COMPUTER MODELING OF ENVIRONMENTAL CHAMBER MEASUREMENTS OF MAXIMUM INCREMENTAL REACTIVITIES OF VOLATILE ORGANIC COMPOUNDS

by

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ABSTRACT

A detailed atmospheric photochemical mechanism which had been previously used in model calculations for developing ozone reactivity scales for volatile organic compounds (VOCs) was evaluated by comparing its predictions with measurements of incremental reactivities in an environmental chamber system. An updated version of this mechanism is also described and evaluated. The experiments consisted of determining the effects of adding representative alkanes, alkenes, aromatic hydrocarbons, aldehydes or CO on NO oxidation, ozone formation and radical levels in a simplified model photochemical smog system representing conditions where ozone formation is most sensitive to VOCs. The published mechanism correctly simulated the observed qualitative reactivity trends, but overpredicted the effect of adding formaldehyde early in the experiments, performed poorly in simulating reactivities of branched alkanes, tended to underpredict the reactivities of alkenes, and did not simulate differences in reactivities of aromatic isomers. The updates to the mechanism improved the simulation results for the branched alkanes and the alkanes, but not for formaldehyde and the aromatics. The implications of these results concerning the development of atmospheric mechanisms for VOCs are discussed.

INTRODUCTION

The formation of ground-level ozone is caused by the gas-phase interactions of emitted volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in the presence of sunlight (NRC, 1991). Development effective control strategies for reducing ozone requires an ability to predictively model the effects of changing VOC and NO_x emissions on ozone. With regard to VOC emissions it is important to recognize that individual VOC compounds can differ significantly in their effects on ozone. Therefore, the model must not only be able to appropriate represent the effects of changing total VOC emissions, but also to appropriately represent the effects of changing the chemical content of the emissions. This is necessary, for example, to assessing the atmospheric effects of alternative fuel use, evaluating control strategies based on solvent substitution, or assessing whether a particular compound is "negligibly reactive", and thus an appropriate candidate for exemption from VOC controls.

The most direct quantitative measure of the degree to which a VOC contributes to ozone formation in a photochemical air pollution episode is its "incremental reactivity" (Carter and Atkinson, 1987; 1989a; Chang and Rudy, 1990; Russell, 1990; Carter, 1991, 1994). This is defined as the amount of additional ozone formation resulting from the addition of a small amount of the compound to the emissions in the episode, divided by the amount of compound added. This depends not only on the VOC and its atmospheric reactions, but also on the conditions of the environment in which the VOC is emitted. Incremental reactivities of VOCs in the atmosphere cannot be measured experimentally because it is not feasible to duplicate in the laboratory all the environmental factors which affect reactivity. They can, however, be calculated using computer airshed models, given a model for airshed conditions and a mechanism for the VOCs' atmospheric chemical reactions. For example, a set of models for airshed conditions throughout the U.S. and a detailed chemical mechanism were used to calculate a "Maximum Incremental Reactivity" (MIR) scale (Carter, 1994). Reactivities in this scale were calculated based on effects of VOCs on ozone formation under relatively high NO_x conditions where changes in VOC emissions have the greatest effect on ozone formation (Carter, 1991, 1994). This scale has been adopted by the California Air Resources Board (ARB) for the derivation of reactivity adjustment factors for use in vehicle emissions standards (CARB 1990, 1991).

However, such model calculations of incremental reactivity can be no more reliable than the chemical mechanisms upon which they are based. To be minimally suitable for this purpose, the mechanisms need to be evaluated under controlled conditions by comparing their predictions against results of environmental chamber experiments in which the VOCs react in the presence of NO_x to form ozone. Although the MIR scale gives reactivity factors for over 100 compounds (Carter, 1994), prior to this study the mechanisms for less than a dozen have been tested against results of environmental chamber experiments. Furthermore, only a few of these experiments provide direct tests of the mechanisms' ability to predict incremental reactivities.

In a companion paper (Carter et al., 1995), we described a study where incremental reactivities of a wide variety of VOCs were measured under high NO_x conditions in an environmental chamber. The results yielded information not only on the effects of these VOCs on NO oxidation and ozone formation in this chamber system, but also information on the relative importance of "direct" and "indirect" factors which affect a VOC's reactivity. More importantly in terms of the discussion here, with these data we now have a means to directly assess test the ability of currently chemical mechanisms to predict a VOC's maximum incremental reactivity.

This paper discusses the performance of two different chemical mechanisms developed by the author in simulating the experimental incremental reactivity data of Carter et al. (1995). Both of these are "detailed" mechanisms in the sense can represent separately the reactions of over 100 types of VOCs emitted into the atmosphere, and thus can, in principle, incorporate our current knowledge concerning their kinetics and mechanisms when calculating their reactivities. [This distinguishes them from "condensed" mechanisms which "lump" a large number of species into broad chemical classes or structural groups for the purpose of computational efficiency (e.g., Gery et al., 1988, Lurmann et al. 1987)]. The first, designated "SAPRC-90", is documented by Carter (1990) and is of significance because it was used to document the "MIR" used in the CARB vehicle emissions regulations. The second, designated "SAPRC-93", is an updated version of this mechanism which incorporates new information concerning some of its aspects, as well as results of model simulations discussed in this paper. The results of this study should give an indication of the capabilities of current detailed chemical mechanisms in simulating maximum incremental reactivities in the atmosphere.

METHODS

Chemical Mechanisms

SAPRC-90 Mechanism. This mechanism is documented by Carter (1990), with updates for various VOCs as described elsewhere (Carter, 1994). It was evaluated extensively against chamber data (Carter and Lurmann, 1991), though the presently available data are sufficient for evaluating reactivity predictions for only a few VOCs. This mechanism was used to calculate the reactivity scales given by Carter (1994), including the MIR scale incorporated in the California Air Resources Board’s Low Emissions Vehicle/Clean Fuels regulations (CARB, 1991). When evaluated using the results of a variety of environmental chamber experiments, it was found to be able to simulate maximum ozone concentrations and rates of NO oxidation and ozone formation to within ±30% for 63% of the experiments, but with a slight bias (~15%) towards overpredicting maximum ozone concentrations in experiments designed to represent ambient mixtures (Carter and Lurmann, 1991). This is comparable or slightly better than the performance of the RADM-II (Stockwell et al., 1990; Carter and Lurmann, 1990) and the Carbon Bond IV (Gery et al., 1988) mechanisms in simulating the same or a similar data base. However, none of these mechanisms have been evaluated using results of incremental reactivity experiments such as those discussed here.

SAPRC-93 Mechanism. This is the same as SAPRC-90 except for the updates and modifications indicated below. Further updates to this mechanism are planned and it has not been as extensively evaluated against the chamber data as the SAPRC-90 mechanism, so this version of the mechanism is considered to be preliminary. It is used here to illustrate how the presently implemented updates affect the simulations of these reactivity experiments. Except as discussed specifically below, the data from this study were not used in the development of this mechanism, although future updates will take these data into account. The differences between the SAPRC-90 and the updated mechanism are as follows:

(1) The formaldehyde absorption cross-sections were updated based on the recent data of Cantrell et al. (1990) and Rogers (1989). This results in a slight increase in the formaldehyde photolysis rate.

(2) The kinetics for the reactions of the acetyl peroxy radical with NO and NO_2, which are involved in the formation and decomposition of PAN, and the kinetics of the thermal decomposition of PAN, were updated based on recent experimental results of Tuazon et al. (1991) and Bridier et al. (1991). This causes the model to predict somewhat higher ozone formation rates than the SAPRC-90 mechanism.

(3) The SAPRC-90 mechanism uses model species ("AFG1" and "AFG2"), whose photolysis rates are adjusted to fit aromatic-NO_x-air chamber experiments, to represent the unknown photoreactive aromatic fragmentation products (Carter, 1990). This approach is still used in the updated mechanism, except that the change in the acetyl peroxy and PAN kinetics required reoptimization of these photolysis rates. In addition, the action spectra (absorption coefficients x quantum yields) for these products were assumed to be proportional for the absorption cross section for acrolein (Gardner et al., 1987), rather than using the somewhat arbitrary action spectrum in the SAPRC-90 mechanism. These changes were found not to significantly affect the performance of the mechanism if the reoptimization is conducted using the same set of experiments as used in the development of SAPRC-90.

(4) The reaction of OH radicals with acetone is assumed to proceed entirely to form, after one NO to NO_2 conversion, acetyl peroxy radicals and formaldehyde, rather than forming 80% methylglyoxal as assumed previously. This is based on updated estimates for alkoxy radical reactions (Atkinson and Carter, 1992). In addition, our model simulations of the acetone quantum yield data of Meyrahn et al. (1986) indicate that the reported quantum yield for 330 nm is probably invalid, and a modified quantum yield spectrum for 325-335 nm was estimated by extrapolating the reported higher wavelength values. These changes had no significant effect on the model simulations discussed here, but were made in conjunction with another study (Carter et al. 1993a).

(5) The mechanisms for the reactions of ozone with alkenes were modified to be consistent with the data of Atkinson and Aschmann (1993), who observed much higher yields of OH radicals than predicted by the SAPRC-90 mechanism. To account for these data, it was assumed that (1) the formation

of OH radicals dominates over other radical-forming fragmentation processes, and (2) in the reactions of unsymmetrical alkenes, the more substituted Criegee biradical, which forms higher OH yields, are formed in relatively higher yields than the less substituted biradicals. The modified ozone reactions for the alkenes discussed in this paper are:

$$\text{Ethene + O3} \rightarrow \text{HCHO + (HCHO2)}$$
$$\text{Propene + O3} \rightarrow \text{0.6 HCHO + 0.4 CCHO + 0.4 (HCHO2) + 0.6 (CCHO2)}$$
$$\underline{\text{trans}}\text{-2-Butene + O3} \rightarrow \text{CCHO + (CCHO2)}$$
$$\text{Isobutene + O3} \rightarrow \text{0.82 HCHO + 0.18 ACET + 0.18 (HCHO2) + 0.82 (C(C)CO2)}$$

where CCHO and ACET represent acetaldehyde and acetone, and (HCHO2), etc., represent the excited Criegee biradicals, which are represented as reacting as follows:

$$\text{(HCHO2)} \xrightarrow{\text{fast}} \text{0.12 CO + 0.12 HO. + 0.12 HO2. + 0.88 (unreactive carbon)}$$

$$\begin{aligned}\text{(CCHO2)} \xrightarrow{\text{fast}} \; & \text{0.3 HCHO + 0.3 CO + 0.6 HO. + 0.3 }\{\text{CCO-O2.+ RCO3.}\}\text{ +} \\ & \text{0.3 }\{\text{RO2-R.+ RO2.}\}\text{ + 0.9 (unreactive carbon)}\end{aligned}$$

$$\text{(C(C)CO2)} \xrightarrow{\text{fast}} \text{HCHO + HO. + }\{\text{R2O2.+ RO2.}\}\text{ + }\{\text{CCO-O2.+ RCO3.}\}$$

[See Carter (1990) for a description of the model species and the methods used to represent peroxy radical reactions.] This is clearly an oversimplification of this complex system (e.g., see Atkinson, 1990, 1994), but is intended to account for the observed OH radical yields and represent the major features affecting these compounds' reactivities. Note that this new mechanism gives substantially higher radical yields in the ozone + alkene systems than the SAPRC-90 mechanism, particularly for internal alkenes.

(6) The reaction of NO with the peroxy radical formed in the reaction of OH radicals with isobutene was assumed to form the corresponding hydroxyalkyl nitrate 10% of the time. This assumption resulted in significant improvements to the fit of model simulations to ozone and PAN yields in isobutene - NO_x - air chamber experiments. Without this assumption, the model with the OH yields indicated by the O_3 + isobutene data of Atkinson and Aschmann (1993) significantly overpredicts O_3 formation rates. If lower radical yields in the O_3 + isobutene reaction are assumed, the model significantly underpredicts PAN (unpublished results from this laboratory).

(7) The representations of isobutane isooctane were modified to improve the model simulations of their reactivities. These changes are discussed in the Results section.

Experiments Modeled

The environmental chamber experiments which were simulated in this study were the "Maximum Incremental Reactivity" experiments described in the companion paper (Carter et al., 1995). Briefly, they consisted of series of repeated 6-hour irradiations of a standard "base case" mixture representing photochemical smog precursors in an indoor environmental chamber, alternating with "test" experiments using the same procedures except that varying amounts of a test VOC was added. The runs were conducted using in a ~3000-liter flexible FEP Teflon reactor and a blacklights light source. The base case mixture consisted of ~3.5 or ~4.5 ppmC of a reactive organic gas (ROG) "mini-surrogate" containing 35% (as carbon) ethene, 50% n-hexane, and 15% m-xylene, and with ~0.5 ppm of oxides of nitrogen (NO_x) in dry (<5% RH), purified air. The mini-surrogate was designed to be an experimentally simple representative of the reactive organic compounds emitted into the atmosphere. Although it is a significant oversimplification of the complex mixture of ROGs present in the atmosphere (see, for example, Jeffries et al. 1989), model calculations show that its use in such experiments provides a more sensitive measure of reactivities than use of more complex mixtures (Carter et al., 1994a). The relatively high NO_x levels (or low ROG/NO_x ratios) were employed to represent "maximum reactivity" conditions where VOCs have the greatest effects on ozone formation (Carter, 1991, 1994).

As discussed by Carter et al. (1995), the reactivity experiments can be grouped into three "sets", with slightly different reaction conditions. In "Set 1", the base case ROG/NO_x ratio was ~7, and apparently there was some contamination by HONO injected with the NO_x (see below). In "Set 2" the NO_x was treated to remove HONO prior to injection, and the O_3 formed in the base case experiments was significantly lower. In "Set 3", which includes the majority of the experiments, the ROG/NO_x ratio was increased to ~9 to increase the O_3 formed in the base case run, while still remaining in the VOC-sensitive "maximum reactivity" regime where O_3 formation was still continuing at the end of the run.

The experiments modeled consisted of all the test experiments listed by Carter et al. (1995) and all of the base case experiments judged to be sufficiently well characterized for modeling. A few base case experiments had uncertain initial reactant concentration because of instrumentation problems and were not modeled. A number of characterization runs were modeled for the purpose of adjusting and evaluating the model for chamber effects, as discussed below.

Chamber Characterization Model

Testing of chemical mechanisms against environmental chamber results requires including appropriate representations of chamber-dependent effects such as wall reactions and characteristics of the light source. The methods used in this study are based on those discussed in detail by Carter and Lurmann (1991), adapted for these specific experiments as discussed by Carter et al. (1993b, 1994b). The specific set of parameters used when modeling the runs for this study are given elsewhere (Carter et al., 1994b). Where possible, the parameters were derived based on analysis of results of characterization experiments carried out in conjunction with these runs. In cases where no data are available for this specific chamber, the parameters used by Carter and Lurmann (1991) for model simulations of runs carried out in the SAPRC ITC were used. The SAPRC ITC is similar in construction to the SARPC ETC chamber used for this study (Carter et al., 1995); both are indoor chambers consisting of 2-mil thick FEP Teflon reaction bags with a blacklight light source. The main difference is that the ETC chamber used dry air, while most ITC runs were humidified to ~50% RH.

Probably the most important single chamber effect is the "chamber radical source", which is discussed by Carter et al. (1982). This effect is represented in our models by a light-dependent OH radical input from an unspecified source (Carter and Lurmann, 1991). As part of a study of effects of chamber and light sources on chamber results, we re-evaluated the radical source assignments for all environmental chambers in our laboratory used for mechanism evaluation experiments (Carter et al. 1994b). It was found that radical source parameter estimates derived from model simulations of NO oxidation rates in n-butane-NO_x and CO-NO_x experiments were much more consistent among chambers and with results of other types of experiments, compared to the radical source estimates derived from rates of decay of organic tracers in the tracer-NO_x-air irradiations (Carter et al., 1982), as used in our previous mechanism evaluation studies (Carter and Lurmann, 1990, 1991; Carter et al., 1993b). The radical source parameters which best fit the results of n-butane-NO_x experiments out in a Teflon Film chamber using dry air, which include outdoor chamber runs carried out at temperatures up to 318°C, are reasonably well fit by the relationship

$$[\text{OH radical input (ppb/min)}] = [\text{NO}_2 \text{ photolysis rate (min}^{-1})] \text{ x } 3.7\text{x}10^{9} \text{ x } e^{-9556/T}$$

where T is in °K. [Note that his gives a somewhat higher radical input rate for these experiments than the assignments used by Carter et al. (1993b).] This is used in all the simulations of all the Set 2 and 3 experiments discussed in this work.

The Set 1 experiments were treated differently because of apparent contamination by nitrous acid (HONO) in the initial NO_x. Even small amounts of HONO can significantly affect the results because its rapid photolysis provides a large and early source of radicals in the experiments (e.g., Carter et al., 1982). Although model simulations of earlier experiments in Teflon film chambers in our laboratories are best fit by assuming initial HONO is negligible (Carter and Lurmann, 1990, 1991), simulation of ETC Set 1 runs could only fit the data if was assumed that ~1.5% of the injected NO_x was in the form of HONO (Carter et al., 1993b). A slightly higher continuous OH radical input ($7x10^{-5}$ x [NO_2 photolysis rate]) was also required to fit the data. The temperature did not vary significantly during the Set 1 runs, so no temperature dependencies are assumed.

The photolysis rates were derived using the measured NO_2 photolysis rates (k_1's), combined with measured spectra of the blacklight light source (Carter et al, 1994b,c). The NO_2 actinometry data for this chamber have been recently re-evaluated (unpublished results), and the revised values are reasonably well fit by the expression k_1 (min^{-1})= 0.35 x (1 - $2.21e^{-0.046xRun\ Number}$), and these assignments were used for modeling. During the Set 1 experiments, the k_1 declined from ~0.43 to 0.36 min^{-1} due to the ageing of the lights (which were new when the series started), but were essentially constant at ~0.36-0.35 min^{-1} for Sets 2 and 3. As discussed by Carter et al. (1995), the results of the Set 1 base case runs are consistent with this decline in light intensity.

Procedure for Modeling Reactivity Data

The procedures for conducting model simulations for comparison with the experimental incremental reactivity measurements was as follows: Each individual test experiment was simulated based on its measured initial reactant concentrations, temperature profiles, light intensity assignments, and chamber effects assignments derived as discussed above. Then a "base case" simulation for the conditions of that experiment, which consisted of repeating the simulation of the test run with the test compound removed, was carried out. If the test compound was a component of the base ROG surrogate (e.g., ethene, n-hexane, or m-xylene), this simulation used the average initial concentration of that component observed in the base case runs. (This is the same procedure as used when deriving the "amount added" for the analysis of the experimentnal data for these runs.) The various measures of incremental or mechanistic reactivity were then derived from these calculations using the exact same analysis procedures as employed for the experimental data (Carter et al., 1995). For example, the simulated IntOH values were derived not from the simulated OH radical concentrations, but from the simulated rates of consumption of the VOC reactant used as the radical tracer in the experimental data analysis.

RESULTS

Simulations of the Base Case Experiments

Representative results of model simulations of individual base case experiments using the SAPRC-90 and the updated mechanisms are shown in the companion paper (Carter et al., 1995). The performance of the mechanisms in simulating the final amounts of O_3 formed plus NO oxidized, d(O_3-NO) (Carter, 1995) in the full data set is shown on Figure 1. The upper part of that figure gives plots of experimental vs calculated d(O_3-NO), with the line showing where the points would lie if they both were equal. The bottom part shows plots of the relationship between the model error [(calculated-experimental)/experimental] and the average temperature, the only experimental parameter which was found to have an apparent effect on model performance.

It can be seen that both mechanisms are able to simulate the O_3 formed and NO oxidized in the base case experiments to within ±25%. The SAPRC-90 mechanism has somewhat less bias in simulating the Set 1 and 2 experiments, but tends to underpredict d(O_3-NO) in the Set 3 runs, particularly at the higher temperatures. The updated mechanism performs somewhat better in simulating the Set 3 runs, though it has a slight but definite bias towards overpredicting d(O_3-NO) in the Set 1 and 2 runs, while still tending to underpredict d(O_3-NO) at temperatures above ~301°K. As discussed in more detail elsewhere (Carter et al., 1994b), these slight biases, and the apparent temperature dependence in the model performance, might in part be due to uncertainties in the chamber characterization model (particularly the radical source), and not necessarily to biases errors in the mechanism.

Simulations of Reactivity Data..

The various measures of reactivity which were obtained from the experiments discussed in this work are discussed in detail in the companion paper (Carter et al., 1995). Briefly, these measures are as follows:

- Incremental Reactivity: This is the change in some measurable quantity caused by adding a VOC to the system, divided by the amount added. This takes into account both how rapidly the VOC reacts and the effects of its reactions on the system.

- Mechanistic Reactivity: This is the change in some measurable quantity caused by adding the VOC, divided by the amount reacted, or incremental reactivity divided by the fraction of the VOC which reacts. This takes into account primarily the effects of the VOC's reactions on the system, with the effects of the reaction rates, to a first approximation at least, being factored out. It also permits comparisons of reaction mechanisms of VOCs with widely differing reaction rates.

- d(O_3-NO): This is the amount of NO consumed + the amount of ozone formed in the experiment, or the change in [O_3]-[NO]. As discussed previously (e.g., Johnson, 1983; Carter and Atkinson, 1987; Carter and Lurmann, 1990, 1991) the chemical processes which cause NO consumption when NO is present are the same as those responsible for O_3 formation once the NO has been consumed. Therefore, reactivities with respect to d(O_3-NO) give a general measure of a VOC's overall potential for forming (or inhibiting) ozone.

- IntOH: This is the integrated OH radical levels. Reactivities relative to IntOH measure the tendency of the VOC's reactions to enhance or inhibit radical levels, and thus their effects on the rates of O_3 formation from the reactions of the other VOCs in the system.

- Direct and Indirect Reactivities: The direct reactivity of a VOC is the amount of O_3 formation and NO oxidation [change in d(O_3-NO)] caused directly by the radicals formed from the reactions of the VOC or its products. The indirect reactivity is the effect of the test VOC on the amount of d(O_3-NO) formed from the reactions the other VOCs present (the base ROG mixture). As discussed in the companion paper (Carter et al., 1995), the indirect d(O_3-NO) reactivities can be estimated from the effect of the VOC on IntOH and the d(O_3-NO)/IntOH ratio observed in the base case experiments, allowing the direct d(O_3-NO) reactivities to be derived from the difference between that and the total reactivity.

The performance of the SAPRC-90 and the updated mechanisms in simulating selected reactivity results are shown in Figures 2-7; these specific examples are discussed in more detail below. Figure 8 shows the overall performance of the two mechanisms in simulating mechanistic reactivities with respect to d(O_3-NO) and IntOH, and in simulating direct mechanistic reactivities for d(O_3-NO). The data shown are the averages of the experimental or calculated results, with the weighting factor in both cases being the reciprocal square of the stated uncertainties of the experimental measurements (Carter et al., 1995). The error bars for the experimental data reflect the standard deviation of the averages and the uncertainty in the data. The "error bars" in the model calculations reflect the variation in the results of the model simulations of the individual experiments which are averaged. This variation, which can be seen to be small compared to experimental uncertainties or differences between experimental and calculated results, is due to the fact that calculated reactivities differ somewhat depending on how much test VOC is added and (to a lesser extent) other experimental conditions.

Direct reactivities are not shown for the more reactive alkenes and aromatics because, as discussed in the companion paper (Carter et al., 1995), they could not be determined with sufficient precision to be meaningful in experiments with compounds with high, positive IntOH reactivities. In addition, such compounds perturb the system to a sufficient extent that the assumptions underlying the derivation of direct reactivities may not be applicable in any case (Carter et al., 1995).

Note that, unlike the data tabulation in Carter et al. (1995) and Figures 2-7, where the reactivities are given on a per mole basis, the units for the d(O_3-NO) and IntOH reactivities in Figure 8 are given on a per mole carbon basis. This is done so the magnitude of the mechanistic reactivities for the differing compounds on a more comparable basis, and because it has a closer relationship to how VOC emissions are quantified. However, the direct mechanistic reactivities are still given on a per-mole basis because the magnitudes are comparable and this is mechanistically more meaningful.

The performance of the mechanisms in simulating the reactivity data for the various VOCs are discussed in the following section.

DISCUSSION

A major objective of this study was to provide data needed to test the ability of chemical mechanisms, such as those used in airshed models, to predict maximum incremental reactivities of VOCs. Previous mechanism evaluations (e.g., Gery et al., 1988, Carter and Lurmann, 1990, 1991) have focused primarily on the ability of mechanisms to simulate results of single VOC-NO_x-air chamber experiments, because they provide a means to test the VOC's mechanism independently of uncertainties in mechanisms of other VOCs. However, such runs represent a chemical environment far different from those most VOCs encounter when they react in the atmosphere. In addition, runs where the only added VOCs are radical inhibiting species such as alkanes are driven almost entirely by chamber effects, rendering them almost useless for mechanism evaluation (Carter et al., 1986; Carter and Lurmann, 1991). Runs employing realistic mixtures of VOCs address these problems, but do not provide a means to unambiguously test mechanisms of a single VOC. Reactivity experiments such as those presented here provide a means to address both these problems. The VOC is reacting in a fairly realistic chemical environment, and the effect of the reactions of a single VOC on the system can at least to some extent be isolated.

Evaluating mechanisms using reactivity experiments is not without compounding effects of uncertainties in the mechanisms for the VOCs present in the base case mixture. If the mechanism cannot accurately simulate the result of the base case experiment, its inability to simulate incremental or mechanistic reactivities might be attributed to this fact rather than errors in the mechanism. Worse yet, errors in the model for the base case mixture may compensate for errors in the mechanism of the added VOC, giving an apparently correct prediction of reactivity for the wrong reason. This does not appear to be major concern in the case of these experiments, since both mechanisms being evaluated can simulate the base case d(O_3-NO) to better than ±25%. The biases that do show up on Figure 8 are not large compared to the uncertainty of most of the incremental or mechanistic reactivity measurements, and would, to some extent at least, be canceled out in reactivity simulations because they would be applicable to both the simulation of the test experiment as well as the base case run. However, the possibility that the relatively good fits in the base case simulations are due to compensating errors, which are no longer compensating when the system is perturbed by the addition of the test VOC, can never be totally ruled out.

Although incremental reactivities (ozone formed per VOC emitted) are the quantities of practical interest in assessing effects of VOCs on ozone, the performance of the mechanism is evaluated in terms of predictions of mechanistic reactivities (ozone formed per VOC reacted) because this is the most uncertain component of reactivity. Since the rate constants for atmospheric reaction of most VOCs are reasonably well known (e.g., see Atkinson, 1989, 1990, 1994 and references therein), if the model can correctly predict mechanistic reactivities it is reasonable to expect it to be able to predict incremental reactivities under chemically similar conditions, provided (of course) that the base case mechanism is correct. If, on the other hand, the model cannot simulate mechanistic reactivities, the incremental reactivity predictions will obviously be meaningless.

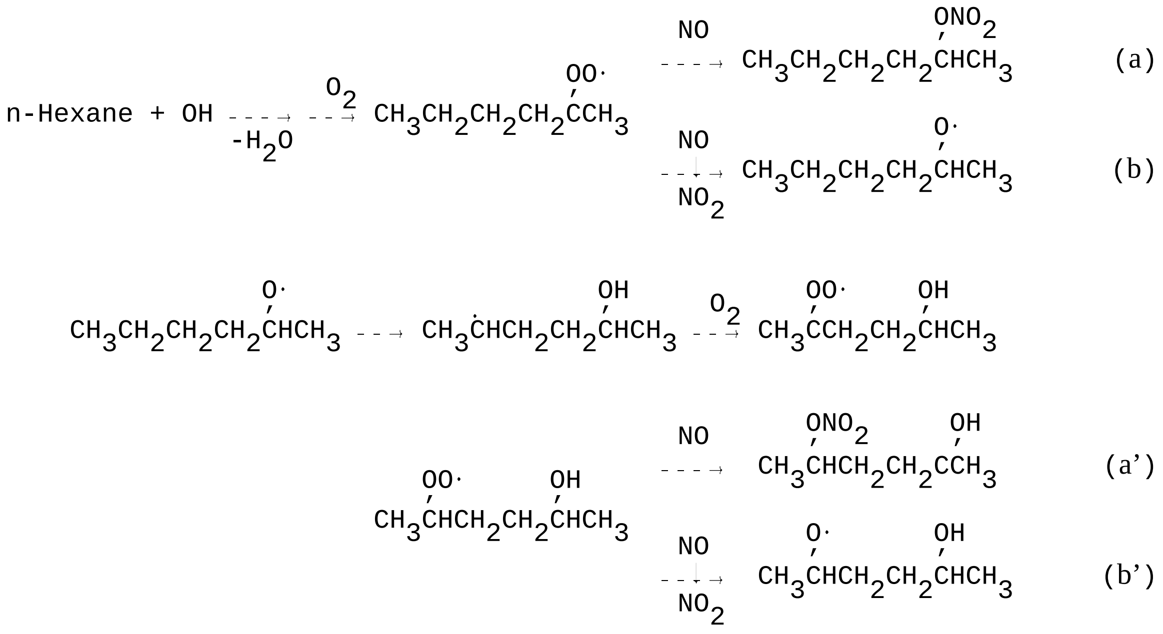
Predictions of mechanistic reactivities in our experiments should also be slightly less sensitive to errors in the model for the base case experiment since they are not sensitive (to a first approximation) to predictions of how rapidly the VOC is reacting. Errors in the base case model could affect predictions of radical levels, which in turn will affect predictions of how rapidly the VOC reacts.

The overall performances of the SAPRC-90 and updated mechanisms in simulating mechanistic reactivities are shown on Figure 8. In most cases, the models correctly predict observed reactivity trends and rankings, and predict direct reactivities to within the experimental uncertainties. However, the SAPRC-90 mechanism gives predictions of d(O_3-NO) and IntOH mechanistic reactivities outside the estimated (one σ) uncertainty ranges of the measurements for somewhat over half of the VOCs studied, and in a few cases the discrepancies are outside the two σ uncertainty ranges. The updated mechanism gives better predictions for the alkenes and branched alkanes, but does not perform significantly better for the other classes of VOCs. The performance of these mechanisms for the individual classes of VOCs, and the differences between them, are discussed below.

Alkanes.

These data provide a significantly better environmental chamber test for alkane mechanisms than has been available previously. Previous relevant chamber data consisted of NO_x-air experiments with alkanes alone, and such experiments have been shown to be so sensitive to chamber-dependent radical sources that the adjustable parameter used to represent this tends to dominate the results of the model simulations (Carter et al., 1982; Carter and Lurmann, 1991). Model simulations of reactivity experiments are much less sensitive to this because the reactions of the base case mixture provide a more important radical source. If the model can adequately simulate the base case experiment, it should be able to simulate the radical inputs in the added alkane runs without the need for a sensitive adjustable parameter.

The major aspect in the alkane mechanisms affecting predictions of their reactivities is the overall alkyl nitrate yield. This is because alkyl nitrate formation is a radical termination process, which is the reason that alkanes have negative IntOH reactivities and therefore low or negative d(O_3-NO) reactivities. Neglecting the apparently anomalous ethane and n-butane runs, the model was found to simulate the reactivities of the n-alkanes reasonably well. This may not seem surprising since alkyl nitrate yields have been directly measured from these compounds (e.g., see Atkinson, 1990; Carter and Atkinson, 1989b), but the measured yields only concern alkyl nitrate formation from the initially formed peroxy radicals. Long chain alkanes such as n-hexane and n-octane are also predicted to form OH-substituted peroxy radicals following 1,5-H shift isomerization, and one might expect radical termination through analogous reactions of these radicals, forming hydroxy nitrates. For example, the reactions below are expected to occur in the n-hexane system following reaction at the 2-position:



$$\text{n-Hexane} + OH \xrightarrow[-H_2O]{} \xrightarrow{O_2} CH_3CH_2CH_2CH_2\overset{OO\cdot}{C}CH_3 \xrightarrow{NO} CH_3CH_2CH_2CH_2\overset{ONO_2}{C}HCH_3 \qquad (a)$$

$$CH_3CH_2CH_2CH_2\overset{OO\cdot}{C}CH_3 \xrightarrow[NO_2]{NO} CH_3CH_2CH_2CH_2\overset{O\cdot}{C}HCH_3 \qquad (b)$$

$$CH_3CH_2CH_2CH_2\overset{O\cdot}{C}HCH_3 \rightarrow CH_3\dot{C}HCH_2CH_2\overset{OH}{C}HCH_3 \xrightarrow{O_2} CH_3\overset{OO\cdot}{C}CH_2CH_2\overset{OH}{C}HCH_3$$

$$CH_3\overset{OO\cdot}{C}HCH_2CH_2\overset{OH}{C}HCH_3 \xrightarrow{NO} CH_3\overset{ONO_2}{C}HCH_2CH_2\overset{OH}{C}CH_3 \qquad (a')$$

$$CH_3\overset{OO\cdot}{C}HCH_2CH_2\overset{OH}{C}HCH_3 \xrightarrow[NO_2]{NO} CH_3\overset{O\cdot}{C}HCH_2CH_2\overset{OH}{C}HCH_3 \qquad (b')$$

If the nitrate yields [e.g., $k'_a/(k'_a+k'_b)$] from these reactions were the same as in the corresponding unsubstituted radical [e.g., $k_a/(k_a+k_b)$], the overall nitrate yield from the alkane would be increased by up to a factor of two. This would significantly affect predictions of the alkane's reactivity, as is shown on Figure 2, which shows experimental and calculated d(O_3-NO) and IntOH mechanistic reactivities for n-octane. It can be seen that while both the SAPRC-90 and the updated mechanisms, which assume that $k'_a/(k'_a+k'_b)=0$, give fairly good fits to the data, while the mechanism which assumes that $k'_a/(k'_a+k'_b) \approx k_a/(k_a+k_b)$ (designated as "RONO2 from OH-RO2.") significant overpredicts the d(O_3-NO) and IntOH inhibition by n-octane. The SAPRC-90 mechanism already assumes that $k'_a/(k'_a+k'_b) = 0$ based on model simulations of single alkane-NO_x-air experiments, but these reactivity experiments provide much stronger support for this assumption because they are highly sensitive to this parameter, and are much less sensitive to uncertain chamber radical sources.

Figure 8 shows that the mechanisms successfully predict the direct reactivities of the alkanes, which are the highest of all the compounds studied. In all cases, the model predictions are within experimental uncertainty of the data. This means that the mechanisms must be predicting approximately the correct number of NO oxidations which occur when the alkanes react. These are relatively high because of the multiple isomerization and decompositions that the intermediate alkoxy radicals can undergo, forming additional peroxy radicals which oxidize NO (Carter and Atkinson, 1985). In contrast to the d(O_3-NO) and IntOH reactivities, the direct reactivities are not highly sensitive to the nitrate yields.

On the other hand, the SAPRC-90 mechanism performed poorly in simulating the isobutane (2-methyl-propane) and isooctane (2,2,4-trimethylpentane) reactivity data. This is shown on Figure 3, where it can be seen that the SAPRC-90 mechanism significantly overpredicts d(O_3-NO) reactivity for isobutane while underpredicting it for isooctane. This can be attributed to factors which are unique for each compound, as discussed below.

Isobutane.

The overprediction by the SAPRC-90 mechanism of the reactivity of isobutane can be attributed to the fact that the mechanism (Carter, 1990) neglects radical termination due to reactions of alkoxy radicals with NO_2. This approximation, which permits significant condensation and is incorporated in most mechanisms currently used in airshed models in the United States (Stockwell et al., 1990; Gery et al., 1988; Lurmann et al., 1987), generally has no consequence for most VOCs. This is because most alkoxy radicals also either react with O_2 or undergo unimolecular reactions sufficiently rapidly that the NO_2 reaction is of negligible importance under atmospheric conditions.

However, the alkoxy + NO_2 reaction may become non-negligible in the case of t-butoxy radicals, which are estimated (Atkinson, 1987) to be formed ~75% of the time following the reaction of OH with isobutane.

$$\mathrm{OH + Isobutane} \xrightarrow[-H_2O]{75\%} (CH_3)_3C\cdot \xrightarrow{O_2} \xrightarrow[NO_2]{NO} (CH_3)_3CO\cdot$$

Since this radical lacks abstractable α- or δ- hydrogens, so the only process competing with the reaction with NO_2

$$(CH_3)_3O\cdot + NO_2 \xrightarrow{M} (CH_3)_3ONO_2$$

is decomposition:

$$(CH_3)_3O\cdot \longrightarrow CH_3\overset{\overset{O}{\parallel}}{C}CH_3 + \dot{C}H_3 \xrightarrow{O_2} \xrightarrow[NO_2]{NO} \xrightarrow{O_2} HCHO + OH$$

The neglect of the alkoxy + NO_2 reaction in effect assumes that the decomposition dominates. However, the high pressure limit for the decomposition reaction is $1.1 \times 10^{+14}\ e^{-7519/T}$ $cm^3\ molec^{-1}\ sec^{-1}$, and at 298K RRKM calculations indicate that the atmospheric rate constant is 79% of the high pressure limit (Batt et al., 1989). The rate constant for the NO_2 reaction has not been measured for isobutoxy radicals, but based on measurements for other alkoxy radicals, Atkinson (1990) estimates that it is $2.3 \times 10^{-11}\ e^{+150/T}$

cm^3 $molec^{-1}$ sec^{-1}. Under typical conditions of our experiments (301 K and $[NO_2]$ = ~0.2 ppm), these rate constants predict that the NO_2 reaction will occur 12% of the time. This is not negligible for a radical termination process such as this.

The updated mechanism was modified to include the NO_2 + t-butoxy reaction, and Figure 3 shows that its predictions are much more consistent with the measured isobutane reactivities. Test calculations showed that the other changes to the updated mechanism did not significantly affect isobutane's predicted reactivity, so the improvement can be attributed entirely to the removal of this approximation.

It should be recognized, however, that the NO_x levels employed in these experiments (~0.5 ppm total) is higher than generally occurs in the atmosphere. Since the importance of the alkoxy + NO_2 reaction decreases as total NO_2 levels decrease, the approximation of neglecting it may not have such an important impact under atmospheric conditions. To assess this, we used the updated mechanism, both with and without the alkoxy + NO_2 reaction, to calculate the atmospheric incremental reactivities of isooctane for the "averaged conditions" airshed scenario we developed previously to represent "maximum incremental reactivity" (MIR) conditions (Carter, 1994). Although MIR scenarios are intended to represent the high end of NO_x conditions in the atmosphere (Carter, 1994), neglecting the alkoxy + NO_2 reaction only caused a ~2% increase in isobutane's calculated atmospheric MIR. Therefore, these data do not indicate that the current models will necessarily incorrectly predict isobutane's reactivity in the atmosphere, only that they cannot be extrapolated to the higher NO_x conditions of these experiments.

Isooctane.

Figure 3 shows that the SAPRC-90 mechanism significantly underpredicts the incremental reactivity of isooctane during the early stages of the experiments. This is most obviously attributed to the isooctane model overpredicting alkyl nitrate formation from the RO_2 + NO reaction, since that it the primary reason why the model predicts it inhibits NO oxidation. There are no available data concerning alkyl nitrate yields from this compound; their yields are estimated based on (1) estimates of relative rates of reactions of OH radicals at the various positions in the isooctane molecule, obtained using group-additivity relationships based on kinetics of OH + alkane reactions (Atkinson, 1987), and (2) estimates of nitrate yields [i.e., $k_a/(k_a+k_b)$] for the reactions of NO with the various expected peroxy radicals, based on nitrate yields from a variety of other alkanes (Carter and Atkinson, 1989b). From this, an overall nitrate yield of 18% is derived. The poor agreement between the SAPRC-90 model and the data shown on Figure 3 indicate that this estimate is an overprediction.

The group-additivity estimates of Atkinson (1987) predict that reaction at the 3-position, giving secondary peroxy radicals, occurs 30% of the time. The nitrate yields from secondary peroxy radicals are estimated to be ~3 times higher than from primary or tertiary radicals (Carter and Atkinson, 1989b), so this accounts for over half the predicted nitrate formation from isooctane. However, this estimate of 30% formation of secondary radicals is probably high because it does not take into account the possibly significant effect of stearic hinderance by the neighboring methyl groups. If the stearic hinderance is assumed to be large enough to inhibit this reaction, then the estimated nitrate yield from isooctane is reduced to 11%. This is assumed in the updated mechanism because, as shown on Figure 3, this gives a much better fit to the experimental reactivity results. Thus the discrepancy in the SAPRC-90 model prediction of isooctane's reactivity can be attributed to stearic effects which are not accounted for in the general alkane estimation methods used to derive the mechanism for this compound (Carter and Atkinson, 1985; Atkinson, 1987).

The sensitivity of predictions of isooctane reactivity to assumptions at this level of detail indicate that mechanisms for other branched alkanes need to be examined on a case-by-case basis. In particular, the reactivity predictions are highly sensitive to estimates concerning fractions of reactions involving formation of secondary vs primary or tertiary radicals, which may vary widely among alkane isomers. Isooctane may provide an extreme example of stearic effects, but it is probably not the only branched alkane where such considerations may be important.

***Alkenes*.**

The mechanisms correctly predict that the alkenes enhance OH radical levels and thus have relatively high d(O_3-NO) mechanistic reactivities. However, as shown on Figure 8, the SAPRC-90 mechanism consistently underpredicts alkene reactivities, particularly for trans-2-butene and isobutene. The updated mechanism, which incorporates the higher radical yields in the O_3 + alkene reactions, performs significantly better, though most mechanistic reactivities are still somewhat underpredicted. The compound most affected by the alkene updates is trans-2-butene. Figure 4, which plots experimental and calculated d(O_3-NO) and IntOH mechanistic reactivity data for a representative trans-2-butene run, shows that the SAPRC-90 mechanism significantly underpredicts both measures of trans-2-butene's reactivity. Therefore, although the updates to the O_3 + alkene mechanisms are probably oversimplifications of these complex systems, they result in a mechanism which performs better in simulating incremental reactivities of alkenes than does the published SAPRC-90 mechanism (Carter, 1990).

Figure 8 shows that the two mechanisms can simulate the direct reactivities of ethene to within the relatively high uncertainties of the measurements. The relatively low direct reactivity for this compound can be attributed to the fact that ethene reacts directly with O_3, causing some O_3 consumption. On the other hand, this ozone reaction causes relatively high indirect (IntOH) reactivities because it results in radical formation, with the net effect being relatively high mechanistic reactivities for this compound. The direct reactivities of the other alkenes are too imprecisely determined to provide a useful test of the mechanism, though similar considerations undoubtedly also apply.

Aromatics.

The mechanisms correctly predict that the alkylbenzenes, like the alkenes, are strong radical initiators and thus have high IntOH and d(O_3-NO) mechanistic reactivities. This is not surprising since the mechanisms were adjusted to simulate this behavior (Carter, 1990) — though none of the data discussed here were used in the optimizations for either mechanism. Figure 8 shows that the updated mechanism gives essentially the same predictions of the aromatic reactivity data as do SAPRC-90; this is as expected since both use essentially the same parameterization of aromatic chemistry, and were both optimized to fit the same set of data. Since the mechanisms were optimized using toluene, m-xylene and 1,3,5-trimethylbenzene runs (Carter, 1990), one would expect it to perform best in simulating reactivities of these compounds. However, the mechanisms slightly underpredict the reactivities of toluene and significantly (by a factor of ~2) underpredict those for 1,3,5-trimethylbenzene. They also underpredict the IntOH reactivities measured for m-xylene, though the data are scattered and may be unreliable (Carter et al., 1995).

Although the SAPRC mechanisms incorporate the appropriate rate constants for the OH reactions of the individual isomers, they assume all xylene isomers form the same products and intermediates, and likewise for the trimethylbenzene isomers. Thus, as shown on Figure 8, they predict that the mechanistic reactivities are similar for all isomers. However, p-xylene and 1,3,5-trimethylbenzene were found to have respectively lower or higher reactivities in these experiments than their other isomers. Thus, the data from these experiments indicate that mechanistic parameters for each isomers should be derived separately. We are currently generating the experimental data necessary to do this.

The model performance in simulating the benzene data suggests other problems with the aromatics mechanisms. As shown on Figures 5 and 8, benzene is the only VOC where there is an experimentally significant discrepancy between the observed and predicted direct mechanistic reactivity. This is despite the fact that the mechanisms give very good simulations of the maximum ozone yields in the added benzene runs, which, unlike all the other reactivity runs in this study, achieve a "true" ozone maximum [see Figure 5 and Carter et al., (1995)]. Although the "direct reactivity" measurement by the end of the added benzene runs was affected by the runs becoming NO_x limited (Carter et al., 1995), Figure 8 shows that the experimental mechanistic reactivities were still significantly lower than predicted by the model earlier in the experiment, before NO_x became limited. Therefore, these data suggest that the SAPRC mechanisms are not correctly representing the number of NO oxidations caused when benzene reacts. This may be true for the other aromatics as well, but for those compounds the effects on radical levels are so large that it overwhelms any direct reactivity effects, and preclude any meaningful direct reactivity measurement.

Aldehydes and Ketones.

The mechanisms are reasonably successful in simulating the reactivity data for acetaldehyde and the 6-hour reactivities of formaldehyde, but overpredict the reactivity of formaldehyde at earlier times in the experiment. Figure 6 shows the experimental and calculated d(O_3-NO) incremental reactivities in the two formaldehyde experiments, and Figure 7 shows the data for for a selected acetaldehyde run. The updated mechanism uses somewhat higher quantum yields for formaldehyde photolysis, causing it to give slightly higher predicted formaldehyde reactivities, but the data are insufficiently precise to permit conclusions as to which mechanism performs better. In both cases, the t=1 hour reactivities are significantly overpredicted, and by essentially the same amount. On the other hand, the updates to the mechanism cause marginally improved predictions in the case of acetaldehyde, as is shown on Figure 7.

It is difficult to account for the reason for the overprediction of the formaldehyde reactivity early in the experiment, since the formaldehyde mechanism is now considered to be reasonably well established. Such a discrepancy is not observed for acetaldehyde. The possibility of the model incorrectly predicting the formaldehyde photolysis rates because of chamber light characterization problems cannot be totally ruled out, but in that case one would expect similar errors for acetaldehyde. Errors in light intensity characterization seem unlikely since this should cause the model to consistently overpredict the rates of reaction in all types of runs. In fact, no such overprediction is observed in simulations of propene-NO_x or ethene-NO_x control experiments. The light spectra in our chamber have been measured by two different spectrometers which give the same results, making it appear unlikely that the discrepancy is due to the model using an incorrect spectral distribution when calculating the formaldehyde and other photolysis rates.

The discrepancy concerning formaldehyde reactivity might also be due to the base ROG reactions being less sensitive to radical input processes at the early stages of the experiments than predicted by this model. This could be the case if both radical initiation and radical terminating processes in the mini-surrogate mechanism were stronger than assumed in this model. Additional runs that we have carried out subsequently, where we investigated the effects of adding formaldehyde to ethylene-NO_x-air irradiations yielded essentially the same discrepancies between experimental results and model predictions (Carter et al., 1994a). Since the modeling of latter experiments does not have the uncertainties in the aromatics mechanism, these data suggest that problems with the mini-surrogate mechanism is not the explanation.

In contrast to formaldehyde, the model successfully simulates all aspects of the reactivity data for acetaldehyde (see Figure 7). The updated mechanism predicts slightly higher reactivities for acetaldehyde because the updated rate constants predict that PAN formation, which is a radical termination process, is slightly slower than predicted by the SAPRC-90 mechanism. Acetaldehyde is unusual in being predicted to have IntOH reactivities which are positive initially but become negative later in the run; this is attributed to the fact that PAN formation becomes increasingly important as the $[NO_2]/[NO]$ ratio increases during the run. This effect on IntOH causes the $d(O_3\text{-}NO)$ mechanistic reactivity to decrease with time during the run. The model predicts that the direct mechanistic reactivity will also decline slightly with time, though not to as great an extent as IntOH reactivity. The experimental measurements of direct reactivities are not sufficiently precise to verify the predicted time-dependence of the direct reactivities.

Alcohols and Ethers.

The mechanisms performed reasonably well in simulating the reactivities of methanol and ethanol, as one would expect since their mechanisms are considered to be well established. Methanol has a high IntOH and $d(O_3\text{-}NO)$ mechanistic reactivity because its major product is formaldehyde, which is a strong radical initiator. Although the model tends to overpredict the initial reactivity of formaldehyde, it gives a reasonably good simulation of the reactivity of methanol, which forms formaldehyde as its major product.

Figure 8 shows that the models also give reasonably good predictions of mechanistic reactivities for isopropanol and dimethyl ether. These and other reactivity data for alcohols and ethers will be discussed in more detail in a subsequent paper.

CONCLUSIONS

The experimental incremental reactivity data from the study of Carter et al. (1995) has provided a useful test of the ability of current detailed chemical mechanisms to predict impacts of VOCs in ozone in radical levels under conditions where ozone formation is most sensitive to VOCs. It has provided the best data yet available for testing the ozone impacts for alkanes without complications of chamber effects, as well as information on the relative reactivities of representative alkenes, aromatic isomers, alcohols, and other compounds. The SAPRC-90 detailed mechanism, which is the basis for the VOC reactivity scale adopted in the California Clean Fuels/Low Emissions Vehicle Regulations (CARB 1990, 1991), performed reasonably well in simulating the general reactivity trends and rankings among the VOCs which were studied, but a number of discrepancies were observed. It preformed poorly in simulating the reactivities of the two branched alkenes studied, underpredicted reactivities of alkenes, and did not predict reactivity differences observed among aromatic isomers. The poor performance in the case of the branched alkanes revealed problems with the generalized alkane reaction mechanism previously developed by the author, and indicates that mechanisms for branched alkanes need to be considered on a case by case basis. An updated mechanism taking into account specific characteristics of the individual compounds preformed significantly better. The updated mechanism which incorporates new data indicating higher radical yields from O_3 + alkene reactions also performed better in simulating these data. However, further updates will be needed to improve the simulations of the relative reactivities of the alkylbenzene isomers or the direct reactivity of benzene. Work is also needed to improve the model simulations of the incremental reactivities of formaldehyde.

It is important to recognize, however, that this study does not provide all the data needed to adequately evaluate the chemical mechanisms used to predict atmospheric reactivities. The present experiments are only suitable for testing mechanisms under high NO_x, maximum reactivity conditions. While this is obviously important, it is also important that the mechanism be tested under conditions where NO_x is limited. Chemical factors involving VOC NO_x sinks, which have essentially no effect on maximum reactivities, become important under NO_x limited conditions, and experiments are needed to test this aspect of the mechanisms. In addition, experiments are needed to determine how reactivities are affected by changes in the composition of the base case ROG mixture, and to determine if reactivities are obtained if sunlight, or light sources with a visible spectrum more closely resembling sunlight, are used. Experiments which address at least some of these additional data needs have been conducted (Carter et. al., 1994a, and will be discussed in a subsequent paper.

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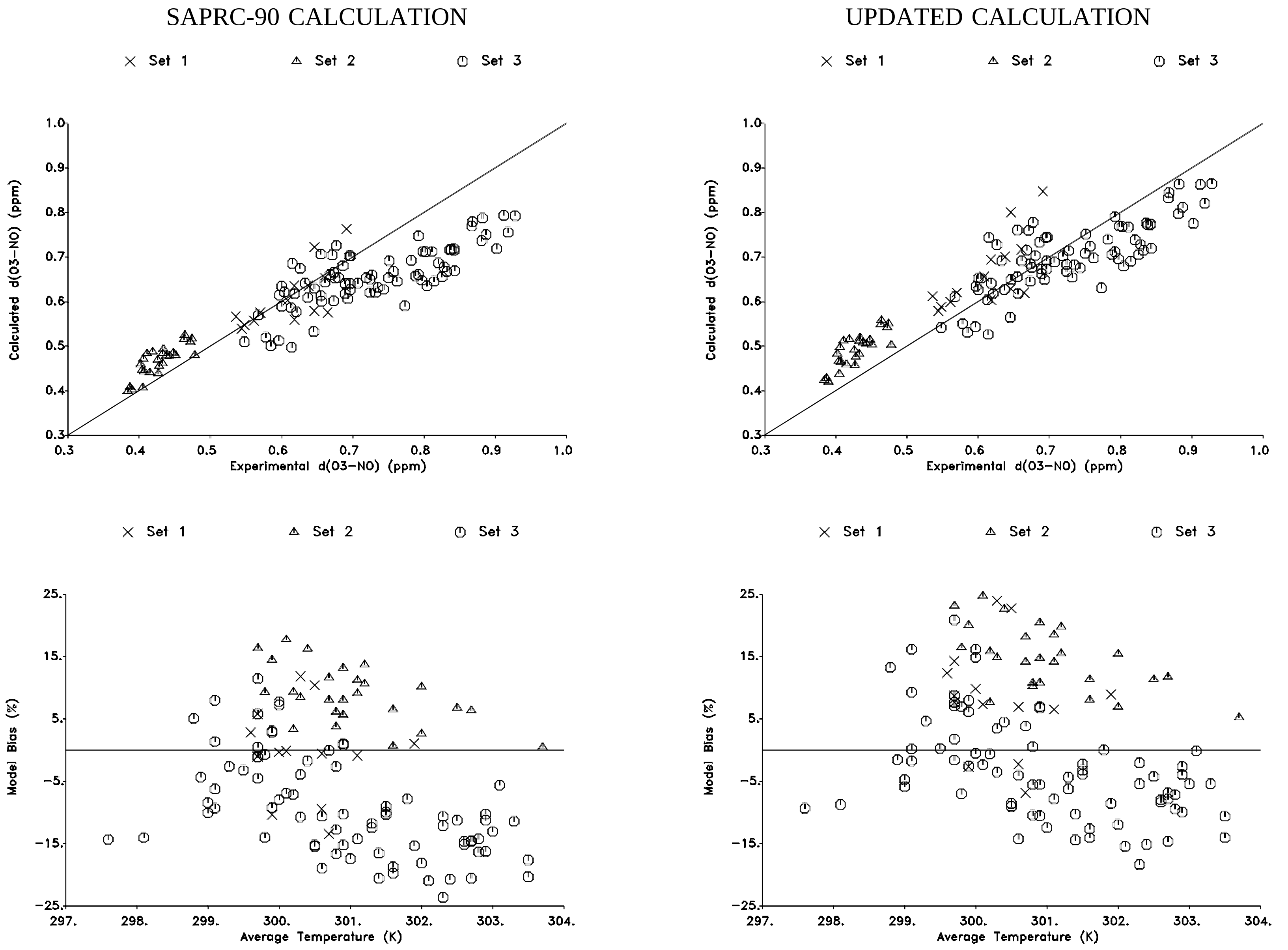

SAPRC-90 CALCULATION

UPDATED CALCULATION

Figure 1. Top plots show experimental vs calculated t=6 hour ozone formed + NO oxidized in the model simulations of the base-case mini-surrogate experiments using the SAPRC-90 and the updated mechanism. The bottom plots show how the biases in these model simulations depend on temperature.

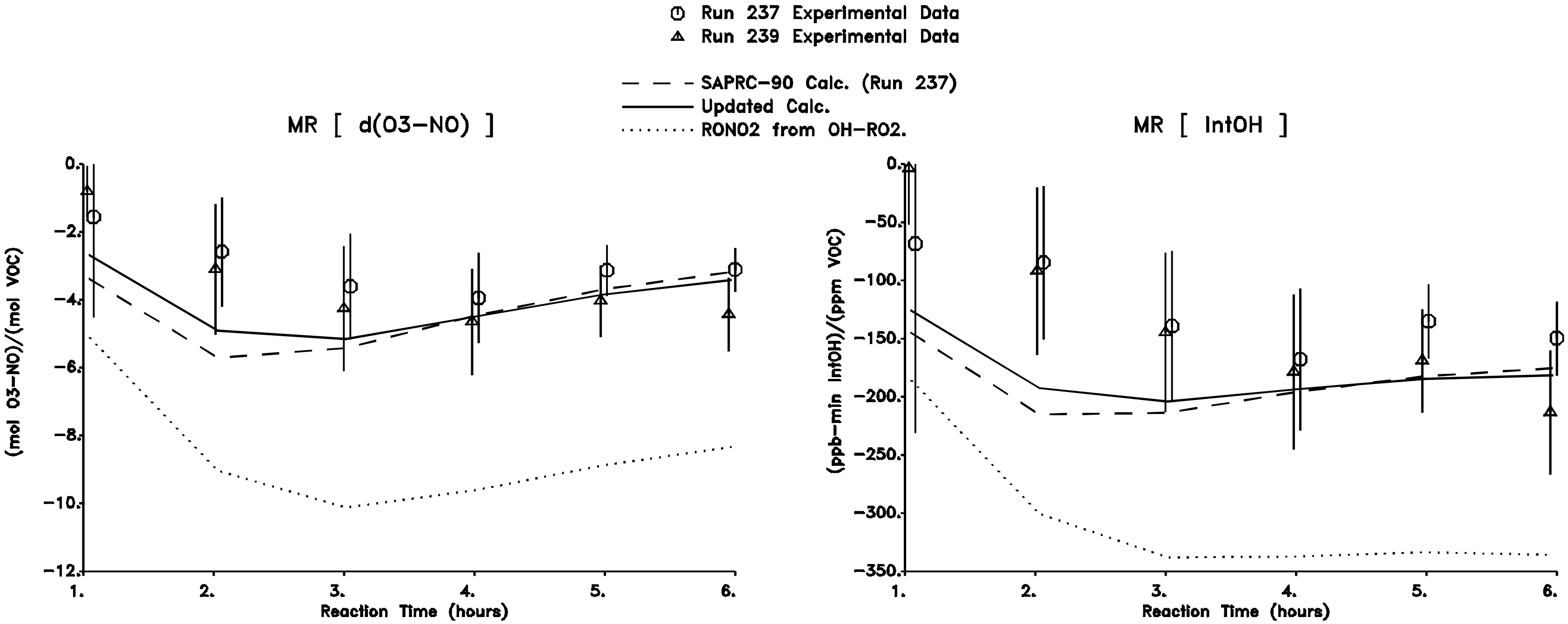

Figure 2. Plots of experimental and calculated d(O_3-NO) and IntOH mechanistic reactivities as a function of reaction time for the n-octane reactivity experiments. The model simulations used either the SAPRC-90, the updated mechanism, or the updated mechanism assuming alkyl nitrate formation occurs from peroxy radicals formed following the isomerization reaction ("RONO2 from OH-RO2.").

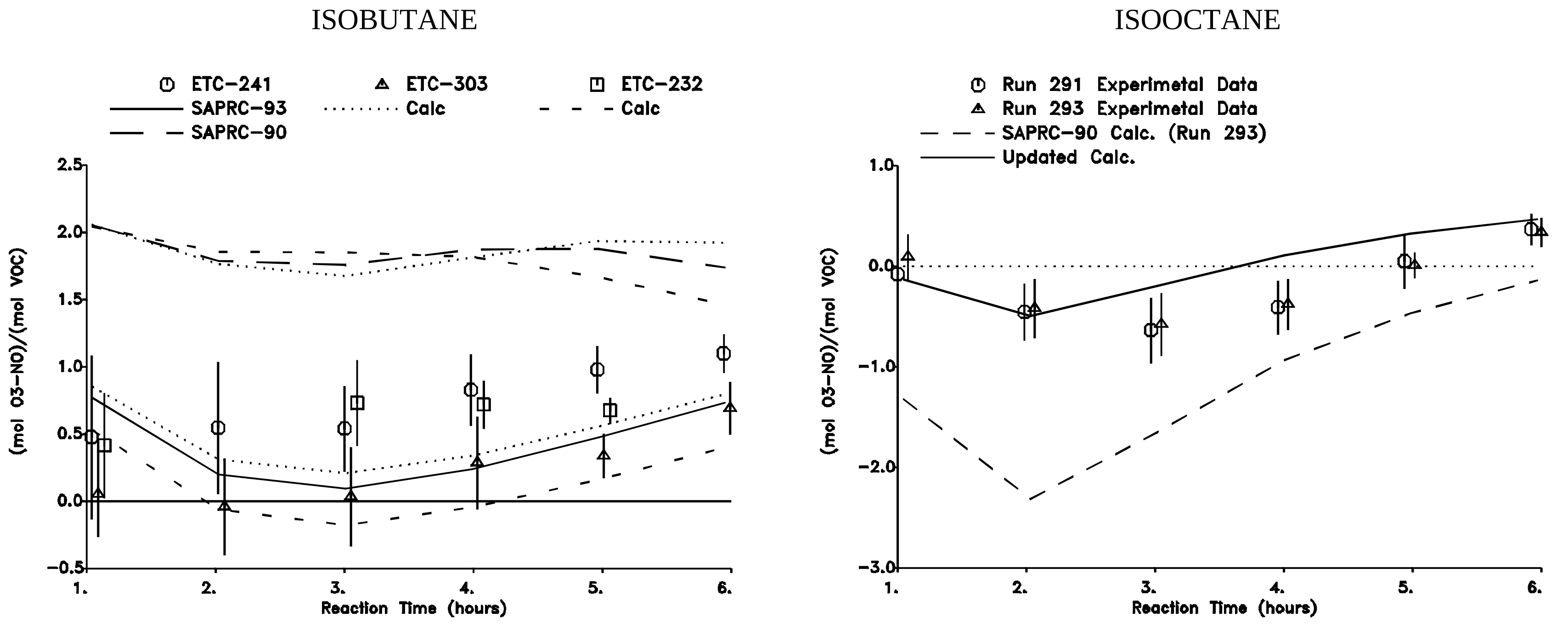

Figure 3. Plots of experimental and calculated d(O_3-NO) mechanistic reactivities as a function of reaction time for the branched alkane reactivity experiments. The model simulations used either the SAPRC-90 or the updated mechanism.

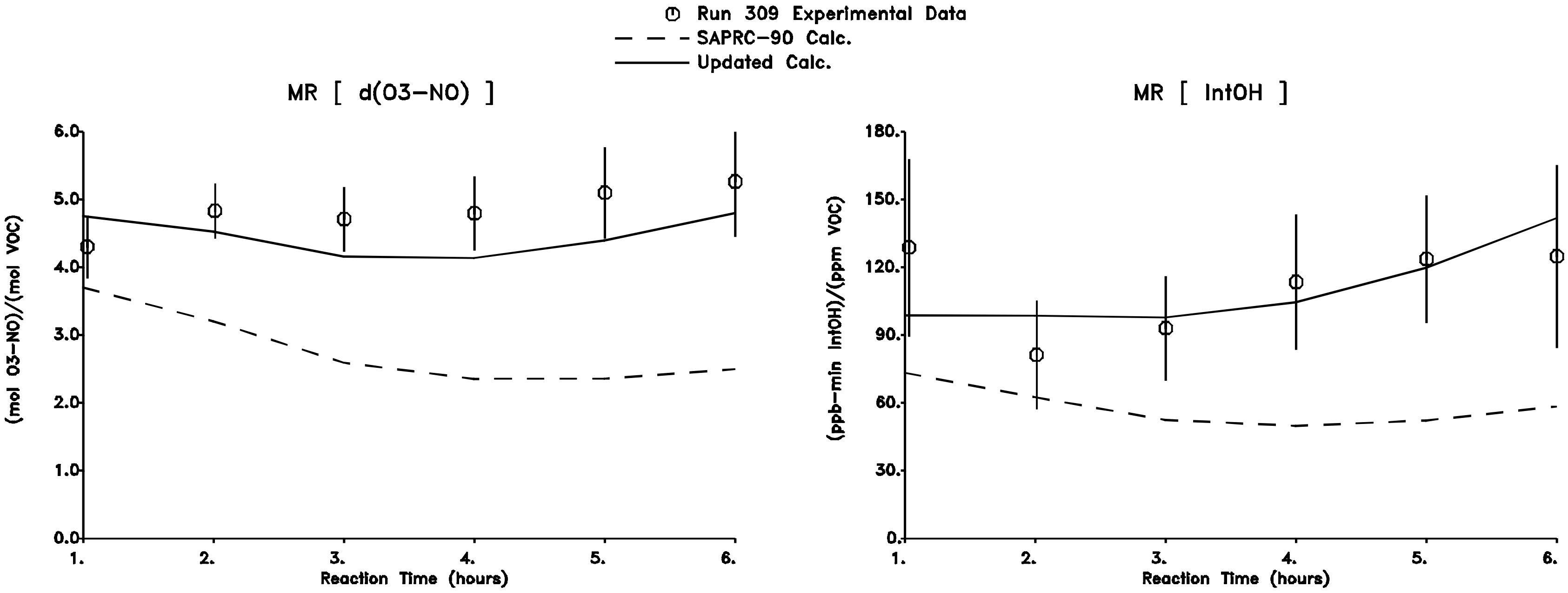

Figure 4. Plots of experimental and calculated d(O_3-NO) and IntOH mechanistic reactivities as a function of reaction time in a selected trans-2-butene reactivity experiment. The model simulations used either the SAPRC-90 or the updated mechanism.

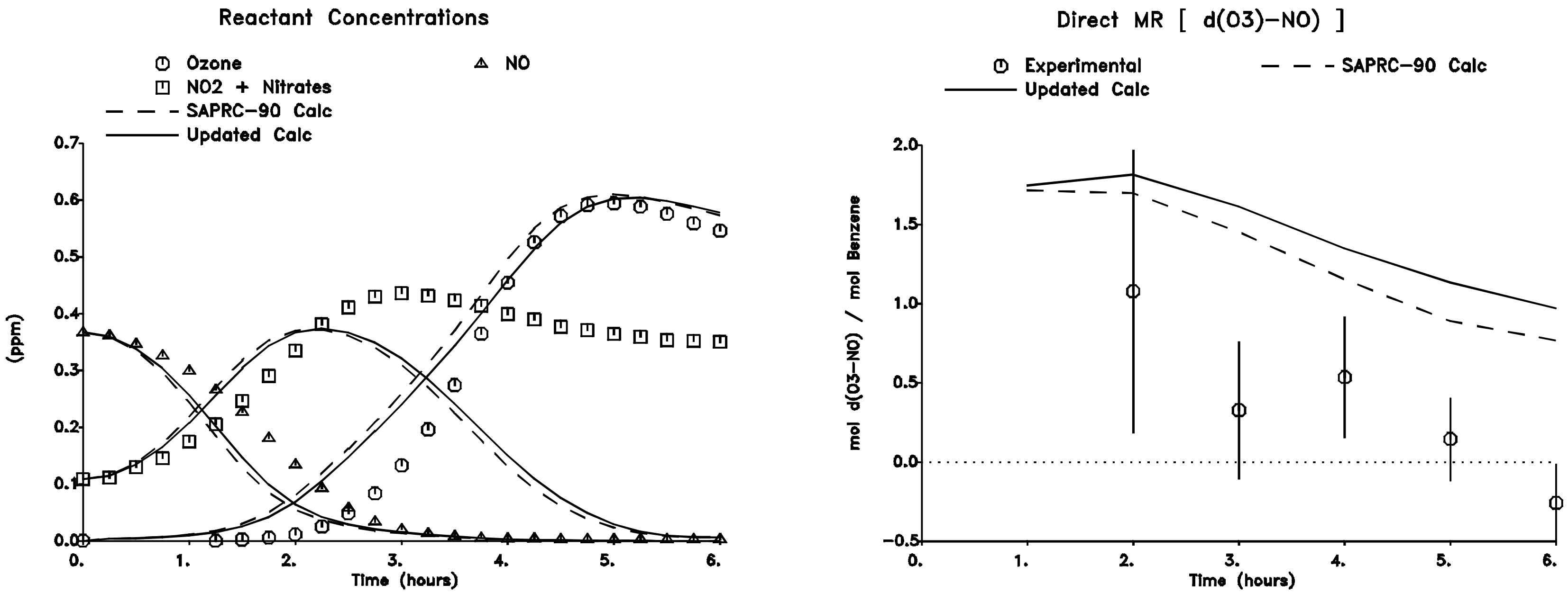

Figure 5. Plots of selected data in a representative added benzene reactivity experiment. Left plot shows concentration-time profiles for selected species as a function of time. Bottom plot shows direct mechanistic reactivities as a function of run duration. The model calculations used either the SAPRC-90 or the updated mechanisms.

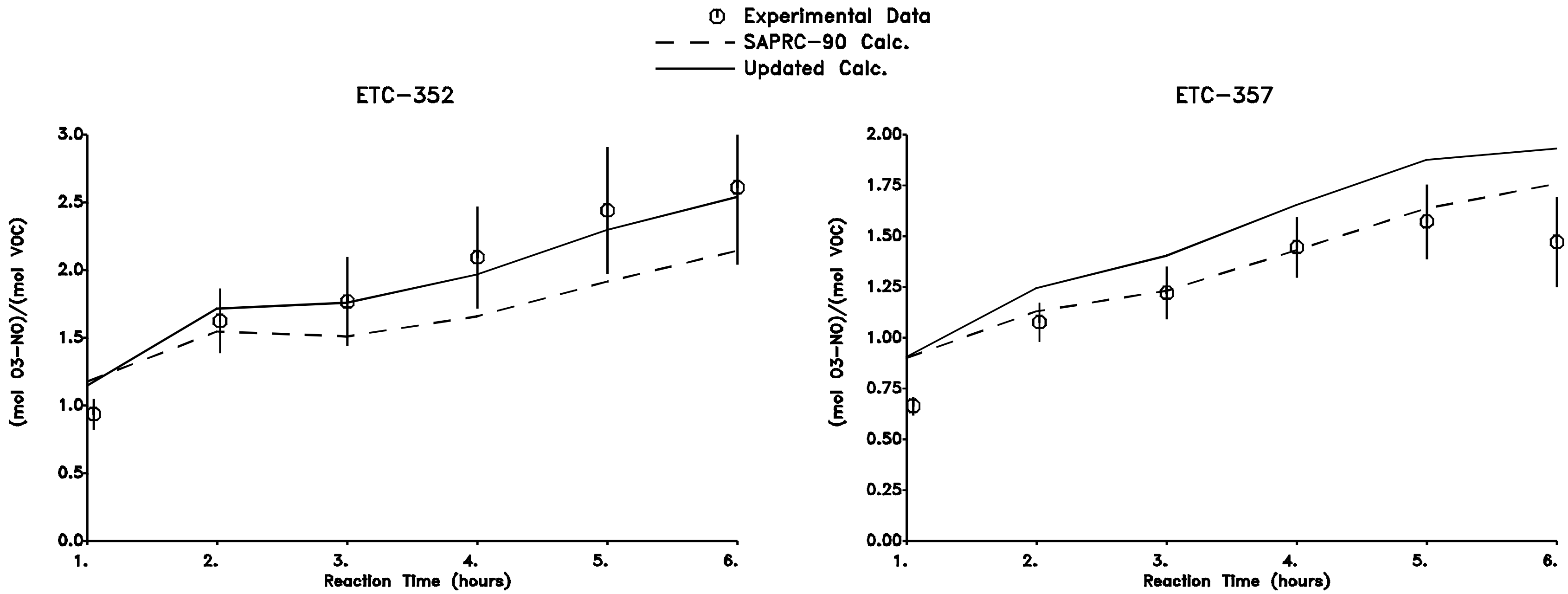

Figure 6. Plots of experimental and calculated d(O_3-NO) incremental reactivities as a function of reaction time in the formaldehyde reactivity experiments. The model calculations used either the SAPRC-90 or the updated mechanism.

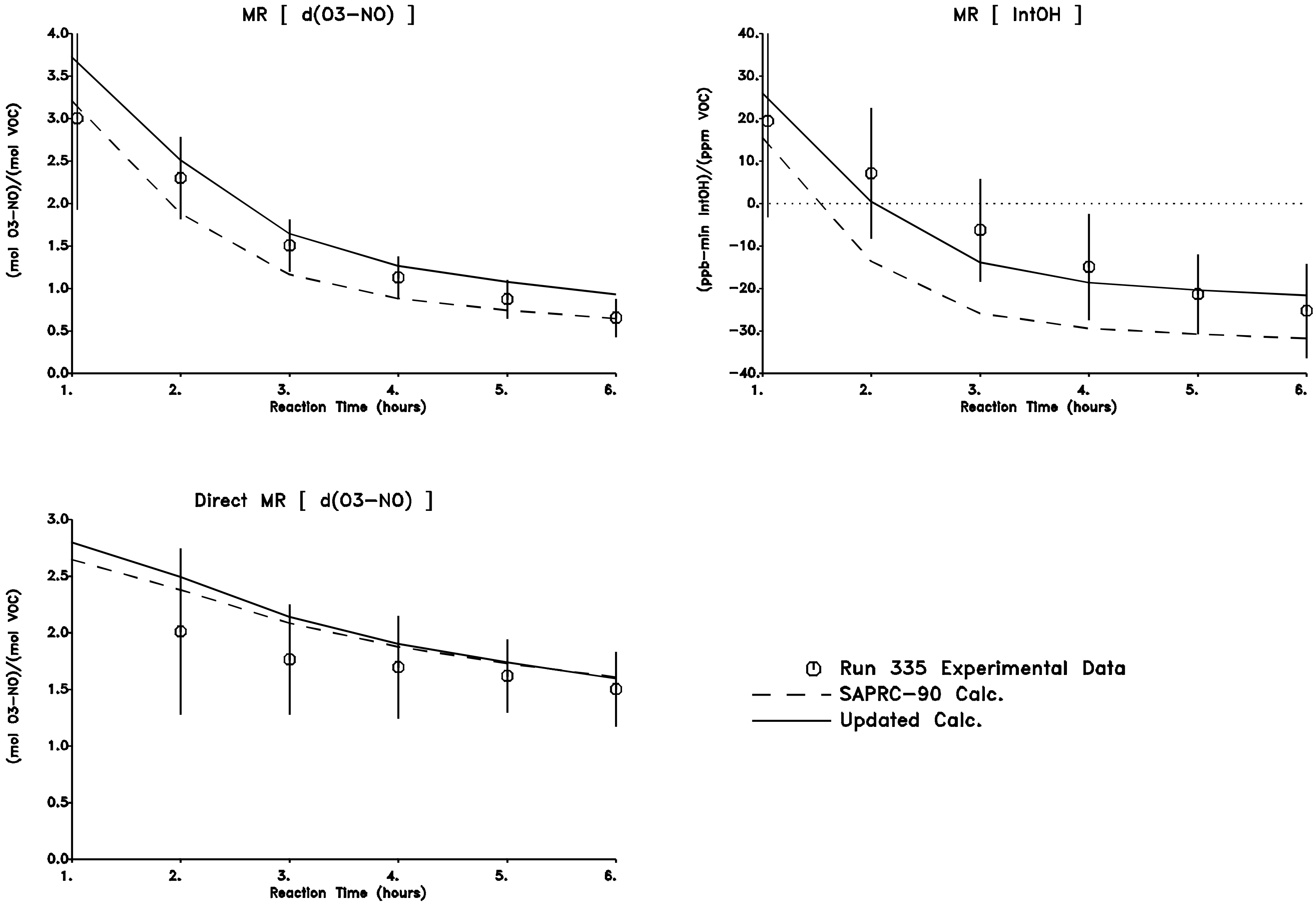

Figure 7. Plots of experimental and calculated d(O_3-NO) and IntOH mechanistic reactivities and direct d(O_3-NO) mechanistic reactivities in a representative acetaldehyde reactivity experiment. The model calculations used either the SAPRC-90 or the updated mechanisms.

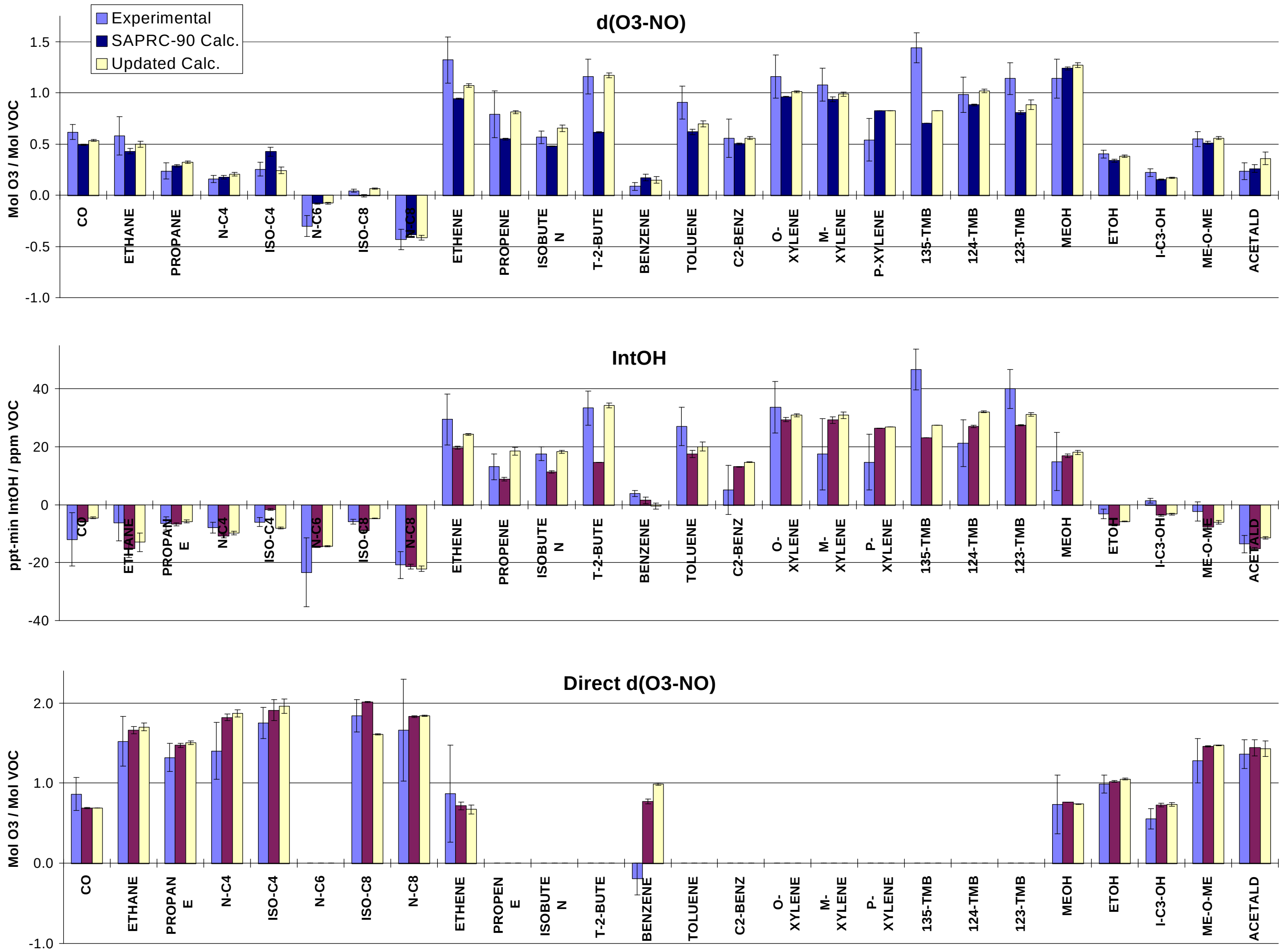

Figure 8. Comparisons of averages of experimental and calculated t=6 hour d(O3-NO) and IntOH mechanistic reactivities and direct d(O3-NO) mechanistic reactivities for all the VOCs studied for which mechanistic reactivities could be derived. The averages are weighed by the reciprocal square of the uncertainty in the experimental average. The error bars show the variability and uncertainty in the experimental measurement and the run-to-run variability in the model calculation.