±0.28
cyclooctane	292-64-8	112.21	AdjP	1			0	6	1.31	0.74	0.32	0.57±0.28
ethylcyclohexane	1678-91-7	112.21	Exp				0	7	1.35	0.78	0.38	0.62±0.26
propyl cyclopentane	2040-96-2	112.21	AdjP				0	7	1.55	0.84	0.40	0.67±0.30
cis-hydrindane; bicyclo[4.3.0]nonane	496-10-6	124.22	AdjP				0	7b	1.16	0.64	0.23	0.47±0.27
c9 bicycloalkanes		124.22	LM				0	8b	1.25	0.71	0.31	0.55±0.26
1,2,3-trimethylcyclohexane	1678-97-3	126.24	AdjP				0	7b	1.08	0.65	0.26	0.48±0.25
1,3,5-trimethylcyclohexane	1839-63-0	126.24	Exp				0	7b	1.03	0.57	0.21	0.42±0.23
c9 cycloalkanes		126.24	LM				0	8b	1.23	0.69	0.31	0.54±0.26
1,1,3-trimethyl cyclohexane	3073-66-3	126.24	Exp	1			0	6b	1.08	0.60	0.25	0.46±0.23

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]				Reactivity (gm O ₃ / gm VOC)					
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
1-ethyl-4-methyl cyclohexane	3728-56-1	126.24	AdjP				0	7b	1.30	0.72	0.30	0.55±0.27
propyl cyclohexane	1678-92-8	126.24	Exp				0	7b	1.17	0.67	0.31	0.52±0.24
c10 bicycloalkanes		138.25	LM				0	8b	0.97	0.57	0.24	0.43±0.22
isobutylcyclohexane; (2- methylpropyl) cyclohexane	1678-98-4	140.27	LM				0	8b	0.88	0.53	0.22	0.40±0.20
sec-butylcyclohexane	7058-01-7	140.27	LM				0	8b	0.88	0.53	0.22	0.40±0.20
c10 cycloalkanes		140.27	LM				0	8b	0.96	0.56	0.23	0.42±0.21
1,3-diethyl-cyclohexane	1678-99-5	140.27	AdjP				0	7b	1.13	0.64	0.26	0.48±0.25
1,4-diethyl-cyclohexane	1679-00-1	140.27	Exp				0	7b	1.11	0.62	0.26	0.47±0.24
1-methyl-3-isopropyl cyclohexane	16580-24-8	140.27	Exp				0	7b	0.90	0.54	0.22	0.40±0.20
butyl cyclohexane	1678-93-9	140.27	Exp	1			0	6b	0.88	0.53	0.22	0.40±0.20
c11 bicycloalkanes		152.28	LM				0	8b	0.80	0.48	0.172	0.34±0.20
c11 cycloalkanes		154.29	LM				0	8b	0.79	0.47	0.169	0.34±0.20
1,3-diethyl-5-methyl cyclohexane	164259-42-1	154.29	Exp				0	7b	0.93	0.52	0.20	0.38±0.21
1-ethyl-2-propyl cyclohexane	62238-33-9	154.29	AdjP				0	7b	0.70	0.44	0.140	0.30±0.20
pentyl cyclohexane	4292-92-6	154.29	Exp				0	7b	0.74	0.45	0.172	0.33±0.18
c12 tricycloalkanes		164.29	LM				0	8b	0.71	0.42	0.130	0.29±0.19
c12 bicycloalkanes		166.30	LM				0	8b	0.70	0.42	0.128	0.29±0.19
c12 cycloalkanes		168.32	LM				0	8b	0.69	0.41	0.127	0.29±0.19
1,3,5-triethyl cyclohexane	164259-43-2	168.32	Exp				0	7b	0.92	0.51	0.20	0.38±0.21
1-methyl-4-pentyl cyclohexane	75736-67-3	168.32	Exp				0	7b	0.62	0.38	0.114	0.26±0.18
hexyl cyclohexane	4292-75-5	168.32	AdjP	1	2		0	2b	0.54	0.34	0.065	0.21±0.18
c13 tricycloalkanes		178.31	LM				0	8b	0.61	0.38	0.111	0.26±0.17
c13 bicycloalkanes		180.33	LM				0	8b	0.61	0.37	0.110	0.25±0.17
c13 cycloalkanes		182.35	LM				0	8b	0.60	0.37	0.109	0.25±0.17
1,3-diethyl-5-propyl cyclohexane		182.35	Exp				0	7b	0.86	0.48	0.193	0.36±0.19
1-methyl-2-hexyl- cyclohexane	92031-93-1	182.35	Exp				0	7b	0.49	0.32	0.086	0.21±0.16
heptyl cyclohexane	5617-41-4	182.35	AdjP				0	7b	0.45	0.30	0.049	0.181±0.166
c14 tricycloalkanes		192.34	LM				0	8b	0.57	0.35	0.101	0.24±0.17
c14 bicycloalkanes		194.36	LM				0	8b	0.57	0.35	0.100	0.23±0.16
c14 cycloalkanes		196.37	LM				0	8b	0.56	0.34	0.099	0.23±0.16
1,3-dipropyl-5-ethyl cyclohexane		196.37	Exp				0	7b	0.82	0.46	0.186	0.34±0.18
<i>trans</i> 1-methyl-4-heptyl cyclohexane	205324-73-8	196.37	Exp				0	7b	0.44	0.29	0.069	0.186±0.148
octyl cyclohexane	1795-15-9	196.37	AdjP		2		0	7b	0.42	0.28	0.044	0.168±0.157
c15 tricycloalkanes		206.37	LM				0	8b	0.54	0.33	0.097	0.22±0.16
c15 bicycloalkanes		208.38	LM				0	8b	0.53	0.33	0.096	0.22±0.15
c15 cycloalkanes		210.40	LM				0	8b	0.53	0.32	0.095	0.22±0.15
1,3,5-tripropyl cyclohexane		210.40	Exp				0	7b	0.78	0.43	0.179	0.33±0.17
1-methyl-2-octyl cyclohexane		210.40	AdjP				0	7b	0.42	0.28	0.075	0.182±0.139
nonyl cyclohexane	2883-02-5	210.40	AdjP				0	7b	0.38	0.26	0.034	0.149±0.149

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]			Unc	Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt		Bias	MIR	MOIR	EBIR	Base
c16 tricycloalkanes		220.39	LM				0	8b	0.50	0.31	0.091	0.21±0.15
c16 bicycloalkanes		222.41	LM				0	8b	0.50	0.31	0.090	0.21±0.14
c16 cycloalkanes		224.43	LM				0	8b	0.47	0.29	0.082	0.196±0.142
1,3-propyl-5-butyl cyclohexane		224.43	Exp				0	7b	0.67	0.38	0.152	0.28±0.16
1-methyl-4-nonyl cyclohexane	39762-40-8	224.43	Exp				0	7b	0.39	0.26	0.065	0.166±0.132
decyl cyclohexane	1795-16-0	224.43	AdjP				0	7b	0.35	0.24	0.031	0.138±0.141
c17 tricycloalkanes		234.42	LM				0	8b	0.47	0.29	0.086	0.197±0.137
c17 bicycloalkanes		236.44	LM				0	8b	0.47	0.29	0.085	0.195±0.136
c17 cycloalkanes		238.45	LM				0	8b	0.44	0.28	0.077	0.184±0.134
c18 tricycloalkanes		248.45	LM				0	8b	0.45	0.27	0.081	0.186±0.129
c18 bicycloalkanes		250.46	LM				0	8b	0.44	0.27	0.080	0.185±0.128
c18 cycloalkanes		252.48	LM				0	8b	0.42	0.26	0.073	0.174±0.127
c19 tricycloalkanes		262.47	LM				0	8b	0.42	0.26	0.076	0.176±0.122
c19 bicycloalkanes		264.49	LM				0	8b	0.42	0.26	0.076	0.175±0.121
c19 cycloalkanes		266.51	LM				0	8b	0.39	0.25	0.069	0.165±0.120
c20 tricycloalkanes		276.50	LM				0	8b	0.40	0.25	0.073	0.167±0.116
c20 bicycloalkanes		278.52	LM				0	8b	0.40	0.24	0.072	0.166±0.115
c20 cycloalkanes		280.53	LM				0	8b	0.37	0.23	0.066	0.157±0.114
c21 tricycloalkanes		290.53	LM				0	8b	0.38	0.23	0.069	0.159±0.110
c21 bicycloalkanes		292.54	LM				0	8b	0.38	0.23	0.069	0.158±0.110
c21 cycloalkanes		294.56	LM				0	8b	0.36	0.22	0.063	0.149±0.108
c22 tricycloalkanes		304.55	LM				0	8b	0.36	0.22	0.066	0.152±0.105
c22 bicycloalkanes		306.57	LM				0	8b	0.36	0.22	0.065	0.151±0.105
c22 cycloalkanes		308.58	LM				0	8b	0.34	0.21	0.060	0.142±0.104
ethene	74-85-1	28.05	Exp	1	1	0	3d	8.88	3.72	2.29	3.47±1.30	
propene	115-07-1	42.08	Exp	1	1	0	3d	11.57	4.53	2.79	4.29±1.66	
1-butene	106-98-9	56.11	Exp	1	3	0	3d	9.57	3.83	2.35	3.59±1.33	
c4 terminal alkenes		56.11	LM				0	7	9.57	3.83	2.35	3.59±1.33
1-pentene	109-67-1	70.13	Exp	1		0	6d	7.07	2.87	1.75	2.67±0.99	
3-methyl-1-butene	563-45-1	70.13	Exp	1		0	6d	6.86	2.80	1.72	2.61±0.95	
c5 terminal alkenes		70.13	LM				0	7	7.07	2.87	1.75	2.67±0.99
1-hexene	592-41-6	84.16	Exp	1	4	0	4d	5.35	2.29	1.41	2.11±0.74	
3,3-dimethyl-1-butene	558-37-2	84.16	Exp	1		0	8d	5.68	2.41	1.50	2.23±0.78	
3-methyl-1-pentene	760-20-3	84.16	Exp			0	8	6.00	2.50	1.52	2.31±0.83	
4-methyl-1-pentene	691-37-2	84.16	Exp			0	8	5.55	2.28	1.37	2.11±0.78	
c6 terminal alkenes		84.16	LM				0	8	5.35	2.29	1.41	2.11±0.74
1-heptene	592-76-7	98.19	AdjP	1		0	8d	4.29	1.86	1.09	1.68±0.61	
3,4-dimethyl-1-pentene	7385-78-6	98.19	Exp			0	8	4.72	1.98	1.18	1.81±0.66	
3-methyl-1-hexene	3404-61-3	98.19	Exp			0	8	4.27	1.86	1.10	1.69±0.61	
1-octene	111-66-0	112.21	Exp			0	8	3.14	1.37	0.77	1.22±0.47	
c8 terminal alkenes		112.21	LM				0	8	3.14	1.37	0.77	1.22±0.47
2,4,4-trimethyl-1-pentene	107-39-1	112.21	Exp			0	8	3.31	1.23	0.66	1.13±0.52	
1-nonene	124-11-8	126.24	Exp			0	8	2.49	1.11	0.60	0.97±0.38	
c9 terminal alkenes		126.24	LM				0	8	2.49	1.11	0.60	0.97±0.38
1-decene	872-05-9	140.27	Exp			0	8	2.07	0.93	0.49	0.80±0.33	
c10 terminal alkenes		140.27	LM				0	8	2.07	0.93	0.49	0.80±0.33
1-undecene	821-95-4	154.29	Exp			0	8	1.77	0.80	0.41	0.68±0.29	

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]					Reactivity (gm O ₃ / gm VOC)					
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base	
c11 terminal alkenes		154.29	LM					0	8	1.77	0.80	0.41	0.68±0.29
c12 terminal alkenes		168.32	LM					0	8	1.56	0.71	0.36	0.60±0.26
1-dodecene	112-41-4	168.32	Exp					0	8	1.56	0.71	0.36	0.60±0.26
1-tridecene	2437-56-1	182.35	Exp					0	8	1.40	0.64	0.32	0.54±0.23
c13 terminal alkenes		182.35	LM					0	8	1.40	0.64	0.32	0.54±0.23
1-tetradecene	1120-36-1	196.37	Exp					0	8	1.27	0.58	0.29	0.49±0.21
c14 terminal alkenes		196.37	LM					0	8	1.27	0.58	0.29	0.49±0.21
1-pentadecene	13360-61-7	210.40	LM					0	8	1.18	0.54	0.27	0.46±0.20
c15 terminal alkenes		210.40	LM					0	8	1.18	0.54	0.27	0.46±0.20
isobutene	115-11-7	56.11	Exp	1	3			0	3	6.31	2.23	1.23	2.10±1.00
2-methyl-1-butene	563-46-2	70.13	Exp	1				0	8	6.38	2.35	1.35	2.21±0.97
2,3-dimethyl-1-butene	563-78-0	84.16	Exp					0	8	4.71	1.78	1.01	1.65±0.71
2-ethyl-1-butene	760-21-4	84.16	Exp					0	8	5.04	1.89	1.06	1.76±0.77
2-methyl-1-pentene	763-29-1	84.16	Exp	1				0	8	5.25	1.94	1.09	1.82±0.80
2,4-dimethyl-1-pentene	2213-32-3	98.19	AdjP					0	8	5.91	2.40	1.42	2.21±0.86
2,3-dimethyl-1-pentene	3404-72-6	98.19	Exp					0	8	5.04	2.10	1.21	1.91±0.74
3,3-dimethyl-1-pentene	3404-73-7	98.19	Exp					0	8	4.75	2.13	1.35	1.96±0.64
2-methyl-1-hexene	6094-02-6	98.19	Exp					0	8	4.99	2.08	1.19	1.89±0.74
2,3,3-trimethyl-1-butene	594-56-9	98.19	Exp					0	8	4.42	1.79	1.06	1.65±0.64
c7 terminal alkenes		98.19	LM					0	8	4.29	1.86	1.09	1.68±0.61
3-methyl-2-isopropyl-1-butene	111823-35-9	112.21	AdjP					0	8	3.21	1.36	0.74	1.21±0.49
4,4-dimethyl-1-pentene	762-62-9	126.24	Exp					0	8	3.02	1.29	0.72	1.15±0.45
<i>cis</i> -2-butene	590-18-1	56.11	Exp	1				0	6	14.26	5.26	3.18	5.06±2.18
<i>trans</i> -2-butene	624-64-6	56.11	Exp	1	1			0	3	15.20	5.51	3.29	5.30±2.37
c4 internal alkenes		56.11	LM					0	7	14.73	5.39	3.23	5.17±2.27
2-methyl-2-butene	513-35-9	70.13	Exp	1				0	6	14.20	4.83	2.73	4.68±2.41
<i>cis</i> -2-pentene	627-20-3	70.13	Exp	1				0	6	10.28	3.99	2.46	3.79±1.47
<i>trans</i> -2-pentene	646-04-8	70.13	Exp	1				0	6	10.47	4.02	2.46	3.82±1.51
2-pentenenes		70.13	LM					0	7	10.38	4.01	2.46	3.80±1.49
c5 internal alkenes		70.13	LM					0	7	10.38	4.01	2.46	3.80±1.49
3-methyl- <i>trans</i> -2-pentene	616-12-6	84.16	Exp					0	7	11.66	4.15	2.39	3.98±1.92
2,3-dimethyl-2-butene	563-79-1	84.16	Exp	1				0	8	12.58	4.03	2.14	3.94±2.30
2-methyl-2-pentene	625-27-4	84.16	Exp	1				0	8	11.03	3.88	2.22	3.73±1.79
<i>cis</i> 4-methyl-2-pentene		84.16	LM					0	8	8.04	3.14	1.91	2.96±1.16
<i>cis</i> -2-hexene	7688-21-3	84.16	Exp					0	8	8.22	3.22	1.98	3.04±1.17
<i>cis</i> -3-hexene	7642-09-3	84.16	Exp					0	8	7.44	3.03	1.89	2.84±1.02
<i>cis</i> -3-methyl-2-pentene	922-62-3	84.16	Exp					0	8	12.52	4.40	2.53	4.23±2.07
<i>trans</i> 3-methyl-2-pentene	20710-38-7	84.16	Exp					0	8	13.20	4.61	2.64	4.44±2.18
<i>trans</i> 4-methyl-2-pentene	674-76-0	84.16	Exp	1				0	8	8.04	3.14	1.91	2.96±1.16
<i>trans</i> -2-hexene	4050-45-7	84.16	Exp					0	8	8.55	3.29	1.99	3.11±1.24
<i>trans</i> -3-hexene	13269-52-8	84.16	Exp					0	8	7.42	3.01	1.87	2.82±1.02
2-hexenes	592-43-8	84.16	LM					0	8	8.38	3.25	1.98	3.08±1.21
c6 internal alkenes		84.16	LM					0	8	8.38	3.25	1.98	3.08±1.21
4,4-dimethyl- <i>cis</i> -2-pentene	762-63-0	98.19	Exp					0	8	6.59	2.56	1.53	2.41±0.98
2,4-dimethyl-2-pentene	625-65-0	98.19	Exp					0	8	9.31	3.27	1.84	3.13±1.53
2-methyl-2-hexene	2738-19-4	98.19	Exp					0	8	9.50	3.33	1.86	3.18±1.57
3-ethyl-2-pentene	816-79-5	98.19	Exp					0	8	9.76	3.54	2.05	3.38±1.60
3-methyl- <i>trans</i> -3-hexene	3899-36-3	98.19	Exp					0	8	9.70	3.54	2.05	3.37±1.54

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]					Reactivity (gm O ₃ / gm VOC)				
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
cis-2-heptene	6443-92-1	98.19	Exp				0	8	7.08	2.79	1.69	2.62±1.03
2-methyl-trans-3-hexene	692-24-0	98.19	Exp				0	8	6.11	2.51	1.55	2.34±0.85
3-methyl-cis-3-hexene	4914-89-0	98.19	Exp				0	8	9.69	3.53	2.05	3.36±1.54
3,4-dimethyl-cis-2-pentene	4914-91-4	98.19	Exp				0	8	9.19	3.23	1.79	3.08±1.56
2,3-dimethyl-2-pentene	10574-37-5	98.19	Exp	1			0	8	9.79	3.27	1.75	3.15±1.74
cis-3-heptene	7642-10-6	98.19	Exp				0	8	6.18	2.54	1.56	2.36±0.86
trans 4,4-dimethyl-2-pentene	690-08-4	98.19	Exp	1			0	8	6.58	2.56	1.53	2.41±0.98
trans-2-heptene	14686-13-6	98.19	Exp	1			0	8	7.06	2.79	1.69	2.62±1.02
trans-3-heptene	14686-14-7	98.19	Exp				0	8	6.17	2.53	1.56	2.36±0.86
2-heptenes		98.19	LM				0	8	6.17	2.54	1.56	2.36±0.86
c7 internal alkenes		98.19	LM				0	8	6.17	2.53	1.56	2.36±0.86
trans-2-octene	13389-42-9	112.21	Exp				0	8	5.92	2.34	1.40	2.19±0.87
2-methyl-2-heptene	627-97-4	112.21	Exp				0	8	8.35	2.95	1.64	2.81±1.38
cis-4-octene	7642-15-1	112.21	AdjP				0	8	4.60	1.93	1.13	1.75±0.67
trans 2,2-dimethyl 3-hexene	690-93-7	112.21	Exp				0	8	4.86	2.05	1.26	1.89±0.68
trans 2,5-dimethyl 3-hexene	692-70-6	112.21	AdjP				0	8	4.68	1.99	1.24	1.84±0.65
trans-3-octene	14919-01-8	112.21	AdjP				0	8	5.20	2.18	1.31	2.00±0.74
trans-4-octene	14850-23-8	112.21	AdjP	1			0	8	4.69	1.94	1.13	1.77±0.69
3-octenes		112.21	LM				0	8	5.20	2.18	1.31	2.00±0.74
c8 internal alkenes		112.21	LM				0	8	4.69	1.94	1.13	1.77±0.69
2,4,4-trimethyl-2-pentene	107-40-4	112.21	Exp				0	8	6.30	2.28	1.26	2.14±1.02
4-nonene	2198-23-4	126.24	LM				0	8	4.42	1.86	1.10	1.69±0.64
3-nonenes		126.24	LM				0	8	4.42	1.86	1.10	1.69±0.64
c9 internal alkenes		126.24	LM				0	8	4.42	1.86	1.10	1.69±0.64
trans-4-nonene	10405-85-3	126.24	AdjP				0	8	4.42	1.86	1.10	1.69±0.64
3,4-diethyl-2-hexene	59643-70-8	140.27	Exp				0	8	3.26	1.44	0.79	1.28±0.51
cis-5-decene	7433-78-5	140.27	AdjP				0	8	3.56	1.52	0.85	1.36±0.55
trans-4-decene	19398-89-1	140.27	AdjP				0	8	3.76	1.59	0.92	1.44±0.56
c10 3-alkenes		140.27	LM				0	8	3.76	1.59	0.92	1.44±0.56
c10 internal alkenes		140.27	LM				0	8	3.76	1.59	0.92	1.44±0.56
trans-5-undecene	764-97-6	154.29	AdjP				0	8	3.49	1.49	0.87	1.35±0.52
c11 3-alkenes		154.29	LM				0	8	3.49	1.49	0.87	1.35±0.52
c11 internal alkenes		154.29	LM				0	8	3.49	1.49	0.87	1.35±0.52
c12 2-alkenes		168.32	LM				0	8	3.05	1.31	0.74	1.17±0.46
c12 3-alkenes		168.32	LM				0	8	3.05	1.31	0.74	1.17±0.46
c12 internal alkenes		168.32	LM				0	8	3.05	1.31	0.74	1.17±0.46
trans-5-dodecene	7206-16-8	168.32	AdjP				0	8	3.05	1.31	0.74	1.17±0.46
trans-5-tridecene	23051-84-5	182.35	Exp				0	8	2.51	1.09	0.62	0.97±0.39
c13 3-alkenes		182.35	LM				0	8	2.51	1.09	0.62	0.97±0.39
c13 internal alkenes		182.35	LM				0	8	2.51	1.09	0.62	0.97±0.39
trans-5-tetradecene	41446-66-6	196.37	Exp				0	8	2.28	0.99	0.57	0.88±0.36
c14 3-alkenes		196.37	LM				0	8	2.28	0.99	0.57	0.88±0.36
c14 internal alkenes		196.37	LM				0	8	2.28	0.99	0.57	0.88±0.36
trans-5-pentadecene	74392-33-9	210.40	Exp				0	8	2.10	0.91	0.52	0.81±0.33
c15 3-alkenes		210.40	LM				0	8	2.10	0.91	0.52	0.81±0.33
c15 internal alkenes		210.40	LM				0	8	2.10	0.91	0.52	0.81±0.33

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
c4 alkenes		56.11	LM				0	8	12.15	4.61	2.79	4.38±1.79
c5 alkenes		70.13	LM				0	8	8.72	3.44	2.10	3.24±1.24
c6 alkenes		84.16	LM				0	8	6.69	2.71	1.63	2.52±0.96
c7 alkenes		98.19	LM				0	8	5.23	2.20	1.33	2.02±0.73
c8 alkenes		112.21	LM				0	8	3.91	1.65	0.95	1.50±0.58
c9 alkenes		126.24	LM				0	8	3.46	1.48	0.85	1.33±0.51
c10 alkenes		140.27	LM				0	8	2.92	1.26	0.71	1.12±0.44
c11 alkenes		154.29	LM				0	8	2.63	1.15	0.64	1.02±0.40
c12 alkenes		168.32	LM				0	8	2.30	1.01	0.55	0.89±0.36
c13 alkenes		182.35	LM				0	8	1.95	0.86	0.47	0.75±0.31
c14 alkenes		196.37	LM				0	8	1.78	0.79	0.43	0.69±0.29
c15 alkenes		210.40	LM				0	8	1.64	0.73	0.39	0.63±0.26
cyclopentene	142-29-0	68.12	Exp	1			0	8	6.69	2.55	1.53	2.41±0.96
3-methylcyclopentene	1120-62-3	82.14	Exp				0	8	5.00	2.03	1.25	1.90±0.70
1-methyl cyclopentene	693-89-0	82.14	AdjP				0	8	12.45	4.46	2.57	4.27±1.99
cyclohexene	110-83-8	82.14	Exp	1	4		0	4	4.89	2.02	1.25	1.88±0.68
1-methyl cyclohexene	591-49-1	96.17	Exp	1			0	8	6.58	2.48	1.42	2.33±1.04
4-methyl cyclohexene	591-47-9	96.17	Exp				0	8	4.08	1.68	1.03	1.56±0.58
1,2-dimethyl cyclohexene	1674-10-8	110.20	Exp				0	8	5.57	2.10	1.11	1.93±0.94
1,2-propadiene (allene)	463-49-0	40.06	Exp	1			0	11	8.15	3.90	2.48	3.55±1.14
1-buten-3-yne (vinyl acetylene)	689-97-4	52.07	LM				0	11	10.32	4.13	2.54	3.87±1.43
1,2-butadiene	590-19-2	54.09	Exp	1			0	11	9.09	3.98	2.50	3.67±1.25
1,3-butadiene	106-99-0	54.09	Exp	1			0	6	12.45	4.77	2.91	4.51±1.73
trans 1,3-pentadiene	2004-70-8	68.12	Exp				0	8	12.33	4.82	2.97	4.54±1.70
cis 1,3-pentadiene	1574-41-0	68.12	LM				0	8	12.33	4.82	2.97	4.54±1.70
1,4-pentadiene	591-93-5	68.12	Exp	1			0	8	9.05	3.73	2.39	3.51±1.20
1,2-pentadiene	591-95-7	68.12	Exp	1			0	11	7.68	3.21	1.99	2.98±1.05
3-methyl-1,2-butadiene	598-25-4	68.12	Exp	1			0	11	10.11	4.01	2.46	3.76±1.40
isoprene	78-79-5	68.12	Exp	1	2		0	1	10.48	3.97	2.36	3.74±1.49
trans,trans-2,4-hexadiene	5194-51-4	82.14	LM				0	8	8.76	3.37	2.04	3.19±1.27
trans 1,3-hexadiene	20237-34-7	82.14	LM				0	8	10.23	3.99	2.47	3.77±1.41
trans 1,4-hexadiene	7319-00-8	82.14	Exp	1			0	8	8.52	3.35	2.04	3.15±1.21
c6 cyclic or di-olefins		82.14	LM				0	8	8.59	3.33	2.03	3.16±1.24
c7 cyclic or di-olefins		96.17	LM				0	8	7.21	2.85	1.72	2.67±1.05
c8 cyclic or di-olefins		110.20	LM				0	8	4.78	1.98	1.16	1.80±0.70
c9 cyclic or di-olefins		124.22	LM				0	8	4.49	1.89	1.12	1.72±0.65
c10 cyclic or di-olefins		138.25	LM				0	8	3.82	1.61	0.94	1.46±0.57
c11 cyclic or di-olefins		152.28	LM				0	8	3.54	1.51	0.88	1.37±0.53
c12 cyclic or di-olefins		166.30	LM				0	8	3.08	1.32	0.75	1.18±0.47
c13 cyclic or di-olefins		180.33	LM				0	8	2.54	1.10	0.63	0.98±0.40
c14 cyclic or di-olefins		194.36	LM				0	8	2.31	1.00	0.57	0.89±0.36
c15 cyclic or di-olefins		208.38	LM				0	8	2.12	0.92	0.52	0.82±0.34
cyclopentadiene	542-92-7	66.10	LM				0	8	6.89	2.63	1.58	2.48±0.98
3-carene	13466-78-9	136.23	Exp	1	3		0	4	3.18	1.26	0.73	1.17±0.47
a-pinene	80-56-8	136.23	Exp	1	2		0	4	4.49	1.66	0.88	1.53±0.72
b-pinene	127-91-3	136.23	Exp	1	2		0	4	3.43	1.41	0.76	1.26±0.53
d-limonene	5989-27-5	136.23	Exp	1	2		0	4	4.50	1.71	0.96	1.60±0.72
sabinene	3387-41-5	136.23	Exp	1	3		0	4	4.08	1.67	0.93	1.51±0.62

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
terpene		136.23	LM				0	8	3.98	1.55	0.84	1.41±0.62
Terpinolene	586-62-9	136.23	Exp				0	8	6.14	2.21	1.17	2.09±1.09
styrene	100-42-5	104.15	Exp	1	2		0	2	1.66	0.186	-0.47	-0.008±0.521
allylbenzene	300-57-2	118.18	LM				0	8	1.46	0.164	-0.41	-0.007±0.460
a-methyl styrene	98-83-9	118.18	LM				0	8	1.46	0.164	-0.41	-0.007±0.460
c9 styrenes		118.18	LM				0	8	1.46	0.164	-0.41	-0.007±0.460
b-methyl styrene	637-50-3	118.18	Exp	1			0	8	0.94	0.113	-0.33	-0.035±0.307
c10 styrenes		132.20	LM				0	8	1.31	0.147	-0.37	-0.006±0.411
benzene	71-43-2	78.11	Exp	1	2	0?	4	0.69	0.104	-0.146	0.042±0.202	
toluene	108-88-3	92.14	Exp	1	2		0	4	3.93	1.38	0.55	1.20±0.70
ethyl benzene	100-41-4	106.17	Exp	1	3		0	4	2.96	1.15	0.50	0.99±0.51
c9 monosubstituted benzenes		120.19	LM				0	8	1.96	0.80	0.35	0.68±0.34
n-propyl benzene	103-65-1	120.19	Exp	1			0	8	1.96	0.80	0.35	0.68±0.34
isopropyl benzene (cumene)	98-82-8	120.19	Exp	1			0	8	2.45	0.94	0.39	0.81±0.43
c10 monosubstituted benzenes		134.22	Exp				0	8	2.29	0.92	0.41	0.79±0.39
n-butyl benzene	104-51-8	134.22	LM				0	8	2.29	0.92	0.41	0.79±0.39
s-butyl benzene	135-98-8	134.22	LM				0	8	2.29	0.92	0.41	0.79±0.39
t-butyl benzene	98-06-6	134.22	Exp	1			0	8	1.91	0.70	0.27	0.60±0.35
n-pentylbenzene	538-68-1	148.24	LM				0	8	2.04	0.84	0.38	0.72±0.34
c11 monosubstituted benzenes		148.24	Exp				0	8	2.04	0.84	0.38	0.72±0.34
c12 monosubstituted benzenes		162.27	Exp				0	8	1.84	0.77	0.36	0.66±0.31
c13 monosubstituted benzenes		176.30	Exp				0	8	1.68	0.71	0.34	0.61±0.28
c14 monosubstituted benzenes		190.32	Exp				0	8	1.54	0.66	0.32	0.57±0.26
c15 monosubstituted benzenes		204.35	Exp				0	8	1.43	0.62	0.30	0.53±0.24
c16 monosubstituted benzenes		218.38	Exp				0	8	1.33	0.58	0.29	0.50±0.22
c17 monosubstituted benzenes		232.40	LM				0	8	1.25	0.55	0.27	0.47±0.20
c18 monosubstituted benzenes		246.43	LM				0	8	1.18	0.52	0.25	0.44±0.19
c19 monosubstituted benzenes		260.46	LM				0	8	1.11	0.49	0.24	0.42±0.18
c20 monosubstituted benzenes		274.48	LM				0	8	1.06	0.46	0.23	0.40±0.17
c21 monosubstituted benzenes		288.51	LM				0	8	1.01	0.44	0.22	0.38±0.16
c22 monosubstituted benzenes		302.54	LM				0	8	0.96	0.42	0.21	0.36±0.16
c8 disubstituted benzenes	1330-20-7	106.17	LM				0	8	7.72	2.59	1.21	2.37±1.26
m-xylene	108-38-3	106.17	Exp	1	1		0	4	9.73	3.20	1.55	2.97±1.57
o-xylene	95-47-6	106.17	Exp	1	2		0	4	7.58	2.58	1.20	2.34±1.24
p-xylene	106-42-3	106.17	Exp	1	3		0	4	5.78	1.98	0.86	1.77±0.97

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]			Reactivity (gm O ₃ / gm VOC)				
				k	a	Bias	Unc	MIR	MOIR	EBIR	Base
c9 disubstituted benzenes		120.19	LM			0	8	5.78	2.01	0.94	1.82±0.94
m-ethyl toluene	620-14-4	120.19	Exp	1		0	8	7.39	2.49	1.20	2.29±1.19
o-ethyl toluene	611-14-3	120.19	Exp	1		0	8	5.54	1.96	0.91	1.76±0.91
p-ethyl toluene	622-96-8	120.19	Exp	1		0	8	4.39	1.59	0.72	1.41±0.73
o-cymene; 1-methyl-2-(1-methylethyl)benzene	527-84-4	134.22	LM			0	8	5.43	1.91	0.91	1.73±0.88
1-methyl-2-n-propylbenzene	1074-17-5	134.22	LM			0	8	5.43	1.91	0.91	1.73±0.88
m-cymene; 1-methyl-3-(1-methylethyl)benzene	535-77-3	134.22	LM			0	8	7.08	2.39	1.17	2.21±1.13
1-methyl-3-n-propylbenzene	1074-43-7	134.22	LM			0	8	7.08	2.39	1.17	2.21±1.13
1-methyl-4-n-propylbenzene	1074-55-1	134.22	LM			0	8	4.39	1.58	0.73	1.41±0.71
c10 disubstituted benzenes		134.22	LM			0	8	5.64	1.96	0.94	1.78±0.91
m-c10 disubstituted benzenes		134.22	Exp			0	8	7.08	2.39	1.17	2.21±1.13
o-c10 disubstituted benzenes		134.22	Exp			0	8	5.43	1.91	0.91	1.73±0.88
p-c10 disubstituted benzenes		134.22	Exp			0	8	4.39	1.58	0.73	1.41±0.71
m-diethyl benzene	141-93-5	134.22	LM			0	8	7.08	2.39	1.17	2.21±1.13
o-diethyl benzene	135-01-3	134.22	LM			0	8	5.43	1.91	0.91	1.73±0.88
1-methyl-4-isopropylbenzene (p-cymene)	99-87-6	134.22	Exp	1		0	8	4.41	1.57	0.71	1.40±0.72
p-diethyl benzene	105-05-5	134.22	LM			0	8	4.39	1.58	0.73	1.41±0.71
m-c11 disubstituted benzenes		148.24	Exp			0	8	6.12	2.08	1.03	1.92±0.98
o-c11 disubstituted benzenes		148.24	Exp			0	8	4.68	1.67	0.80	1.51±0.75
p-c11 disubstituted benzenes		148.24	Exp			0	8	3.82	1.40	0.66	1.25±0.62
1-butyl-2-methylbenzene		148.24	LM			0	8	4.68	1.67	0.80	1.51±0.75
1-ethyl-2-n-propylbenzene		148.24	LM			0	8	4.68	1.67	0.80	1.51±0.75
o-t-butyl toluene; 1-(1,1-dimethylethyl)-2-methylbenzene	1074-92-6	148.24	LM			0	8	4.68	1.67	0.80	1.51±0.75
1-methyl-3-n-butylbenzene	1595-04-6	148.24	LM			0	8	6.12	2.08	1.03	1.92±0.98
p-Isobutyl toluene; 1-methyl-4(2-methylpropyl)benzene	5161-04-6	148.24	LM			0	8	3.82	1.40	0.66	1.25±0.62
c11 disubstituted benzenes		148.24	LM			0	8	4.88	1.72	0.83	1.56±0.78
m-c12 disubstituted benzenes		162.27	Exp			0	8	5.48	1.87	0.92	1.73±0.87
o-c12 disubstituted benzenes		162.27	Exp			0	8	4.18	1.50	0.72	1.35±0.67
p-c12 disubstituted benzenes		162.27	Exp			0	8	3.43	1.26	0.60	1.13±0.55

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
1,3-di-n-propylbenzene		162.27	LM				0	8	4.18	1.50	0.72	1.35±0.67
1,4 diisopropyl benzene		162.27	LM				0	8	3.43	1.26	0.60	1.13±0.55
3-isopropyl cumene; 1,3- diisopropyl benzene	99-62-7	162.27	LM				0	8	5.48	1.87	0.92	1.73±0.87
c12 disubstituted benzenes		162.27	LM				0	8	4.36	1.54	0.75	1.40±0.70
m-c13 disubstituted benzenes		176.30	Exp				0	8	4.90	1.68	0.83	1.55±0.78
o-c13 disubstituted benzenes		176.30	Exp				0	8	3.73	1.35	0.66	1.22±0.60
p-c13 disubstituted benzenes		176.30	Exp				0	8	3.08	1.15	0.55	1.02±0.49
c13 disubstituted benzenes		176.30	LM				0	8	3.90	1.39	0.68	1.27±0.62
m-c14 disubstituted benzenes		190.32	Exp				0	8	4.42	1.53	0.76	1.41±0.70
o-c14 disubstituted benzenes		190.32	Exp				0	8	3.36	1.23	0.60	1.11±0.54
p-c14 disubstituted benzenes		190.32	Exp				0	8	2.79	1.05	0.51	0.93±0.44
c14 disubstituted benzenes		190.32	LM				0	8	3.52	1.27	0.62	1.15±0.56
c15 disubstituted benzenes		204.35	LM				0	8	3.20	1.16	0.58	1.06±0.51
m-c15 disubstituted benzenes		204.35	Exp				0	8	4.02	1.40	0.70	1.29±0.64
o-c15 disubstituted benzenes		204.35	Exp				0	8	3.05	1.12	0.55	1.01±0.49
p-c15 disubstituted benzenes		204.35	Exp				0	8	2.54	0.96	0.47	0.86±0.40
m-c16 disubstituted benzenes		218.38	Exp				0	8	3.68	1.29	0.65	1.19±0.58
o-c16 disubstituted benzenes		218.38	Exp				0	8	2.79	1.04	0.51	0.93±0.44
p-c16 disubstituted benzenes		218.38	Exp				0	8	2.33	0.89	0.44	0.80±0.37
c16 disubstituted benzenes		218.38	LM				0	8	2.93	1.07	0.53	0.97±0.46
c17 disubstituted benzenes		232.40	LM				0	8	2.76	1.01	0.50	0.91±0.44
c18 disubstituted benzenes		246.43	LM				0	8	2.60	0.95	0.47	0.86±0.41
c19 disubstituted benzenes		260.46	LM				0	8	2.46	0.90	0.45	0.82±0.39
c20 disubstituted benzenes		274.48	LM				0	8	2.33	0.85	0.42	0.77±0.37
c21 disubstituted benzenes		288.51	LM				0	8	2.22	0.81	0.40	0.74±0.35
c22 disubstituted benzenes		302.54	LM				0	8	2.12	0.77	0.39	0.70±0.33
isomers of ethylbenzene		106.17	LM				0	8	5.38	1.88	0.86	1.69±0.89
isomers of propylbenzene		120.19	LM				0	8	6.19	2.18	1.10	2.00±0.97
c9 trisubstituted benzenes	25551-13-7	120.19	LM				0	8	10.84	3.72	2.02	3.50±1.66
1,2,3-trimethyl benzene	526-73-8	120.19	Exp	1	2	0	4	11.94	4.07	2.19	3.83±1.83	
1,2,4-trimethyl benzene	95-63-6	120.19	Exp	1	2	0	4	8.83	3.14	1.71	2.93±1.34	
1,3,5-trimethyl benzene	108-67-8	120.19	Exp	1	2	0	4	11.75	3.96	2.15	3.76±1.81	
1,2,3-c10 trisubstituted benzenes		134.22	Exp				0	8	10.16	3.50	1.90	3.29±1.55
1,2,4-c10 trisubstituted benzenes		134.22	Exp				0	8	7.54	2.71	1.48	2.53±1.14

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]			Reactivity (gm O ₃ / gm VOC)				
				k	a	Bias	Unc	MIR	MOIR	EBIR	Base
1,3,5-c10 trisubstituted benzenes		134.22	Exp			0	8	10.10	3.43	1.87	3.25±1.55
1,2,3,4-tetramethylbenzene	488-23-3	134.22	LM			0	8	9.26	3.21	1.75	3.02±1.41
1,2,4,5-tetramethylbenzene	95-93-2	134.22	LM			0	8	9.26	3.21	1.75	3.02±1.41
1,2-dimethyl-3-ethylbenzene	933-98-2	134.22	LM			0	8	10.16	3.50	1.90	3.29±1.55
1,2-dimethyl-4-ethylbenzene	934-80-5	134.22	LM			0	8	7.54	2.71	1.48	2.53±1.14
1,3-dimethyl-2-ethylbenzene	2870-04-4	134.22	LM			0	8	10.16	3.50	1.90	3.29±1.55
1,3-dimethyl-4-ethylbenzene	874-41-9	134.22	LM			0	8	7.54	2.71	1.48	2.53±1.14
1,3-dimethyl-5-ethylbenzene	934-74-7	134.22	LM			0	8	10.10	3.43	1.87	3.25±1.55
1,4-dimethyl-2-ethylbenzene	1758-88-9	134.22	LM			0	8	7.54	2.71	1.48	2.53±1.14
1,2,3,5 tetramethyl benzene	527-53-7	134.22	LM			0	8	9.26	3.21	1.75	3.02±1.41
isomers of butylbenzene		134.22	LM			0	8	5.55	1.98	1.01	1.81±0.87
c10 trisubstituted benzenes		134.22	LM			0	8	9.26	3.21	1.75	3.02±1.41
c10 tetrasubstituted benzenes		134.22	LM			0	8	9.26	3.21	1.75	3.02±1.41
1,2,3-c11 trisubstituted benzenes		148.24	Exp			0	8	8.88	3.07	1.67	2.89±1.36
1,2,4-c11 trisubstituted benzenes		148.24	Exp			0	8	6.61	2.39	1.31	2.23±1.00
1,3,5-c11 trisubstituted benzenes		148.24	Exp			0	8	8.91	3.03	1.65	2.87±1.37
pentamethylbenzene	700-12-9	148.24	LM			0	8	8.13	2.83	1.54	2.66±1.24
1-methyl-3,5-diethylbenzene	2050-24-0	148.24	LM			0	8	8.91	3.03	1.65	2.87±1.37
isomers of pentylbenzene		148.24	LM			0	8	4.86	1.75	0.89	1.60±0.76
c11 trisubstituted benzenes		148.24	LM			0	8	8.13	2.83	1.54	2.66±1.24
c11 tetrasubstituted benzenes		148.24	LM			0	8	8.13	2.83	1.54	2.66±1.24
c11 pentasubstituted benzenes		148.24	LM			0	8	8.13	2.83	1.54	2.66±1.24
1,2,3-c12 trisubstituted benzenes		162.27	Exp			0	8	7.95	2.76	1.49	2.59±1.22
1,2,4-c12 trisubstituted benzenes		162.27	Exp			0	8	5.93	2.15	1.18	2.00±0.90
1,3,5-c12 trisubstituted benzenes		162.27	Exp			0	8	8.02	2.73	1.49	2.58±1.23
1-(1,1-dimethylethyl)-3,5-dimethylbenzene	98-19-1	162.27	LM			0	8	8.02	2.73	1.49	2.58±1.23
isomers of hexylbenzene		162.27	LM			0	8	4.37	1.57	0.80	1.44±0.68
c12 trisubstituted benzenes		162.27	LM			0	8	7.30	2.55	1.39	2.39±1.11
c12 tetrasubstituted benzenes		162.27	LM			0	8	7.30	2.55	1.39	2.39±1.11
c12 pentasubstituted benzenes		162.27	LM			0	8	7.30	2.55	1.39	2.39±1.11

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)					
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base	
c12 hexasubstituted benzenes		162.27	LM					0	8	7.30	2.55	1.39	2.39±1.11
1,2,3-c13 trisubstituted benzenes		176.30	Exp					0	8	7.11	2.48	1.34	2.33±1.09
1,2,4-c13 trisubstituted benzenes		176.30	Exp					0	8	5.33	1.94	1.06	1.80±0.80
1,3,5-c13 trisubstituted benzenes		176.30	Exp					0	8	7.23	2.47	1.35	2.34±1.11
c13 trisubstituted benzenes		176.30	LM					0	8	6.56	2.30	1.25	2.15±1.00
1,2,3-c14 trisubstituted benzenes		190.32	Exp					0	8	6.48	2.26	1.23	2.12±0.99
1,2,4-c14 trisubstituted benzenes		190.32	Exp					0	8	4.86	1.77	0.97	1.65±0.73
1,3,5-c14 trisubstituted benzenes		190.32	Exp					0	8	6.63	2.27	1.23	2.14±1.02
c14 trisubstituted benzenes		190.32	LM					0	8	5.98	2.10	1.15	1.97±0.91
c15 trisubstituted benzenes		204.35	LM					0	8	5.49	1.93	1.05	1.81±0.83
1,2,3-c15 trisubstituted benzenes		204.35	Exp					0	8	5.92	2.07	1.13	1.94±0.90
1,2,4-c15 trisubstituted benzenes		204.35	Exp					0	8	4.45	1.63	0.89	1.51±0.67
1,3,5-c15 trisubstituted benzenes		204.35	Exp					0	8	6.09	2.09	1.14	1.97±0.93
1,2,3-c16 trisubstituted benzenes		218.38	Exp					0	8	5.43	1.91	1.04	1.79±0.83
1,2,4-c16 trisubstituted benzenes		218.38	Exp					0	8	4.09	1.50	0.82	1.39±0.62
1,3,5-c16 trisubstituted benzenes		218.38	Exp					0	8	5.62	1.93	1.05	1.82±0.86
c16 trisubstituted benzenes		218.38	LM					0	8	5.04	1.78	0.97	1.67±0.77
c17 trisubstituted benzenes		232.40	LM					0	8	4.74	1.67	0.91	1.57±0.72
c18 trisubstituted benzenes		246.43	LM					0	8	4.47	1.58	0.86	1.48±0.68
c19 trisubstituted benzenes		260.46	LM					0	8	4.23	1.49	0.81	1.40±0.64
c20 trisubstituted benzenes		274.48	LM					0	8	4.01	1.42	0.77	1.33±0.61
c21 trisubstituted benzenes		288.51	LM					0	8	3.82	1.35	0.74	1.26±0.58
c22 trisubstituted benzenes		302.54	LM					0	8	3.64	1.29	0.70	1.20±0.55
indene	95-13-6	116.16	LM					0	10	1.49	0.167	-0.42	-0.007±0.468
indan	496-11-7	118.18	LM					0	10	3.24	1.15	0.44	0.99±0.56
naphthalene	91-20-3	128.17	Exp	1	4	+	5	3.28	1.14	0.48	0.41	0.90±0.51	
methyl indans		132.20	LM					0	10	2.89	1.03	0.39	0.89±0.50
tetralin	119-64-2	132.20	Exp	1	4	+	5	2.89	1.03	0.39	0.39	0.89±0.50	
methyl naphthalenes	1321-94-4	142.20	Exp			+	10	3.00	1.02	0.41	0.41	0.90±0.51	
1-methyl naphthalene	90-12-0	142.20	LM			+	10	3.00	1.02	0.41	0.41	0.90±0.51	
2-methyl naphthalene	91-57-6	142.20	LM			+	10	3.00	1.02	0.41	0.41	0.90±0.51	
c11 tetralin or indan		146.23	LM			+	10	2.61	0.93	0.35	0.35	0.80±0.45	
1-ethylnaphthalene	1127-76-0	156.22	LM			+	10	2.73	0.93	0.37	0.37	0.82±0.46	
c12 naphthalenes		156.22	LM			+	10	3.85	1.30	0.60	0.60	1.19±0.62	
c12 monosubstituted naphthalene		156.22	LM			+	10	2.73	0.93	0.37	0.37	0.82±0.46	

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
c12 disubstituted naphthalenes		156.22	LM				+	10	4.96	1.67	0.82	1.55±0.78
2,3-dimethyl naphthalene dimethyl naphthalenes	581-40-8	156.22	Exp	1	4		+	5	4.96	1.67	0.82	1.55±0.78
c12 tetralin or indan		156.22	LM				+	10	4.96	1.67	0.82	1.55±0.78
c13 naphthalenes		160.26	LM				0	10	2.39	0.85	0.32	0.73±0.41
c13 monosubstituted naphthalene		170.25	LM				0	10	3.53	1.19	0.55	1.09±0.57
c13 disubstituted naphthalenes		170.25	LM				0	10	2.51	0.85	0.34	0.76±0.42
c13 trisubstituted naphthalenes		170.25	LM				0	10	4.55	1.53	0.75	1.42±0.72
c13 tetralin or indan		170.25	LM				0	10	4.55	1.53	0.75	1.42±0.72
c14 naphthalenes		174.28	LM				0	10	2.19	0.78	0.30	0.67±0.38
c14 tetralin or indan		184.28	LM				0	10	3.26	1.10	0.51	1.01±0.53
c15 naphthalenes		188.31	LM				0	10	2.03	0.72	0.28	0.62±0.35
c15 tetralin or indan		198.30	LM				0	10	3.03	1.02	0.47	0.93±0.49
c16 naphthalenes		202.34	LM				0	10	1.89	0.67	0.26	0.58±0.33
c16 tetralin or indan		212.33	LM				0	10	2.83	0.96	0.44	0.87±0.46
c17 naphthalenes		216.36	LM				0	10	1.77	0.63	0.24	0.54±0.30
c17 tetralin or indan		226.36	LM				0	10	2.65	0.90	0.41	0.82±0.43
c18 naphthalenes		230.39	LM				0	10	1.66	0.59	0.22	0.51±0.29
c18 tetralin or indan		240.38	LM				0	10	2.50	0.84	0.39	0.77±0.40
c19 naphthalenes		244.41	LM				0	10	1.56	0.56	0.21	0.48±0.27
c19 tetralin or indan		254.41	LM				0	10	2.36	0.80	0.37	0.73±0.38
c20 naphthalenes		258.44	LM				0	10	1.48	0.53	0.20	0.45±0.25
c20 tetralin or indan		268.44	LM				0	10	2.24	0.76	0.35	0.69±0.36
c21 naphthalenes		272.47	LM				0	10	1.40	0.50	0.190	0.43±0.24
c21 tetralin or indan		282.46	LM				0	10	2.13	0.72	0.33	0.66±0.34
c22 naphthalenes		286.49	LM				0	10	1.33	0.47	0.181	0.41±0.23
c22 tetralin or indan		296.49	LM				0	10	2.03	0.68	0.31	0.63±0.33
acetylene	74-86-2	300.52	LM				0	10	1.27	0.45	0.172	0.39±0.22
methyl acetylene	74-99-7	26.04	Exp	1	2		-	3	0.95	0.38	0.20	0.35±0.16
1,3-butadiyne	460-12-8	40.06	Exp	1			-	7	6.67	2.51	1.39	2.33±1.05
2-butyne	503-17-3	50.06	Exp				0	11	5.56	2.56	1.65	2.36±0.80
ethyl acetylene	107-00-6	54.09	Exp	1			0	10	16.34	5.63	3.19	5.38±2.50
methanol	67-56-1	54.09	Exp	1			-	7	6.05	2.27	1.26	2.10±0.94
ethanol	64-17-5	32.04	Exp	1	3		0	2	0.66	0.32	0.20	0.29±0.10
isopropyl alcohol	67-63-0	46.07	Exp	1	3		0	2	1.45	0.84	0.57	0.75±0.23
n-propyl alcohol	71-23-8	60.10	Exp	1	2		0	2	0.59	0.35	0.26	0.32±0.07
isobutyl alcohol	78-83-1	60.10	Exp	1			0	6	2.39	1.23	0.79	1.10±0.37
n-butyl alcohol	71-36-3	74.12	Exp	1			0	6	2.42	1.16	0.72	1.04±0.35
s-butyl alcohol	78-92-2	74.12	Exp	1			0	6	2.77	1.38	0.88	1.24±0.41
t-butyl alcohol	75-65-0	74.12	Exp	1	2		+	2	1.29	0.73	0.50	0.66±0.18
cyclopentanol	96-41-3	86.13	Exp	1			0	6	0.39	0.22	0.141	0.195±0.056
2-pentanol	6032-29-7	88.15	Exp	1			0	6	1.65	0.87	0.57	0.78±0.23
3-pentanol	584-02-1	88.15	Exp	1			0	6	1.53	0.83	0.55	0.74±0.22
pentyl alcohol	71-41-0	88.15	Exp	1			0	6	1.56	0.82	0.55	0.75±0.22
									2.72	1.33	0.84	1.20±0.40

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
isoamyl alcohol (3-methyl-1-butanol)	123-51-3	88.15	Exp	1			0	6	3.06	1.42	0.90	1.30±0.43
2-methyl-1-butanol	137-32-6	88.15	Exp				0	7	2.31	1.14	0.72	1.03±0.33
cyclohexanol	108-93-0	100.16	AdjP	1			0	6	1.83	1.01	0.63	0.88±0.28
1-hexanol	111-27-3	102.17	AdjP	1			0	6	2.56	1.29	0.81	1.15±0.38
2-hexanol	626-93-7	102.17	AdjP	1			0	6	1.96	1.14	0.73	1.00±0.31
4-methyl-2-pentanol (methyl isobutyl carbinol)	108-11-2	102.17	AdjP				0	7	2.52	1.34	0.87	1.20±0.36
1-heptanol	111-70-6	116.20	Exp	1			0	6	1.74	0.91	0.55	0.80±0.27
dimethylpentanol (2,3-dimethyl-1-pentanol)	10143-23-4	116.20	Exp				0	7	2.13	1.05	0.64	0.94±0.31
1-octanol	111-87-5	130.23	Exp	1	2	+	2	2	1.33	0.73	0.40	0.61±0.23
2-ethyl-1-hexanol	104-76-7	130.23	Exp				0	7	1.90	0.94	0.54	0.82±0.29
2-octanol	4128-31-8	130.23	Exp	1	2	+	2	2	1.84	0.98	0.59	0.85±0.29
3-octanol	20296-29-1	130.23	Exp	1	2	+	2	2	2.15	1.10	0.67	0.96±0.33
4-octanol	589-62-8	130.23	AdjP	1			0	6	2.09	1.10	0.65	0.95±0.33
5-methyl-1-heptanol	7212-53-5	130.23	AdjP				0	7	1.69	0.85	0.47	0.73±0.27
trimethylcyclohexanol	1321-60-4	142.24	AdjP				0	7	1.73	0.92	0.50	0.77±0.30
dimethylheptanol (2,6-dimethyl-2-heptanol)	13254-34-7	144.25	Exp				0	7	0.87	0.48	0.24	0.39±0.16
2,6-dimethyl-4-heptanol	108-82-7	144.25	AdjP				0	7	1.96	0.99	0.56	0.85±0.32
menthol	89-78-1	156.27	Exp				0	7	1.34	0.70	0.40	0.60±0.22
8-methyl-1-nonanol (isodecyl alcohol)	25339-17-7	158.28	Exp				0	7	0.97	0.53	0.26	0.43±0.18
1-decanol	112-30-1	158.28	Exp				0	7	0.98	0.53	0.27	0.43±0.18
3,7-dimethyl-1-octanol	106-21-8	158.28	Exp				0	7	1.11	0.58	0.30	0.48±0.20
Trimethylnonanol, threo/erythro; 2,6,8-trimethyl-4-nonanol	123-17-1	186.33	AdjP				0	7	1.23	0.64	0.31	0.52±0.23
ethylene glycol	107-21-1	62.07	Exp	1	2	0	2	2	3.03	1.49	1.00	1.37±0.41
propylene glycol	57-55-6	76.09	AdjP	1	2	0	2	2	2.50	1.16	0.75	1.07±0.34
glycerol	56-81-5	92.09	AdjP				0	7	3.07	1.36	0.84	1.25±0.45
1,3-butanediol	107-88-0	90.12	Exp	1			0	6	3.22	1.58	1.02	1.43±0.45
1,2-butanediol	584-03-2	90.12	AdjP	1			0	6	2.45	1.11	0.72	1.03±0.33
1,4-butanediol	110-63-4	90.12	Exp				0	7	2.62	1.24	0.78	1.13±0.39
2,3-butanediol		90.12	AdjP	1			0	6	4.25	1.86	1.08	1.68±0.70
pentaerythritol	115-77-5	136.15	AdjP				0	7	2.10	0.98	0.62	0.89±0.30
1,2-dihydroxy hexane	6920-22-5	118.17	AdjP				0	7	2.45	1.18	0.73	1.06±0.36
2-methyl-2,4-pentanediol	107-41-5	118.17	Exp	1			0	6	1.40	0.68	0.44	0.62±0.19
2-ethyl-1,3-hexanediol	94-96-2	146.23	AdjP				0	7	1.94	0.98	0.60	0.87±0.30
dimethyl ether	115-10-6	46.07	Exp	1	3	0	2	2	0.76	0.54	0.43	0.50±0.09
trimethylene oxide	503-30-0	58.08	Exp	1			0	6	4.31	2.41	1.74	2.22±0.61
1,3-dioxolane	646-06-0	74.08	Exp				0	7	4.77	2.21	1.59	2.10±0.58
dimethoxy methane	109-87-5	76.09	AdjP	1			0	6	0.89	0.64	0.50	0.59±0.11
tetrahydrofuran	109-99-9	72.11	Exp	1			0	6	4.11	2.11	1.41	1.92±0.56
diethyl ether	60-29-7	74.12	Exp	1	2	0	2	2	3.65	1.73	1.12	1.59±0.49
1,4-dioxane	123-91-1	88.11	Exp				0	7	2.49	1.29	0.90	1.19±0.32
alpha-methyltetrahydrofuran	96-47-9	86.13	Exp	1			0	6	3.78	1.87	1.22	1.69±0.52

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]					Reactivity (gm O ₃ / gm VOC)			
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR
tetrahydropyran	142-68-7	86.13	Exp	1		0	6	3.04	1.65	1.07	1.47±0.43
ethyl isopropyl ether	625-54-7	88.15	Exp			0	7	3.65	1.62	1.04	1.50±0.49
methyl n-butyl ether	628-28-4	88.15	Exp	1		0	6	3.00	1.57	1.04	1.42±0.42
methyl t-butyl ether	1634-04-4	88.15	Exp	1	3	0	2	0.70	0.43	0.29	0.38±0.10
2,2-dimethoxy propane	77-76-9	104.15	Exp			0	7	0.46	0.29	0.20	0.26±0.06
di n-propyl ether	111-43-3	102.17	Exp	1		0	6	2.93	1.55	1.04	1.40±0.40
ethyl n-butyl ether	628-81-9	102.17	Exp	1		0	6	3.34	1.61	1.03	1.46±0.46
ethyl t-butyl ether	637-92-3	102.17	Exp	1		0	6	1.94	0.97	0.62	0.88±0.27
methyl t-amyl ether	994-05-8	102.17	Exp	1		0	6	1.61	0.90	0.59	0.80±0.23
diisopropyl ether	108-20-3	102.17	Exp			0	7	3.44	1.45	0.89	1.34±0.48
ethylene glycol diethyl ether; 1,2-diethoxyethane	629-14-1	118.17	Exp			0	7	2.82	1.40	0.90	1.26±0.38
acetal (1,1-diethoxyethane)	105-57-7	118.17	Exp			0	7	3.47	1.51	0.97	1.40±0.46
4,4-dimethyl-3-oxahexane	919-94-8	116.20	Exp			0	7	1.87	0.94	0.58	0.84±0.27
2-butyl tetrahydrofuran	1004-29-1	128.21	Exp			0	7	1.99	0.99	0.55	0.85±0.32
di-isobutyl ether	628-55-7	130.23	Exp	1		0	6	1.11	0.63	0.38	0.54±0.17
di-n-butyl ether	142-96-1	130.23	Exp	1		0	6	2.70	1.33	0.82	1.18±0.39
2-methoxy-1-(2-methoxy-1-methylethoxy)-propane; dipropylene glycol dimethyl ether	89399-28-0	162.23	AdjP			0	7	1.92	0.95	0.62	0.86±0.26
di-n-pentyl ether	693-65-2	158.28	AdjP	1		0	6	2.00	1.07	0.64	0.92±0.32
2-methoxyethanol	109-86-4	76.09	Exp	1		0	6	2.86	1.29	0.84	1.20±0.39
1-methoxy-2-propanol	107-98-2	90.12	AdjP	1	2	0	2	2.34	1.22	0.85	1.12±0.31
2-ethoxyethanol	110-80-5	90.12	Exp	1	3	0	2	3.61	1.62	1.03	1.49±0.49
2-methoxy-1-propanol	1589-47-5	90.12	Exp			0	7	2.96	1.21	0.75	1.13±0.41
3-methoxy-1-propanol	1320-67-8	90.12	Exp			0	7	3.76	1.63	1.03	1.52±0.52
diethylene glycol	111-46-6	106.12	AdjP			0	7	3.27	1.43	0.90	1.32±0.45
tetrahydro-2-furanmethanol	97-99-4	102.13	Exp			0	7	3.22	1.40	0.87	1.29±0.44
1-ethoxy-2-propanol	1569-02-4	104.15	Exp			0	7	2.96	1.47	0.94	1.33±0.41
2-propoxyethanol	2807-30-9	104.15	AdjP			0	7	3.19	1.50	0.98	1.38±0.43
3-ethoxy-1-propanol	111-35-3	104.15	Exp	1		0	6	3.98	1.75	1.09	1.61±0.55
3-methoxy-1-butanol	2517-43-3	104.15	Exp	1		0	6	3.81	1.56	0.97	1.46±0.53
2-(2-methoxyethoxy) ethanol	111-77-3	120.15	AdjP			0	7	2.55	1.26	0.85	1.16±0.33
1-propoxy-2-propanol (propylene glycol n-propyl ether)	1569-01-3	118.17	AdjP			0	7	2.56	1.32	0.89	1.20±0.34
2-butoxyethanol	111-76-2	118.17	Exp	1	2	0	2	2.80	1.26	0.76	1.14±0.39
3 methoxy -3 methyl-butanol	56539-66-3	118.17	Exp			0	7	1.46	0.77	0.49	0.69±0.22
n-propoxypropanol	30136-13-1	118.17	Exp			0	7	3.65	1.66	1.05	1.52±0.50
2-(2-ethoxyethoxy) ethanol	111-90-0	134.17	Exp	1	3	0	2	3.13	1.46	0.91	1.32±0.44
dipropylene glycol isomer (1-[2-hydroxypropyl]-2-propanol)	110-98-5	134.17	AdjP			0	7	2.20	1.14	0.76	1.04±0.30
triethylene glycol	112-27-6	150.17	Exp			0	7	3.13	1.46	0.91	1.32±0.44
1-tert-butoxy-2-propanol	57018-52-7	132.20	AdjP			0	7	1.53	0.81	0.51	0.72±0.22
2-tert-butoxy-1-propanol	94023-15-1	132.20	Exp			0	7	1.78	0.72	0.41	0.66±0.26

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]			Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt Bias	Unc	MIR	MOIR	EBIR	Base
n-butoxy-2-propanol (propylene glycol n-butyl ether)	5131-66-8	132.20	Exp			0	7	2.59	1.28	0.81	1.15±0.37
2-(2-propoxyethoxy) ethanol	6881-94-3	148.20	Exp			0	7	2.72	1.32	0.83	1.18±0.38
dipropylene glycol methyl ether isomer (1-methoxy-2- [2-hydroxypropoxy]- propane)		148.20	AdjP			0	7	1.88	0.96	0.64	0.87±0.25
dipropylene glycol methyl ether isomer (2-[2- methoxypropoxy]-1- propanol)	13588-28-8	148.20	AdjP			0	7	2.48	1.13	0.72	1.04±0.34
2-[2-(2-methoxyethoxy) ethoxy] ethanol	112-35-6	164.20	Exp			0	7	2.44	1.22	0.77	1.09±0.35
2-hexyloxyethanol	112-25-4	146.23	AdjP			0	7	1.98	0.99	0.58	0.86±0.30
2,2,4-trimethyl-1,3- pentanediol	144-19-4	146.23	Exp			0	7	1.46	0.77	0.48	0.68±0.22
2-(2-butoxyethoxy)-ethanol	112-34-5	162.23	Exp	2		0	7	2.27	1.09	0.65	0.96±0.34
dipropylene glycol ethyl ether	15764-24-6	162.23	Exp			0	7	2.61	1.20	0.72	1.07±0.37
2-[2-(2-ethoxyethoxy) ethoxy] ethanol	112-50-5	178.23	Exp			0	7	2.33	1.15	0.71	1.02±0.34
tetraethylene glycol	112-60-7	194.23	Exp			0	7	2.39	1.15	0.71	1.03±0.35
1-(butoxyethoxy)-2- propanol	124-16-3	176.25	AdjP			0	7	1.81	0.95	0.59	0.83±0.26
2-[2-(2-propoxyethoxy) ethoxy] ethanol	23305-64-8	192.25	Exp			0	7	2.05	1.02	0.62	0.90±0.30
tripropylene glycol	24800-44-0	192.25	Exp			0	7	2.07	1.04	0.64	0.92±0.31
2,5,8,11-tetraoxatridecan- 13-ol	23783-42-8	208.25	Exp			0	7	1.85	0.94	0.57	0.83±0.28
2-(2-ethylhexyloxy) ethanol	1559-35-9	174.28	AdjP			0	7	1.44	0.76	0.38	0.62±0.26
2-(2-hexyloxyethoxy) ethanol	112-59-4	190.28	AdjP			0	7	1.72	0.90	0.52	0.77±0.27
glycol ether dpnb {1-(2- butoxy-1-methylethoxy)-2- propanol}	29911-28-2	190.28	AdjP			0	7	1.72	0.87	0.53	0.77±0.25
2-[2-(2-butoxyethoxy) ethoxy] ethanol	143-22-6	206.28	Exp			0	7	1.85	0.92	0.55	0.81±0.28
tripropylene glycol monomethyl ether	25498-49-1	206.28	Exp			0	7	1.81	0.91	0.55	0.80±0.27
diethylene glycol mono(2- ethylhexyl) ether	1559-36-0	218.33	Exp			0	7	1.45	0.75	0.42	0.64±0.24
3,6,9,12-tetraoxa- hexadecan-1-ol	1559-34-8	250.33	AdjP			0	7	1.61	0.82	0.49	0.71±0.25
tripropylene glycol n-butyl ether	55934-93-5	248.36	Exp			0	7	1.55	0.75	0.43	0.65±0.24
methyl formate	107-31-3	60.05	Exp	1		0	6	0.053	0.043	0.035	0.040±0.007
ethyl formate	109-94-4	74.08	Exp	1		0	6	0.45	0.27	0.193	0.25±0.07

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]					Reactivity (gm O ₃ / gm VOC)			
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR
methyl acetate	79-20-9	74.08	Exp	1	2	0	2	0.067	0.055	0.043	0.050±0.010
gamma-butyrolactone	96-48-0	86.09	Exp			0	7	0.90	0.56	0.38	0.50±0.14
ethyl acetate	141-78-6	88.11	Exp	1	2	0	3	0.59	0.35	0.23	0.31±0.09
methyl propionate	554-12-1	88.11	Exp	1		0	6	0.63	0.32	0.20	0.29±0.10
n-propyl formate	110-74-7	88.11	Exp	1		0	6	0.72	0.44	0.29	0.39±0.13
isopropyl formate	625-55-8	88.11	Exp			0	7	0.34	0.24	0.176	0.22±0.05
ethyl propionate	105-37-3	102.13	Exp	1		0	6	0.73	0.42	0.27	0.37±0.11
isopropyl acetate	108-21-4	102.13	Exp	1	2	0	2	1.03	0.57	0.39	0.52±0.14
methyl butyrate	623-42-7	102.13	Exp	1		0	6	1.05	0.55	0.34	0.49±0.16
methyl isobutyrate	547-63-7	102.13	Exp	1	2	0	2	0.58	0.33	0.21	0.29±0.10
n-butyl formate	592-84-7	102.13	Exp	1		0	6	0.77	0.48	0.32	0.42±0.13
propyl acetate	109-60-4	102.13	Exp	1		0	6	0.72	0.45	0.30	0.40±0.12
ethyl butyrate	105-54-4	116.16	Exp	1		0	6	1.11	0.60	0.38	0.53±0.17
isobutyl acetate	110-19-0	116.16	Exp			0	7	0.58	0.40	0.28	0.35±0.08
methyl pivalate	598-98-1	116.16	Exp	1	2	0	2	0.33	0.20	0.120	0.169±0.055
n-butyl acetate	123-86-4	116.16	Exp	1	2	0,+	2	0.77	0.49	0.31	0.42±0.13
n-propyl propionate	106-36-5	116.16	Exp	1		0	6	0.78	0.47	0.30	0.41±0.14
s-butyl acetate	105-46-4	116.16	Exp	1		0	6	1.24	0.75	0.51	0.67±0.18
t-butyl acetate	540-88-5	116.16	Exp	1	3	0	2	0.172	0.097	0.059	0.084±0.027
butyl propionate	590-01-2	130.18	Exp			0	7	0.78	0.48	0.29	0.40±0.14
amyl acetate	628-63-7	130.18	AdjP			0	7	0.77	0.49	0.28	0.41±0.14
n-propyl butyrate	105-66-8	130.18	Exp	1		0	6	0.98	0.56	0.34	0.49±0.16
isoamyl acetate (3-methylbutyl acetate)	123-92-2	130.18	Exp			0	7	1.01	0.60	0.36	0.51±0.17
2-methyl-1-butyl acetate	624-41-9	130.18	Exp			0	7	1.01	0.62	0.40	0.54±0.15
ethyl 3-ethoxy propionate	763-69-9	146.18	AdjP			0	7	3.50	1.44	0.84	1.32±0.51
hexyl acetates		144.21	LM			0	7	0.72	0.46	0.24	0.37±0.14
2,3-dimethylbutyl acetate		144.21	Exp			0	7	0.69	0.43	0.25	0.36±0.12
2-methylpentyl acetate		144.21	Exp			0	7	0.90	0.53	0.29	0.44±0.17
3-methylpentyl acetate		144.21	AdjP			0	7	0.99	0.59	0.33	0.49±0.17
4-methylpentyl acetate		144.21	Exp			0	7	0.75	0.45	0.24	0.36±0.14
isobutyl isobutyrate	97-85-8	144.21	Exp			0	7	0.55	0.35	0.20	0.29±0.09
n-butyl butyrate	109-21-7	144.21	Exp	1		0	6	1.01	0.57	0.32	0.48±0.17
n-hexyl acetate	142-92-7	144.21	AdjP			0	7	0.62	0.41	0.20	0.32±0.13
methyl amyl acetate (4-methyl-2-pentanol acetate)	108-84-9	144.21	Exp			0	7	1.27	0.67	0.37	0.56±0.21
n-pentyl propionate	624-54-4	144.21	AdjP			0	7	0.65	0.40	0.20	0.32±0.13
2,4-dimethylpentyl acetate		158.24	Exp			0	7	0.84	0.47	0.22	0.37±0.16
2-methylhexyl acetate		158.24	AdjP			0	7	0.62	0.39	0.162	0.29±0.14
3-ethylpentyl acetate		158.24	Exp			0	7	1.01	0.59	0.31	0.48±0.19
3-methylhexyl acetate		158.24	Exp			0	7	0.81	0.49	0.24	0.38±0.16
4-methylhexyl acetate		158.24	Exp			0	7	0.74	0.44	0.21	0.35±0.15
5-methylhexyl acetate		158.24	AdjP			0	7	0.52	0.33	0.123	0.24±0.13
isoamyl isobutyrate	2050-01-3	158.24	Exp			0	7	0.75	0.43	0.22	0.35±0.14
n-heptyl acetate	112-06-1	158.24	Exp			0	7	0.57	0.38	0.161	0.28±0.14
2,4-dimethylhexyl acetate		172.26	AdjP			0	7	0.68	0.41	0.162	0.30±0.16
2-ethyl-hexyl acetate	103-09-3	172.26	AdjP			0	7	0.58	0.36	0.125	0.26±0.15
3,4-dimethylhexyl acetate		172.26	AdjP			0	7	0.79	0.48	0.23	0.38±0.16
3,5-dimethylhexyl acetate		172.26	Exp			0	7	0.90	0.51	0.23	0.40±0.18

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
3-ethylhexyl acetate		172.26	Exp				0	7	0.82	0.49	0.23	0.38±0.17
3-methylheptyl acetate		172.26	Exp				0	7	0.59	0.38	0.149	0.28±0.15
4,5-dimethylhexyl acetate		172.26	AdjP				0	7	0.61	0.37	0.156	0.28±0.14
4-methylheptyl acetate		172.26	Exp				0	7	0.58	0.36	0.142	0.26±0.14
5-methylheptyl acetate		172.26	AdjP				0	7	0.53	0.34	0.113	0.24±0.15
n-octyl acetate	112-14-1	172.26	Exp				0	7	0.50	0.33	0.120	0.23±0.13
2,3,5-teimethylhexyl acetate		186.29	AdjP				0	7	0.77	0.45	0.20	0.35±0.16
2,3-dimethylheptyl acetate		186.29	Exp				0	7	0.63	0.40	0.168	0.30±0.15
2,4-dimethylheptyl acetate		186.29	AdjP				0	7	0.60	0.36	0.111	0.25±0.16
2,5-dimethylheptyl acetate		186.29	Exp				0	7	0.70	0.43	0.179	0.32±0.16
2-methyloctyl acetate		186.29	AdjP				0	7	0.44	0.29	0.068	0.185±0.138
3,5-dimethylheptyl acetate		186.29	AdjP				0	7	0.72	0.42	0.158	0.31±0.17
3,6-dimethylheptyl acetate		186.29	Exp				0	7	0.69	0.42	0.163	0.31±0.16
3-ethylheptyl acetate		186.29	Exp				0	7	0.55	0.35	0.126	0.25±0.14
4,5-dimethylheptyl acetate		186.29	AdjP				0	7	0.61	0.38	0.149	0.28±0.14
4,6-dimethylheptyl acetate		186.29	Exp				0	7	0.70	0.40	0.160	0.30±0.16
4-methyloctyl acetate		186.29	Exp				0	7	0.54	0.34	0.122	0.24±0.14
5-methyloctyl acetate		186.29	AdjP				0	7	0.48	0.31	0.082	0.20±0.14
n-nonyl acetate	143-13-5	186.29	Exp				0	7	0.45	0.30	0.096	0.20±0.13
3,6-dimethyloctyl acetate		200.32	Exp				0	7	0.70	0.42	0.171	0.31±0.16
3-isopropylheptyl acetate		200.32	AdjP				0	7	0.46	0.30	0.082	0.20±0.14
4,6-dimethyloctyl acetate		200.32	Exp				0	7	0.68	0.40	0.153	0.29±0.16
3,5,7-trimethyloctyl acetate		214.34	AdjP				0	7	0.57	0.34	0.104	0.24±0.15
3-ethyl-6-methyloctyl acetate		214.34	AdjP				0	7	0.55	0.34	0.104	0.23±0.15
4,7-dimethylnonyl acetate		214.34	AdjP				0	7	0.43	0.27	0.057	0.171±0.136
methyl dodecanoate {methyl laurate}	111-82-0	214.34	Exp				0	7	0.40	0.26	0.074	0.175±0.118
2,3,5,7-tetramethyloctyl acetate		228.37	Exp				0	7	0.54	0.33	0.113	0.23±0.14
3,5,7-trimethylnonyl acetate		228.37	AdjP				0	7	0.54	0.32	0.099	0.22±0.14
3,6,8-trimethylnonyl acetate		228.37	AdjP				0	7	0.51	0.31	0.077	0.20±0.15
2,4,6,8-tetramethylnonyl acetate		242.40	AdjP				0	7	0.43	0.26	0.057	0.168±0.134
3-ethyl-6,7-dimethylnonyl acetate		242.40	AdjP				0	7	0.53	0.33	0.104	0.23±0.15
4,7,9-trimethyldecyl acetate		242.40	AdjP				0	7	0.35	0.22	0.022	0.126±0.128
methyl myristate {methyl tetradecanoate}	124-10-7	242.40	Exp				0	7	0.37	0.24	0.067	0.159±0.110
2,3,5,6,8-pentaamethylnonyl acetate		256.42	Exp				0	7	0.57	0.35	0.136	0.26±0.14
3,5,7,9-tetramethyldecyl acetate		256.42	AdjP				0	7	0.40	0.25	0.046	0.155±0.136
5-ethyl-3,6,8-trimethylnonyl acetate		256.42	AdjP				0	7	0.69	0.40	0.154	0.30±0.16
dimethyl carbonate	616-38-6	90.08	Exp	1	2	0	2	0.055	0.045	0.035	0.041±0.008	

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
propylene carbonate	108-32-7	102.09	Exp	1	2	+	2	0.26	0.184	0.137	0.166±0.037	
methyl lactate	547-64-8	104.10	Exp	1			0	6	2.63	1.06	0.58	0.96±0.43
2-methoxyethyl acetate	110-49-6	118.13	Exp				0	7	1.08	0.65	0.47	0.59±0.14
ethyl lactate	97-64-3	118.13	Exp	1			0	6	2.42	1.04	0.60	0.94±0.38
methyl isopropyl carbonate	51729-83-0	118.13	Exp	1	2		0	2	0.59	0.34	0.23	0.31±0.08
1-methoxy-2-propyl acetate	108-65-6	132.16	Exp	1	2	0,+	2	1.63	0.83	0.56	0.76±0.21	
2-ethoxyethyl acetate	111-15-9	132.16	Exp				0	7	1.76	0.89	0.58	0.80±0.24
2-methoxy-1-propyl acetate	70657-70-4	132.16	Exp				0	7	1.06	0.59	0.41	0.54±0.13
methoxypropanol acetate	84540-57-8	132.16	Exp				0	7	1.76	0.93	0.60	0.83±0.26
dimethyl succinate	106-65-0	146.14	Exp	1	2		0	2	0.21	0.131	0.081	0.113±0.034
ethylene glycol diacetate	111-55-7	146.14	Exp				0	7	0.62	0.37	0.24	0.32±0.11
diisopropyl carbonate	6482-34-4	146.18	Exp				0	7	0.94	0.49	0.30	0.43±0.14
1,2-propylene glycol diacetate	623-84-7	160.17	Exp				0	7	0.57	0.36	0.24	0.32±0.08
dimethyl glutarate	1119-40-0	160.17	AdjP	1	2		0	2	0.39	0.22	0.108	0.179±0.075
2-butoxyethyl acetate	112-07-2	160.21	Exp				0	7	1.52	0.80	0.50	0.70±0.22
dimethyl adipate	627-93-0	174.19	AdjP	1			0	6	1.72	0.80	0.44	0.70±0.27
2-(2-ethoxyethoxy) ethyl acetate	112-15-2	176.21	AdjP				0	7	1.39	0.74	0.47	0.65±0.20
dipropylene glycol n-propyl ether isomer #1		176.25	AdjP				0	7	1.89	0.96	0.60	0.85±0.27
dipropylene glycol methyl ether acetate isomer #1		190.24	AdjP				0	7	1.30	0.68	0.42	0.59±0.19
dipropylene glycol methyl ether acetate isomer #2		190.24	AdjP				0	7	1.43	0.72	0.44	0.64±0.21
dipropylene glycol methyl ether acetate isomers	88917-22-0	190.24	LM				0	7	1.37	0.70	0.43	0.62±0.20
glyceryl triacetate	102-76-1	218.20	Exp				0	7	0.50	0.31	0.178	0.26±0.09
2-(2-butoxyethoxy) ethyl acetate	124-17-4	204.26	Exp				0	7	1.29	0.68	0.40	0.58±0.20
substituted c7 ester (c12)		216.32	LM				0	7	0.75	0.39	0.20	0.32±0.13
1-hydroxy-2,2,4-trimethylpentyl-3-isobutyrate	18491-15-1	216.32	Exp				0	7	0.84	0.40	0.21	0.34±0.14
3-hydroxy-2,2,4-trimethylpentyl-1-isobutyrate	77-68-9	216.32	AdjP				0	7	0.71	0.39	0.191	0.31±0.13
texanol isomers	25265-77-4	216.32	LM	1	2		0	2	0.75	0.39	0.20	0.32±0.13
substituted c9 ester (c12)		216.32	LM				0	7	0.75	0.39	0.20	0.32±0.13
dimethyl sebacate	106-79-6	230.30	Exp				0	7	0.38	0.23	0.070	0.161±0.102
diisopropyl adipate	6938-94-9	230.30	Exp				0	7	1.22	0.52	0.22	0.43±0.22
triethyl citrate	77-93-0	276.28	Exp				0	8	0.66	0.31	0.155	0.26±0.11
2,2,4-trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	286.41	Exp				0	7	0.33	0.20	0.062	0.140±0.088
ethylene oxide	75-21-8	44.05	Exp	1			0	6	0.036	0.032	0.026	0.029±0.005
propylene oxide	75-56-9	58.08	Exp	1			0	6	0.28	0.21	0.159	0.188±0.037
1,2-epoxybutane	106-88-7	72.11	Exp	1			0	6	0.85	0.62	0.46	0.55±0.13
formic acid	64-18-6	46.03	Exp	1			0	6	0.062	0.045	0.035	0.041±0.008
acetic acid	64-19-7	60.05	Exp	1			0	6	0.67	0.32	0.20	0.29±0.10

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]					Reactivity (gm O ₃ / gm VOC)				
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
glycolic acid	79-14-1	76.05	AdjP				0	8	2.35	0.92	0.49	0.84±0.39
peroxyacetic acid	79-21-0	76.05	LM				0	8	0.53	0.26	0.162	0.23±0.08
acrylic acid	79-10-7	72.06	AdjP				0	8	11.38	4.00	2.27	3.81±1.76
propionic acid	79-09-4	74.08	Exp				0	7	1.18	0.57	0.34	0.51±0.19
methacrylic acid	79-41-4	86.09	Exp				0	8	18.56	6.17	3.52	5.95±2.85
isobutyric acid	79-31-2	88.11	Exp				0	7	1.16	0.59	0.38	0.53±0.17
butanoic acid	107-92-6	88.11	AdjP				0	7	1.76	0.88	0.55	0.79±0.26
malic acid	6915-15-7	134.09	AdjP				0	8	6.92	2.44	1.33	2.29±1.08
3-methylbutanoic acid	503-74-2	102.13	AdjP				0	7	4.17	1.69	0.98	1.56±0.64
adipic acid	124-04-9	146.14	AdjP				0	8	2.95	1.41	0.88	1.27±0.43
2-ethyl hexanoic acid	149-57-5	144.21	Exp				0	7	3.21	1.39	0.75	1.23±0.50
methyl acrylate	96-33-3	86.09	Exp				0	8	11.50	3.90	2.19	3.73±1.77
vinyl acetate	108-05-4	86.09	Exp				0	8	3.16	1.21	0.72	1.14±0.46
2-methyl-3-butene-2-ol	115-18-4	86.13	Exp	1			0	8	4.81	2.00	1.29	1.88±0.64
ethyl acrylate	140-88-5	100.12	Exp				0	8	7.71	2.87	1.67	2.70±1.13
methyl methacrylate	80-62-6	100.12	Exp				0	8	15.67	5.20	2.95	5.02±2.41
ethyl methacrylate	97-63-2	114.14	Exp				0	8	12.50	4.21	2.38	4.04±1.92
hydroxypropyl acrylate	2918-23-2	130.14	Exp				0	8	4.82	1.94	1.16	1.80±0.68
n-butyl acrylate	141-32-2	128.17	Exp				0	8	4.95	1.91	1.08	1.76±0.73
isobutyl acrylate	106-63-8	128.17	AdjP				0	8	4.64	1.81	1.01	1.66±0.69
butyl methacrylate	97-88-1	142.20	Exp				0	8	8.71	2.96	1.64	2.82±1.34
isobutyl methacrylate	97-86-9	142.20	Exp				0	8	8.63	2.93	1.62	2.79±1.34
α-terpineol	98-55-5	154.25	Exp				0	8	4.62	1.67	0.90	1.57±0.78
Citronellol (3,7-dimethyl-6-octen-1-ol)	106-22-9	154.25	Exp				0	8	5.80	2.05	1.12	1.94±0.97
Linalool	78-70-6	156.27	Exp				0	8	5.44	1.96	1.09	1.85±0.91
Geraniol	106-24-1	172.26	Exp				0	8	5.10	1.88	1.06	1.78±0.86
2-ethyl-hexyl acrylate	103-11-7	184.28	Exp				0	8	2.46	0.96	0.47	0.85±0.39
Hexyl cinnamal	101-86-0	216.32	LM				0	10	2.93	1.08	0.64	1.03±0.42
furan	110-00-9	68.07	Exp	1	3	-	4	9.03	3.57	2.10	3.33±1.34	
2-methyl furan	534-22-5	82.10	Exp	1	3	0	4	8.20	3.19	1.88	2.99±1.21	
3-methyl furan	930-27-8	82.10	Exp	1	3	0	4	6.77	2.77	1.68	2.58±0.97	
2-ethyl furan	3208-16-0	96.13	LM				0	8	7.01	2.72	1.61	2.55±1.03
2,5-dimethyl furan	625-86-5	96.13	Exp	1	3	0	4	7.78	2.96	1.75	2.79±1.15	
formaldehyde	50-00-0	30.03	Exp	1	1	0	1 b	9.59	2.89	1.41	2.79±1.68	
acetaldehyde	75-07-0	44.05	Exp	1	2	0	1	6.46	2.53	1.62	2.42±0.86	
propionaldehyde	123-38-6	58.08	Exp	1		0	6	6.96	2.72	1.72	2.58±0.93	
2-methylpropanal	78-84-2	72.11	Exp	1		0	7	5.15	2.08	1.35	1.98±0.67	
butanal	123-72-8	72.11	Exp	1		0	7	5.85	2.30	1.45	2.18±0.78	
c4 aldehydes		72.11	LM			0	7	5.85	2.30	1.45	2.18±0.78	
2,2-dimethylpropanal (pivaldehyde)	630-19-3	86.13	Exp	1		0	8	4.80	1.88	1.21	1.80±0.63	
3-methylbutanal (isovaleraldehyde)	590-86-3	86.13	Exp	1		0	8	4.89	1.91	1.22	1.82±0.65	
pentanal (valeraldehyde)	110-62-3	86.13	Exp	1		0	8	4.98	1.98	1.26	1.88±0.66	
c5 aldehydes		86.13	LM			0	8	4.98	1.98	1.26	1.88±0.66	
glutaraldehyde	111-30-8	100.12	Exp			0	8	4.21	1.70	1.13	1.62±0.54	
hexanal	66-25-1	100.16	Exp	1		0	8	4.26	1.70	1.08	1.60±0.56	
c6 aldehydes		100.16	LM			0	8	4.26	1.70	1.08	1.60±0.56	

Table C-1 (continued)

Description	CAS	MWt [a]	Codes [b]					Reactivity (gm O ₃ / gm VOC)			
			Rep	k	a	Expt	Bias	Unc	MIR	MOIR	EBIR
heptanal	111-71-7	114.19	Exp	1		0	8	3.60	1.43	0.90	1.35±0.48
c7 aldehydes		114.19	LM			0	8	3.60	1.43	0.90	1.35±0.48
2-methyl-hexanal	925-54-2	114.19	Exp			0	8	3.45	1.41	0.88	1.32±0.46
octanal	124-13-0	128.21	Exp			0	8	3.08	1.22	0.74	1.14±0.42
c8 aldehydes		128.21	LM			0	8	3.08	1.22	0.74	1.14±0.42
Hydroxycitronellal	107-75-5	154.25	Exp			0	8	2.54	1.02	0.61	0.94±0.35
glyoxal	107-22-2	58.04	Exp	1		0	6	12.59	3.95	2.02	3.81±2.18
methyl glyoxal	78-98-8	72.06	Exp	1		0	6	16.60	5.25	2.85	5.10±2.70
acrolein	107-02-8	56.06	Exp	1	3	0	2	7.37	2.69	1.62	2.56±1.02
crotonaldehyde	4170-30-3	70.09	Exp	1		0	8	9.34	3.35	1.98	3.20±1.34
methacrolein	78-85-3	70.09	Exp	1	2	0	2	5.96	2.19	1.34	2.09±0.81
hydroxy methacrolein	40364-84-9	86.09	Exp			0	8	6.16	2.36	1.42	2.22±0.85
lumped c5+ unsaturated carbonyl species		100.12	Exp			0	8	6.33	2.34	1.39	2.22±0.90
Cinnamic aldehyde	104-55-2	132.16	LM			0	10	4.79	1.77	1.05	1.68±0.68
Amyl cinnamal	122-40-7	202.29	LM			0	10	3.13	1.16	0.69	1.10±0.45
benzaldehyde	100-52-7	106.12	Exp	1	3	0	2	-0.71	-0.73	-1.05	-0.89±0.26
tolualdehyde		120.15	LM			0	7	-0.63	-0.65	-0.93	-0.78±0.23
acetone	67-64-1	58.08	Exp	1	1	0	2	0.35	0.146	0.088	0.135±0.049
cyclobutanone	1191-95-3	70.09	Exp	1		0	8	0.58	0.34	0.23	0.30±0.09
methyl ethyl ketone	78-93-3	72.11	Exp	1	2	0	2	1.45	0.62	0.37	0.56±0.20
cyclopentanone	120-92-3	84.12	Exp	1		0	8	1.08	0.65	0.42	0.57±0.17
c5 cyclic ketones		84.12	LM			0	8	1.08	0.65	0.42	0.57±0.17
2-pentanone	107-87-9	86.13	Exp	1	2	0	2	2.72	1.33	0.85	1.21±0.38
3-pentanone	96-22-0	86.13	Exp	1		0	6	1.18	0.59	0.37	0.52±0.18
c5 ketones		86.13	LM			0	7	2.72	1.33	0.85	1.21±0.38
methyl isopropyl ketone	563-80-4	86.13	Exp	1		0	6	1.60	0.79	0.50	0.71±0.22
2,4-pentanedione	123-54-6	100.12	Exp			0	8	0.99	0.38	0.22	0.35±0.14
cyclohexanone	108-94-1	98.14	Exp	1	2	0	2	1.25	0.72	0.42	0.61±0.22
c6 cyclic ketones		98.14	LM			0	7	1.25	0.72	0.42	0.61±0.22
4-methyl-2-pentanone	108-10-1	100.16	Exp	1	2	0	3	3.78	1.67	1.07	1.55±0.51
methyl n-butyl ketone	591-78-6	100.16	Exp	1		0	8	3.02	1.49	0.94	1.34±0.43
methyl t-butyl ketone	75-97-8	100.16	Exp	1		0	8	0.62	0.32	0.20	0.29±0.09
c6 ketones		100.16	LM			0	8	3.02	1.49	0.94	1.34±0.43
c7 cyclic ketones		112.17	LM			0	8	1.09	0.63	0.37	0.53±0.19
2-heptanone	110-43-0	114.19	Exp	1	3	?	4	2.23	1.16	0.69	1.01±0.34
2-methyl-3-hexanone	7379-12-6	114.19	Exp			0	8	1.44	0.77	0.47	0.67±0.23
di-isopropyl ketone	565-80-0	114.19	Exp	1		0	8	1.23	0.67	0.40	0.58±0.21
c7 ketones		114.19	LM			0	8	2.23	1.16	0.69	1.01±0.34
5-methyl-2-hexanone	110-12-3	114.19	AdjP	1		0	8	2.28	1.19	0.76	1.06±0.33
3-methyl-2-hexanone	2550-21-2	114.19	Exp			0	8	2.43	1.25	0.77	1.10±0.37
c8 cyclic ketones		126.20	LM			0	8	0.97	0.56	0.33	0.47±0.17
2-octanone	111-13-7	128.21	Exp	1		0	8	1.29	0.73	0.39	0.60±0.23
c8 ketones		128.21	LM			0	8	1.29	0.73	0.39	0.60±0.23
c9 cyclic ketones		140.22	LM			0	8	0.87	0.50	0.30	0.43±0.15
2-propyl cyclohexanone	94-65-5	140.22	AdjP			0	8	1.40	0.76	0.38	0.62±0.27
4-propyl cyclohexanone	40649-36-3	140.22	Exp			0	8	1.72	0.89	0.49	0.75±0.29
2-nonanone	821-55-6	142.24	Exp	1		0	8	0.98	0.57	0.27	0.44±0.19

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)			
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR
di-isobutyl ketone (2,6-dimethyl-4-heptanone)	108-83-8	142.24	Exp	1		0	8	2.57	1.15	0.68	1.03±0.37
c9 ketones		142.24	LM			0	8	0.98	0.57	0.27	0.44±0.19
camphor	76-22-2	152.23	Exp			0	8	0.43	0.26	0.089	0.184±0.112
c10 cyclic ketones		154.25	LM			0	8	0.79	0.46	0.27	0.39±0.14
2-decanone	693-54-9	156.27	AdjP	1		0	8	0.80	0.48	0.187	0.35±0.19
c10 ketones		156.27	LM			0	8	0.80	0.48	0.187	0.35±0.19
2,6,8-trimethyl-4-nonanone; isobutyl heptyl ketone	123-18-2	184.32	Exp			0	8	1.56	0.75	0.39	0.63±0.26
biacetyl	431-03-8	86.09	Exp	1		0	6	20.10	6.46	3.68	6.31±3.15
methylvinyl ketone	78-94-4	70.09	Exp	1	3	0	2	9.56	3.68	2.24	3.47±1.35
mesityl oxide (2-methyl-2-penten-4-one)	141-79-7	98.14	LM			0	8	6.46	2.39	1.41	2.26±0.92
isophorone {3,5,5-trimethyl-2-cyclohexenone}	78-59-1	138.21	LM			0	8	4.58	1.70	1.00	1.60±0.65
1-nonene-4-one	61168-10-3	140.22	Exp			0	8	3.00	1.24	0.71	1.12±0.43
hydroxy acetone	116-09-6	74.08	Exp	1		0	8	3.21	1.20	0.66	1.11±0.49
dihydroxyacetone	96-26-4	90.08	Exp			0	8	3.72	1.43	0.80	1.32±0.57
methoxy acetone	5878-19-3	88.11	Exp	1		0	8	1.96	0.95	0.63	0.88±0.25
diacetone alcohol	123-42-2	116.16	Exp			0	8	0.56	0.30	0.184	0.26±0.09
phenol	108-95-2	94.11	LM			0	8	2.75	0.163	-0.89	-0.057±0.876
c7 alkyl phenols	1319-77-3	108.14	LM			0	5	2.40	0.142	-0.78	-0.050±0.762
<i>m</i> -cresol	108-39-4	108.14	LM		4	-0	5	2.40	0.142	-0.78	-0.050±0.762
<i>p</i> -cresol	106-44-5	108.14	LM		4	0?	5	2.40	0.142	-0.78	-0.050±0.762
<i>o</i> -cresol	95-48-7	108.14	Exp	1	4	?	5	2.40	0.142	-0.78	-0.050±0.762
4-vinylphenol	2628-17-3	120.15	LM			0	11	1.44	0.161	-0.41	-0.007±0.452
2,4-dimethyl phenol	105-67-9	122.16	LM			0	8	2.12	0.125	-0.69	-0.044±0.675
2,5-dimethyl phenol		122.16	LM			0	8	2.12	0.125	-0.69	-0.044±0.675
3,4-dimethyl phenol	95-65-8	122.16	LM			0	8	2.12	0.125	-0.69	-0.044±0.675
2,3-dimethyl phenol	526-75-0	122.16	LM			0	8	2.12	0.125	-0.69	-0.044±0.675
2,6-dimethyl phenol	576-26-1	122.16	LM			0	8	2.12	0.125	-0.69	-0.044±0.675
c8 alkyl phenols		122.16	LM			0	8	2.12	0.125	-0.69	-0.044±0.675
methylparaben (4-hydroxybenzoic acid, methyl ester)	99-76-3	152.15	LM			0	11	1.70	0.101	-0.55	-0.036±0.542
2,3,5-trimethyl phenol	697-82-5	136.19	LM			0	8	1.90	0.113	-0.62	-0.039±0.606
2,3,6-trimethyl phenol	2416-94-6	136.19	LM			0	8	1.90	0.113	-0.62	-0.039±0.606
c9 alkyl phenols		136.19	LM			0	8	1.90	0.113	-0.62	-0.039±0.606
c10 alkyl phenols		150.22	LM			0	8	1.73	0.102	-0.56	-0.036±0.549
propylparaben	94-13-3	180.20	LM			0	11	1.44	0.085	-0.47	-0.030±0.458
c11 alkyl phenols		164.24	LM			0	8	1.58	0.094	-0.51	-0.033±0.502
c12 alkyl phenols		178.27	LM			0	8	1.45	0.086	-0.47	-0.030±0.463
2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol	128-37-0	220.35	LM			0	10	1.18	0.070	-0.38	-0.024±0.374
benzyl alcohol	100-51-6	108.14	Exp	1	2	0	4	5.08	1.77	0.85	1.62±0.82
methoxybenzene; anisole	100-66-3	108.14	Exp	1		0	8	6.61	2.25	1.04	2.05±1.09
beta-phenethyl alcohol	98-85-1	122.16	LM			-	11	4.49	1.57	0.76	1.44±0.73

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)				
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
2-phenoxyethanol; ethylene glycol phenyl ether	122-99-6	138.16	Exp				0	8	4.43	1.64	0.85	1.50±0.69
phthalic anhydride	85-44-9	148.12	Exp				0	8	2.53	0.92	0.41	0.81±0.44
cinnamic alcohol	104-54-1	134.18	LM				-1	10	0.83	0.099	-0.29	-0.031±0.270
1-phenoxy-2-propanol	770-35-4	152.19	LM				0	8	1.55	0.63	0.28	0.54±0.27
anethol	104-46-1	148.20	LM				0	11	0.75	0.090	-0.26	-0.028±0.245
1,2-diacetyl benzene	704-00-7	162.19	Exp	1			0	8	2.20	0.80	0.34	0.70±0.39
diethyl phthalate	84-66-2	222.24	Exp				0	8	1.58	0.59	0.26	0.52±0.27
2-ethylhexyl benzoate	5444-75-7	234.33	Exp				0	10	0.92	0.42	0.176	0.34±0.17
Di n-butyl phthalate	84-74-2	278.34	Exp				0	8	1.21	0.48	0.22	0.42±0.20
nitrobenzene	98-95-3	123.11	Exp	1			0	8	0.054	0.007	-0.013	0.002±0.016
m-nitrotoluene	99-08-1	137.14	Exp	1			0	8	0.49	0.165	0.035	0.130±0.102
para toluene isocyanate	622-58-2	133.15	Exp	1	2		0	5	1.04	-0.077	-0.52	-0.167±0.377
2,4-toluene diisocyanate	584-84-9	174.16	Exp	1	2		0	5	-0.084	-0.54	-0.82	-0.61±0.24
2,6-toluene diisocyanate	91-08-7	174.16	LM		4		0	5	-0.084	-0.54	-0.82	-0.61±0.24
toluene diisocyanate (mixed isomers)	26471-62-5	174.16	LM				0	5	-0.084	-0.54	-0.82	-0.61±0.24
methylene diphenylene diisocyanate	101-68-8	250.25	Exp				0	8	0.88	0.020	-0.31	-0.044±0.273
methylamine	74-89-5	31.06	Exp	1			+	13 a,n	7.25	4.04	2.60	3.57±1.10
dimethyl amine	124-40-3	45.08	Exp	1			+	13 a,n	2.65	1.84	1.33	1.61±0.57
ethyl amine	75-04-7	45.08	Exp	1			+	13 a,n	5.45	2.97	1.91	2.63±0.81
trimethyl amine	75-50-3	59.11	Exp	1			+	13 a,n	5.27	2.75	1.81	2.48±0.75
isopropylamine	75-31-0	59.11	Exp		4a		+	12 a,n	6.97	3.26	2.06	2.97±0.97
t-butyl amine	75-64-9	73.14	Exp	1	4a		-	12 a	-3.26	-1.06	-0.44	-0.99±0.70
triethyl amine	121-44-8	101.19	Exp				+	13 a,n	3.07	1.48	0.91	1.31±0.45
triethylene diamine	280-57-9	112.17	LM				+	13 a,n	2.77	1.33	0.82	1.18±0.40
ethanolamine	141-43-5	61.08	Exp		3a		+	12 a,n	6.59	2.99	1.85	2.72±0.93
dimethylaminoethanol	108-01-0	89.14	Exp	1			+	13 a,n	5.15	2.21	1.40	2.05±0.70
2-amino-1-butanol	96-20-8	89.14	Exp				+	13 a,n	4.79	2.14	1.31	1.95±0.67
2-amino-2-methyl-1-propanol	124-68-5	89.14	Exp		3a		-	12 a	-2.68	-0.80	-0.30	-0.76±0.62
diethanol amine	111-42-2	105.14	Exp				+	13 a,n	2.22	1.08	0.70	0.98±0.32
triethanolamine	102-71-6	149.19	Exp				+	13 a,n	3.25	1.37	0.81	1.25±0.46
triisopropanolamine	122-20-3	191.27	Exp				+	13 a,n	1.99	0.96	0.60	0.86±0.29
methyl nitrite	624-91-9	61.04	Exp	1			0	6	10.94	4.76	4.20	5.05±1.35
acrylonitrile	107-13-1	53.06	Exp	1			0	10	2.18	1.09	0.73	1.01±0.29
1-nitropropane	108-03-2	89.09	Exp				0	8	0.20	0.147	0.108	0.131±0.029
ethyl methyl ketone oxime	96-29-7	87.12	Exp				0	10	1.55	1.32	1.45	1.40±0.30
n-methyl-2-pyrrolidone	872-50-4	99.13	Exp	1	2		0	2	2.28	1.16	0.68	1.01±0.35
lauryl pyrrolidone	2687-96-9	253.42	LM				0	11	0.89	0.45	0.27	0.40±0.14
methyl chloride	74-87-3	50.49	Exp	1			0	10	0.037	0.020	0.013	0.018±0.005
dichloromethane	75-09-2	84.93	Exp	1			0	10	0.038	0.026	0.018	0.023±0.006
methyl bromide	74-83-9	94.94	Exp	1			0	10	0.018	0.010	0.006	0.009±0.003
chloroform	67-66-3	119.38	Exp	1			0	10	0.020	0.014	0.010	0.012±0.003
carbon tetrachloride	56-23-5	153.82	LM				0	1	0	0	0	0
methylene bromide	74-95-3	173.83	LM				0	1	0	0	0	0
ethyl chloride	75-00-3	64.51	Exp	1			0	10	0.27	0.168	0.111	0.147±0.044
1,1-dichloroethane	75-34-3	98.96	Exp	1			0	10	0.065	0.043	0.030	0.038±0.009

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]				Reactivity (gm O ₃ / gm VOC)			
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR
1,2-dichloroethane	107-06-2	98.96	Exp	1		0	10	0.21	0.099	0.058	0.088±0.032
ethyl bromide	74-96-4	108.97	Exp	1		0	20	0.121	0.075	0.050	0.066±0.020
1,1,1-trichloroethane	71-55-6	133.40	Exp	1		0	10	0.005	0.003	0.002	0.003±0.001
1,1,2-trichloroethane	79-00-5	133.40	Exp	1		0	10	0.082	0.043	0.026	0.038±0.012
1,2-dibromoethane	106-93-4	187.86	Exp	1		0	20	0.098	0.047	0.028	0.042±0.015
1,2-dichloropropane	78-87-5	112.99	Exp			0	10	0.28	0.136	0.082	0.121±0.042
n-propyl bromide	106-94-5	122.99	Exp	1	2x	-,+2	20n	0.40	0.22	0.135	0.190±0.061
1-chlorobutane	109-69-3	92.57	Exp			0	10	1.04	0.59	0.37	0.52±0.16
n-butyl bromide	109-65-9	137.02	Exp	1	2x	-,+2	20n	0.78	0.44	0.28	0.38±0.12
3-(chloromethyl)-heptane	123-04-6	148.67	LM			0	10	0.86	0.53	0.27	0.42±0.17
vinyl chloride	75-01-4	62.50	Exp	1		0	10	2.71	1.42	0.95	1.29±0.37
1,1-dichloroethene	75-35-4	96.94	Exp			0	10	2.76	1.22	0.82	1.13±0.36
trans-1,2-dichloroethene	156-60-5	96.94	Exp	1		0	10	1.66	0.75	0.44	0.67±0.25
cis-1,2-dichloroethene		96.94	LM			0	10	1.66	0.75	0.44	0.67±0.25
trichloroethylene	79-01-6	131.39	Exp	1	2x	+2	20	0.61	0.33	0.21	0.29±0.09
perchloroethylene	127-18-4	165.83	Exp	1		0	10	0.029	0.020	0.013	0.017±0.005
3-chloropropene		76.52	Exp			0	10	12.20	4.04	2.20	3.84±1.89
trans-1,3-dichloropropene	10061-02-6	110.97	Exp	1	2m	0	3	5.00	1.83	1.03	1.71±0.76
cis-1,3-dichloropropene	10061-01-5	110.97	Exp	1	2m	0	3	3.66	1.44	0.83	1.33±0.55
1,3-dichloropropene mixture		110.97	LM	1	2	0	2	4.25	1.61	0.92	1.49±0.64
2-(cl-methyl)-3-cl-propene	1871-57-4	125.00	Exp	1	4	-	20	6.75	2.30	1.30	2.18±1.01
monochlorobenzene	108-90-7	112.56	Exp	1		0	8	0.31	0.045	-0.068	0.017±0.091
p-dichlorobenzene	106-46-7	147.00	Exp			0	10	0.171	0.025	-0.039	0.009±0.051
o-dichlorobenzene	95-50-1	147.00	LM			0	8	0.171	0.025	-0.039	0.009±0.051
hexafluorobenzene	392-56-3	186.05	Exp	1		0	8	0.045	0.006	-0.011	0.002±0.014
2-chlorotoluene	95-49-8	126.58	LM			1	8	2.86	1.00	0.40	0.88±0.51
benzotrifluoride	98-08-8	146.11	Exp	1		0	8	0.29	0.109	0.042	0.092±0.053
p-trifluoromethyl-cl-benzene	98-56-6	180.55	Exp	1		0	8	0.122	0.047	0.018	0.039±0.023
methyl nonafluorobutyl ether	163702-07-6	234.06	Exp			0	8	0.051	0.041	0.030	0.036±0.008
methyl nonafluoroisobutyl ether	163702-08-7	234.06	LM			0	8	0.051	0.041	0.030	0.036±0.008
ethyl nonafluorobutyl ether	163702-05-4	264.09	Exp			+	8	0.190	0.124	0.084	0.108±0.026
ethyl nonafluoroisobutyl ether	163702-06-5	264.09	LM			+	8	0.190	0.124	0.084	0.108±0.026
chloroacetaldehyde	107-20-0	78.50	Exp	1		0	7	12.44	3.72	1.85	3.58±2.05
chloropicrin	76-06-2	164.38	Exp	1	2	0	1	1.87	1.08	1.16	1.18±0.19
hexamethyldisiloxane	107-46-0	162.38	Exp	1	3	0	5	-0.030	0.020	0.032	0.020±0.020
hydroxymethyldisiloxane		164.35	Exp	1	3	0	5	-0.137	-0.019	0.015	-0.015±0.043
d4 cyclosiloxane	556-67-2	296.62	Exp	1	3	0	5	-0.059	-0.014	0.001	-0.011±0.016
d5 cyclosiloxane	541-02-6	370.77	Exp	1	4	0	5	-0.070	-0.016	0.001	-0.014±0.019
carbon disulfide	75-15-0	76.14	Exp	1	2	0	2	0.23	0.159	0.125	0.147±0.026
methyl isothiocyanate	556-61-6	73.12	Exp	1	2	0	2	0.31	0.21	0.186	0.20±0.03
dimethyl sulfoxide	67-68-5	78.13	Exp	1	2	-2,0	4	6.63	2.47	1.54	2.37±0.97
molinate		187.30	Exp			0	7	1.43	0.70	0.43	0.62±0.21
eptc (s-ethyl dipropylthiocarbamate)	759-94-4	189.32	Exp	1	2	0	2	1.57	0.82	0.50	0.72±0.24

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]			Reactivity (gm O ₃ / gm VOC)					
				k	a	Expt	Bias	Unc	MIR	MOIR	EBIR	Base
pebulate		203.34	Exp				0	7	1.58	0.79	0.46	0.69±0.25
thiobencarb		257.78	Exp				0	8	0.64	0.27	0.100	0.21±0.12
methyl iodide	74-88-4	141.94	Exp				0	3	-0.52	-2.02	-2.65	-2.11±0.68
Base ROG Mixture		14.44	Mix				0	7	3.56	1.46	0.81	1.32±0.53
Final LEV -- RFA		14.03	Mix				0	7	3.48	1.43	0.77	1.28±0.54
TLEV Exhaust -- RFA		14.04	Mix				0	7	3.95	1.58	0.86	1.43±0.61
TLEV Exhaust -- Phase 2		14.12	Mix				0	7	3.91	1.58	0.87	1.43±0.60
Final LEV -- Phase 2		14.22	Mix				0	7	3.39	1.40	0.77	1.26±0.52
TLEV Exhaust -- LPG		14.86	Mix				0	7	2.02	0.89	0.55	0.82±0.28
TLEV Exhaust -- CNG		15.22	Mix				0	7	0.71	0.34	0.22	0.31±0.10
TLEV Exhaust -- E-85		20.74	Mix				0	7	2.48	1.18	0.75	1.08±0.35
TLEV Exhaust -- M-85		27.45	Mix				0	7	1.56	0.62	0.35	0.57±0.24
Composite mineral spirit (naphthas or lactol spirits) (CARB Profile ID 802)		14.06	Mix				0	7	1.75	0.80	0.36	0.66±0.31
Safety-Kleen Mineral Spirits "A" (Type I-B, 91% Alkanes)		14.08	Mix	2	0,+		7		1.09	0.57	0.23	0.44±0.22
Safety-Kleen Mineral Spirits "B" (Type II-C)		14.10	Mix	2	0,+		7		0.62	0.38	0.127	0.27±0.17
Safety-Kleen Mineral Spirits "C" (Type II-C)		14.11	Mix	2	0,+		7		0.62	0.39	0.126	0.27±0.17
Exxon Exxol(r) D95 Fluid		14.11	Mix	2	0		7		0.53	0.33	0.104	0.23±0.15
Safety-Kleen Mineral Spirits "D" (Type II-C)		14.12	Mix	2	0,+		7		0.62	0.39	0.127	0.27±0.17
Exxon Isopar(r) M Fluid		14.15	Mix	2	0		7		0.51	0.33	0.099	0.22±0.15
Thinning Solvent/Mineral Spirits (Cal Poly Slo. 1996)		14.40	Mix				0	7	1.79	0.85	0.41	0.71±0.30
Aromatic 100		13.36	Mix	2	0		7		7.55	2.62	1.34	2.43±1.19
Kerosene		13.94	Mix	2	0		7		1.45	0.67	0.29	0.54±0.26
Regular mineral spirits		13.97	Mix	2	0		7		1.73	0.78	0.34	0.64±0.30
Reduced Aromatics Mineral Spirits		14.05	Mix	2	0		7		1.06	0.56	0.22	0.43±0.22
Dearomatized Alkanes, mixed, predominately C10- C12		14.09	Mix	2	0		7		0.77	0.46	0.172	0.34±0.19
VMP Naphtha		14.16	Mix	2	0		7		1.10	0.64	0.29	0.50±0.23
Synthetic isoparaffinic alkane mixture, predominately C10-C12		14.20	Mix	2	0		7		0.66	0.41	0.139	0.29±0.17
ASTM-3C1 "Highly Branched" rep'n		14.20	Mix				0	7	1.00	0.59	0.26	0.45±0.21
Oxo-Tridecyl Acetate		16.19	Mix				0	7	0.52	0.31	0.106	0.22±0.14
Oxo-Dodecyl Acetate		16.30	Mix				0	7	0.56	0.33	0.114	0.24±0.14
Oxo-Decyl Acetate		16.71	Mix	2	0		7		0.64	0.39	0.151	0.29±0.15
Oxo-Nonyl Acetate		16.89	Mix				0	7	0.67	0.40	0.159	0.30±0.16
Oxo-Octyl Acetate		17.23	Mix				0	7	0.76	0.46	0.20	0.35±0.16
Oxo-Heptyl Acetate		17.58	Mix				0	7	0.79	0.47	0.23	0.37±0.16
Oxo-Hexyl Acetate		18.02	Mix				0	7	0.83	0.51	0.27	0.41±0.16

Table C-1 (continued)

Description	CAS	MWt [a]	Rep	Codes [b]			Reactivity (gm O ₃ / gm VOC)				
				k	a	Bias	Unc	MIR	MOIR	EBIR	Base
Unspeciated C6 Alkanes (n-, br-, and cyc-)		14.25	Mix			0	8	1.25	0.80	0.49	0.68±0.22
Unspeciated C7 Alkanes (n-, br-, and cyc-)		14.22	Mix			0	8	1.26	0.77	0.41	0.62±0.23
Unspeciated C8 Aromatics		13.27	Mix			0	8	7.56	2.56	1.20	2.34±1.23
Unspeciated C8 Alkanes (n-, br-, and cyc-)		14.19	Mix			0	8	1.16	0.70	0.34	0.55±0.23
Unspeciated C9 Aromatics		13.34	Mix			0	8	8.11	2.82	1.47	2.62±1.27
Unspeciated C9 Alkanes (n-, br-, and cyc-)		14.18	Mix			0	8	0.96	0.57	0.24	0.43±0.21
Unspeciated C10 Aromatics		13.39	Mix			0	8	7.21	2.52	1.31	2.34±1.12
Unspeciated C10 Alkanes (n-, br-, and cyc-)		14.16	Mix			0	8	0.79	0.48	0.186	0.35±0.19
Unspeciated C11 Aromatics		13.43	Mix			0	8	7.02	2.46	1.31	2.29±1.08
Unspeciated C11 Alkanes (n-, br-, and cyc-)		14.15	Mix			0	8	0.64	0.40	0.131	0.28±0.17
Unspeciated C12 Aromatics		13.32	Mix			0	8	5.70	1.98	1.03	1.84±0.88
Unspeciated C12 Alkanes (n-, br-, and cyc-)		14.14	Mix			0	8	0.59	0.37	0.118	0.26±0.16
Unspeciated C13 Aromatics		13.53	Mix			0	8	5.72	2.01	1.08	1.88±0.88
Unspeciated C13 Alkanes (n-, br-, and cyc-)		14.13	Mix			0	8	0.53	0.34	0.106	0.23±0.15
Unspeciated C14 Aromatics		13.56	Mix			0	8	5.22	1.84	0.98	1.72±0.80
Unspeciated C14 Alkanes (n-, br-, and cyc-)		14.12	Mix			0	8	0.50	0.32	0.100	0.22±0.15
Unspeciated C15 Aromatics		13.59	Mix			0	8	4.77	1.69	0.90	1.58±0.73
Unspeciated C15 Alkanes (n-, br-, and cyc-)		14.12	Mix			0	8	0.47	0.30	0.097	0.21±0.14
Unspeciated C16 Aromatics		13.62	Mix			0	8	4.39	1.56	0.83	1.45±0.67
Unspeciated C16 Alkanes (n-, br-, and cyc-)		14.11	Mix			0	8	0.43	0.28	0.087	0.190±0.131

[a] Molecular weights for complex mixtures (base ROG mixture and mixtures listed below it) are given on a per carbon basis.

[b] Codes used in this tabulation are as follows:

"Rep" ... Codes for method used to represent the VOC in the mechanism

Exp An explicit mechanism assignment has been made for this compound or model species. See Carter (2007a) or Table A-1 for the mechanism.

AdjP An explicit mechanism assignment has been made for this compound and the adjusted product version of the mechanism has been used when calculating its atmospheric reactivity values. The adjusted product mechanism is given in Carter et al (2007a).

Table C-1 (continued)

LM	This compound is represented using the "Lumped Molecule" method. See Carter et al (2007a) or Table A-2.	
Mix	This is represented by a complex mixture of detailed model species. The compositions of these mixtures are given in Carter et al (2007a).	
"k a"	... Codes indicating of measurement data for the reaction rate constants	
1	The OH radical rate constant has been measured. See Carter (2007a) or Table A-1 for the rate constant and reference citation. If the compound is consumed primarily by photolysis, this code means that absorption cross section and quantum yield are available and given by Carter (2007a).	
blank	The OH radical rate constant or (if primarily photoreactive) the photolysis rate parameters had to be estimated. See Carter (2007a) for documentation of the estimation method used.	
"Expt"	... Environmental Chamber Data Availability Codes (if blank, no suitable evaluation data are available).	
1	Extensive evaluation data for a variety of conditions.	
2	Sufficient data available. At least 2 and often 3 types of evaluation experiments to test data under different conditions.	
3	Limited evaluation data; usually representing one set of conditions, or some inconsistencies in evaluation results.	
3a	Evaluation data exist for 2 or more sets of conditions, but uncertainties exist concerning amount of compound available to react in the gas phase. See Carter and Warren (2007).	
4	Data from only a single experiment is available, results from different experiments gave inconsistent results, or problems exist with the data.	
4a	Data from only a single experiment is available, and uncertainties exist concerning the amount of compound available for reaction in the gas phase. See Carter and Warren (2007).	
m	This compound was studied in a mixture with the other isomer. Since the reactivities of the two isomers are different, the uncertainty classification has been increased over that of the mixture that was studied.	
x	No attempt was made to improve the mechanism performance to fit the available data.	
"Bias"	... Probable reactivity prediction bias codes (if blank, this compound has not been rated)	
	<u>Chamber data available</u>	<u>No chamber data available</u>
0	No apparent bias	Direction of bias is unknown
+	Some indication of positive bias	Positive bias considered to be more likely than not
-	Some indication of negative bias	Negative bias is considered to be more likely than not
±2	Bias found to be relatively large	Bias may be relatively large
x,x	If two codes given, the first indicates observed or probable bias for predictions of rates of NO oxidation and O ₃ formation, which is important in affecting MIR reactivity, and the second indicates observed or probable bias for low NO _x conditions. E.g. "0,+" if chamber data available indicates that the model simulated rates of NO oxidation and O ₃ formation but overpredicted final O ₃ yields in NO _x -limited experiments.	
?	There is some inconsistency in the data concerning this bias indication (or lack thereof), or the bias is unknown but may be large.	

Table C-1 (continued)

- a The reactivity predictions and representation in the mechanism is based on the assumption that this compound is completely available for reaction in the gas phase. This is likely not to be the case for this compound. Thus the reactivity estimate may be high for compounds that have positive O₃ impacts and low for compounds that are calculated to be inhibitors.

"Unc" ... Uncertainty codes (if blank, this compound has not been rated)

The following codes are used when experimental data are available to evaluate the reactivity predictions of the mechanism and the mechanism was (or would have been) adjusted to fit the data as appropriate to improve the fits.

- 1 The mechanism appears to be reasonably well established or at least its predictions appear to be reasonably well evaluated. This does not rule out possible changes in reactivity values if the base mechanism, scenario conditions, or reactivity metrics are changed. Also used for compounds known or expected to be inert or to have upper limit reactivities much less than methane.
- 2 The mechanism has been evaluated at least to some extent, rate constant data are available for its major reactions, and is not considered to have large uncertainties. If a likely bias is indicated it is probably not large.
- 3 The mechanism has been evaluated at least to some extent and rate constant data are available for its major reactions, but the mechanism has some uncertainties or apparent inconsistencies with available laboratory data, or there are some uncertainties in the evaluation data. If a likely bias is indicated it is probably not large.
- 4 The mechanism has been evaluated at least to some extent and rate constant data are available for its major reactions, but the mechanism has some uncertainties, apparent inconsistencies with available laboratory data exist that may be significant, or the available evaluation database is limited or has problems. If a likely bias of ± 1 is indicated it is probably not large.
- 5 A highly parameterized mechanism has been adjusted to simulate chamber data. The appropriateness of the parameterization, and its ability to extrapolate to ambient conditions, is uncertain.

The following codes are used for compounds for which no experimental data exist to evaluate reactivity predictions of the mechanism, or where such data, if any, were not taken into account when developing the mechanism.

- 6 The mechanism has not been evaluated but at least the important reaction rate(s) have been measured and the methods used to estimate the mechanism have been found to generally perform reasonably well for compounds where evaluation data are available, or the mechanisms are not expected to be highly complex. If a likely bias is indicated it is based on evaluation results for similar compounds.
- 7 The mechanism has not been evaluated and the reaction rates had to be estimated, but the methods used to estimate the rate constant(s) and mechanism have been found to generally perform reasonably well for compounds where evaluation data are available. If a likely bias is indicated it is based on evaluation results for similar compounds. This code is also used for lumped molecule or mixture representations that are considered to be reasonably appropriate.
- 8 The estimated mechanism and/or relevant rate constant(s) or photolysis rates have some uncertainties, but mechanisms based on similar assumptions have been found to perform satisfactorily for related compounds, or the mechanisms are not expected to be highly complex. The applicability of these assumptions to this compound, or the extrapolation of mechanisms for smaller compounds to one of this size, has some uncertainty. This code is also used for lumped molecule representations whose appropriateness has some uncertainty.

Table C-1 (continued)

The uncertainty codes below mean that use of the reactivity values in regulatory applications is problematical.

- 10 The estimated mechanism is sufficiently uncertain that it needs to be evaluated. This code is also used for lumped molecule representations whose appropriateness is considered to be highly uncertain. However, the representation employed is the current best estimate, and the direction of the bias is unknown.
- 11 The estimated mechanism is extremely uncertain that it needs to be evaluated. This code is also used for lumped molecule representations whose appropriateness is questionable, but no better alternative exists, and the bias of using the representation is unknown. However, the representation employed is the current best estimate, and the direction of the bias is unknown.
- 12 An estimated mechanism for the gas-phase reactions for this compound has been developed and has been evaluated at least qualitatively against available chamber data, but its estimated atmospheric ozone impact is highly uncertain because the amount of emitted compound available for reaction in the gas-phase is unknown. One important issue is that this compound may be removed by gas-phase reaction with HNO₃, whose presence depends on ambient conditions and may not be appropriately represented in the scenarios used for reactivity assessment. For such compounds two reactivity values are given, and "upper limit magnitude" reactivity value based on assuming that all the emitted VOC is available for gas-phase reaction and that reaction with HNO₃ is negligible (as may be applicable if the HNO₃ formed in gas-phase reactions is removed from the gas phase by other means) and one also assuming that all the emitted VOC is available for gas-phase reaction except that the reaction with gas-phase HNO₃ is fast and there is no other sink for HNO₃ formed in the gas-phase reactions.
- 13 Same as code 12 except that no chamber data are available to test the estimated gas-phase mechanism.
- 20 The representation or estimated mechanism used is considered to be biased, and the direction of the likely bias is indicated by the bias code. Best estimate mechanisms have not been developed.

Additional codes used where applicable

- s Portions of the mechanism are unknown or highly uncertain and simplified or parameterized representation has been adjusted at least in part to fit available data for this or related compounds. This is used primarily for alkylbenzenes.
- d Portions of this mechanism appear to be inconsistent with available laboratory data. This is used primarily for the 1-alkenes, where radical yields in O₃ reactions have to be reduced to simulate chamber data.
- u The mechanism is unknown and a parameterized mechanism adjusted to fit the data for this or related compounds employed.
- m This uncertainty code is only applicable for mixtures whose composition has been analyzed using state-of-the-science methods. Rating of effects of compositional uncertainties is beyond the scope of the project (but see discussion in Carter and Malkina (2005) for hydrocarbon mixtures).
- b The reactivity predictions may be more sensitive than usual to changes in the base mechanism or scenario conditions.
- n Chamber data for this or related compounds suggest that the mechanism may overpredict ozone under conditions where NO_x is limited. This should affect MIR values but will lead to too high reactivities in lower NO_x scenarios.

Table C-1 (continued)

- a This compound may react with HNO_3 to form a non-volatile salt, which may reduce the availability for this compound to react in the gas phase. The importance of this process under atmospheric conditions is uncertain because (a) the salt may revolatilize to the gas-phase species and the equilibrium constant is unknown, (b) the sources and other sinks for HNO_3 may vary significantly from scenario to scenario and have not been established for the reactivity assessment scenarios, and (c) if ammonia or other amines are present they may compete for the HNO_3 and reduce the importance of this process for this amine, and the importance of these processes have not been established for the reactivity scenarios. In order to derive an upper limit ozone impact estimate, the reactivities of these compounds have been calculated assuming that removal by reaction with HNO_3 is uncertain. If this process is important, the magnitude of the actual ozone impact may be an order of magnitude or more low. Therefore, the tabulated reactivity values are upper limits for positively reactive compounds, and lower limits for ozone inhibitors.
- + This may appropriately be considered to be an upper limit estimate in the ozone impact of this compound.
- This may appropriately be considered to be an upper limit estimate in the amount of ozone inhibition caused by this compound. The upper limit reactivity is zero.