

**DEVELOPMENT OF OZONE REACTIVITY SCALES
FOR VOLATILE ORGANIC COMPOUNDS**

by

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Abstract

Methods for ranking photochemical ozone formation reactivities of volatile organic compounds (VOCs) are discussed. Photochemical mechanisms for the atmospheric reactions of 118 VOCs were used to calculate their effects on ozone formation under various NO_x conditions in model scenarios representing 39 different urban areas. Their effects on ozone were used to derive 18 different ozone reactivity scales, one of which is the Maximum Incremental Reactivity (MIR) scale used in the new California Low Emission Vehicle and Clean Fuel Regulations. These scales are based on 3 different methods for quantifying ozone impacts and on 6 different approaches for dealing with the dependencies of reactivity on NO_x . The predictions of the scales are compared, the reasons for their similarities and differences are discussed, and the sensitivities of the scales to NO_x and other scenario conditions are examined. Scales based on peak ozone levels were highly dependent on NO_x , but those based on integrated ozone were less sensitive to NO_x and tended to be similar to the MIR scale. It is concluded that the MIR scale or one based on integrated ozone is appropriate for applications requiring use of a single reactivity scale.

Implications

Control strategies which encourage use of VOCs which form less ozone per gram emitted may provide a less costly way to achieve ozone reductions. An example of this is to encourage use of alternative fuels for motor vehicles. Practical implementation of such strategies requires some means to quantify ozone formation potentials of VOCs. This paper discusses various methods to do this.

About the Author

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Introduction

The formation of ground-level ozone is a serious air pollution problem in many areas. Ozone is not emitted directly, but is formed from the photochemical interactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x). Many different types of VOCs are emitted into the atmosphere, each reacting at different rates and with different reaction mechanisms.¹ Because of this, VOCs can differ significantly in their effects on ozone formation. These differences in effects on ozone formation are referred to as the ozone "reactivities" of the VOCs. Although in the past such differences have often been neglected and all non-exempt VOCs have been regulated equally, in recent years it has become recognized that control strategies which encourage the use of less reactive VOCs could provide a cost-effective means to achieve ozone reductions. An example of this is to encourage the use of alternative fuels for motor vehicles. However, practical implementation of such strategies requires some means to quantify the reactivities of VOCs.

There are a number of ways to quantify VOC reactivities, but the most relevant measure of the effect of a VOC on ozone is the actual change in ozone formation in an airshed resulting from changing the emissions of the VOC in that airshed. This depends not only on how rapidly the VOC reacts and the nature of its atmospheric reaction mechanism, but also the nature of the airshed where it is emitted, including the effects of the other pollutants which are present. Although the effect of VOCs on ozone formation can be measured in environmental chamber experiments, the fact that these effects depend on the environment where the VOCs react means that one cannot necessarily assume that quantitative ozone impacts in the atmosphere will necessarily be the same as those measured in the laboratory. However, the effect of a VOC on ozone in the atmosphere can be estimated using computer airshed models. While the results of such calculations are no more reliable than the models of the chemical reactions and the air pollution episode being considered, modeling provides the most realistic and flexible means to assess the many factors which affect ozone formation from VOCs and for the development of VOC reactivity scales.

The effect of changing the emissions of a given VOC on ozone formation in a particular episode will in general depend on the magnitude of the emission change and on whether the VOC is being added to, subtracted from, or replacing a portion of the base case (i.e., present day) emissions. To remove the dependence on this, it was proposed to use "incremental reactivity" to quantify ozone impacts of VOCs.² This is defined as the change on ozone caused by adding an arbitrarily small amount of the test VOC to the emissions in the episode, divided by the amount of test VOC added. This can also be thought of as

the partial derivative of ozone with respect to emissions of the VOC. Note that this does not necessarily predict the effects of large changes in emissions, as might occur, for example, if all the motor vehicles in an airshed were converted to another type of fuel. However, Chang and Rudy³ found that incremental reactivities give good approximations to effects on ozone of alternative fuel substitution scenarios involving changing up to 30% of the total VOC emissions. In any case, incremental reactivities will predict the direction of an initial ozone trend which results when a control strategy is being phased in.

Incremental reactivities have been investigated in a number of computer modeling studies,³⁻⁹ and the VOC's reaction mechanism was found to be important in affecting its incremental reactivity. Some compounds can cause the formation of 10 or more additional molecules of ozone per carbon atom reacted, either directly or through its effects on reactions of other compounds, while others cause almost no ozone formation when they react, or even cause ozone formation to be reduced⁹. The predictions that VOCs have variable effects on ozone formation, even after differences in how rapidly they react are taken into account, and that some have negative effects on ozone formation under some conditions, have been verified experimentally^{2,10}.

The modeling studies also predict that incremental reactivities depend significantly on the environmental conditions, particularly on the relative availability of NO_x^{5,9}. NO_x availability has traditionally been measured by the ratio of total emissions of reactive organic gases (ROG) to NO_x. In general, VOCs have the largest incremental reactivities under relatively high NO_x conditions (i.e., low ROG/NO_x ratios) and have much lower, in some cases even negative, reactivities under conditions where NO_x is limited (high ROG/NO_x ratios). This is because under high NO_x conditions the amount of ozone formed is determined by the levels of radicals formed from the reactions of the VOCs, while under lower NO_x conditions it is the availability of NO_x, which must be present in order for ozone to be formed, which limits ozone formation. Other aspects of the environment in which the VOC is emitted, such as nature of the other organics emitted into the airshed,^{8,11} the amount of dilution occurring,⁹ etc., can also be important in affecting VOC reactivities, though investigations of these aspects are more limited.

The fact that incremental reactivities depend on environmental conditions means that no single scale can predict incremental reactivities, or even ratios of incremental reactivities, under all conditions. Thus the concept of a "reactivity scale" oversimplifies the complexities of the effects of VOC emissions on ozone formation. Nevertheless, for some regulatory applications, the only practical choice is between using some reactivity scale or ignoring reactivity altogether. The latter would be the appropriate choice if reactivities were so variable that all VOCs could be considered to be the same to within this variability.

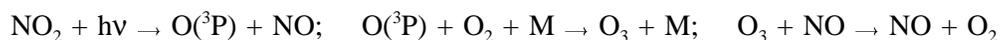
If this is not the case, and if the policy is adopted to use a reactivity scale, the issue becomes how one would develop a scale whose use would result in the greatest overall air quality improvement for the range of conditions where it will be applied.

An example of a case where the policy was adopted to use a reactivity scale is the "Low-Emission Vehicles and Clean Fuels" regulations in California.¹² In this regulation, non methane organic gas (NMOG) exhaust standards for alternatively fueled vehicles are determined using reactivity adjustment factors (RAFTs), which are intended to relate the differences in ozone formation potential of the exhausts compared to that of conventionally fueled vehicles.¹² The regulation as presently adopted utilizes the maximum incremental reactivity (MIR) scale developed by this author to calculate these RAFTs.¹³

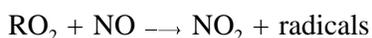
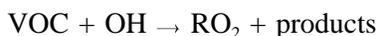
This paper gives the results of an investigation of alternative approaches for developing reactivity scales, and describes the development of the MIR and other reactivity scales.

Chemical Basis of Reactivity

This section gives a summary of the fundamentals of the chemistry of O₃ formation, which may be useful for an understanding of this work. The only significant process forming O₃ in the lower atmosphere is the photolysis of NO₂, which is reversed by the rapid reaction of O₃ with NO.



This results in O₃ being in a photostationary state dictated by the NO₂ photolysis rate and the [NO₂]/[NO] ratio. If reactive VOCs were not present, then significant amounts of O₃ would not be formed. When VOCs are present, they react to form radicals which either consume NO or convert NO to NO₂, which, because of the photostationary state relationship, causes O₃ to increase. Although many types of reactions are involved¹, the major processes can be summarized as follows:



The rate of ozone increase caused by these processes is dependent on the amounts of VOCs present, the rate constants for the VOC's initial reactions, and the level of OH radicals and other species with which the VOCs might react. Ozone production continues as long as sufficient NO_x is present that reactions of peroxy radicals (RO_2) with NO_x compete effectively with their reactions with other peroxy radicals.

Note that the OH radical levels are particularly important in affecting the O_3 formation rate in the presence of NO_x because reaction with OH is a major (and in many cases the only) process causing most VOCs to react. Thus if a VOC reacts in such a way that it initiates radical levels (or forms a product which does), then it would enhance the rate of ozone formation from all VOCs present. This would give it a high incremental reactivity compared to other VOCs. If the VOC has radical termination process when it reacts in the presence of NO_x , it will cause all VOCs to react slower and form less O_3 . In some cases this reduced O_3 formation from other VOCs may be more than enough to counter the ozone formation formed from the VOC's direct reactions. In such cases the VOC would have a negative incremental reactivity in the presence of NO_x .

Ozone formation stops once NO_x is consumed to sufficiently low levels. Since NO_x is removed from the atmosphere more rapidly than VOCs (since most VOCs form product VOCs which also react), it is NO_x availability which ultimately limits O_3 formation. If the NO_x levels are sufficiently high that it is not consumed before the end of the day, then it is mainly the rate of the VOC's reactions, and their effects on OH radicals, which affect incremental reactivity. Indeed, NO_x inhibits O_3 under high NO_x conditions because reaction of OH with NO_2 is an important radical terminating process. If, however, NO_x is consumed before the end of the day, then O_3 is NO_x -limited, and increasing NO_x would cause increased O_3 formation. Under such conditions, if a VOC's reactions caused NO_x to be removed more rapidly than if the VOC were absent (such as, for example, by forming nitrogen-containing products such as PAN's from aldehydes and nitrophenols from aromatics), then this would have a negative effect on O_3 yields, and tend to reduce a VOCs incremental reactivity. Under highly NO_x -limited scenarios, this becomes sufficiently important to cause negative incremental reactivities for VOCs with significant NO_x sinks in their mechanisms — even for those which may have highly positive effects on O_3 under conditions where NO_x is plentiful.

Thus NO_x conditions are a major factor affecting reactivity. However, other scenario conditions will also affect reactivity, by affecting how rapidly NO_x is removed, by affecting overall radical levels and thus how rapidly NO_x and VOCs react, and by affecting other factors determining the efficiency of ozone

formation. This results in variations of incremental reactivities among the different airshed conditions, even those with similar NO_x levels. The relative importance of these factors are investigated in this work.

Methods

This paper uses a number of specialized terms and abbreviations. To assist the reader in following this discussion, Table I gives a summary of these terms and abbreviations. These are discussed in more detail below.

Scenarios Used for Reactivity Assessment

The assessment of ozone reactivities of VOCs under a variety of conditions requires calculating their effects on ozone formation using a set of model scenarios which represent a realistic distribution of environmental conditions. An extensive set of pollution scenarios has been developed for conducting analyses of effects of ROG and NO_x controls on ozone formation using the EKMA modeling approach¹⁴⁻¹⁸. The EKMA approach involves use of single-cell box models to simulate how ozone formation in one day episodes is affected by changes in ROG and NO_x inputs. Although single-cell models cannot represent realistic pollution episodes in great detail, they can represent dynamic injection of pollutants, time-varying changes of inversion heights with entrainment of pollutants from aloft as the inversion height increases throughout the day, and time-varying photolysis rates, temperatures, and humidities^{14,16,19}. Thus, they can be used to simulate a wide range of the chemical conditions which affect ozone formation from ROG and NO_x. These are the same as those affecting VOC reactivity. Therefore, at least to the extent they are suitable for their intended purpose, an appropriate set of EKMA scenarios should also be suitable for assessing methods to develop reactivity scales encompassing a wide range of conditions.

Base Case Scenarios. The set of EKMA scenarios used in this study were developed by the United States EPA for assessing how various ROG and NO_x control strategies would affect ozone nonattainment in various areas of the country.¹⁸ The characteristics of these scenarios and the methods used to derive their input data are described in more detail elsewhere.^{18,20} Briefly, 39 urban areas in the United States were selected based on geographical representativeness of ozone nonattainment areas and data availability, and a representative high ozone episode was selected for each. These were based on

Table I. Summary of terms and abbreviations.

Types of Scenarios and Scenario Characteristics

EKMA Scenario	A model for an air pollution episode which can be represented in the EKMA model formulation. This involves a single-cell box model with a fraction of ROG and NO _x pollutants present initially and the remainder emitted throughout the day, time-varying changes in inversion heights and entrainment of pollutants from aloft as the height raises, and time-varying humidities and temperatures.
Base ROG Mixture	The mixture of reactive organic gases (ROGs) initially present or emitted in the EKMA scenarios except for biogenic VOCs, VOCs present aloft, or VOCs added for the purpose of calculating their incremental reactivities.
NO _x (or ROG) inputs	The sum of the initial NO _x (or base ROG) and the total emitted NO _x (or base ROG) in the scenarios, in units of moles (or moles carbon) per unit area.
NO _x Availability	The condition of whether NO _x is limiting O ₃ formation or whether NO _x is in excess, and the degree to which this is the case.
Base Case Scenario	An EKMA scenario whose inputs are derived to represent a specific ozone exceedence episode in an area of the United States.
MIR Scenario.	Maximum Incremental Reactivity (MIR) Scenario. A scenario derived by adjusting the NO _x emissions in a base case scenario to yield the highest incremental reactivity of the base ROG mixture.
MOR Scenario.	Maximum Ozone Reactivity (MOR) Scenario. A scenario derived by adjusting the NO _x emissions in a base case scenario to yield the highest peak ozone concentration.
EBIR Scenario.	Equal Benefit Incremental Reactivity (EBIR) Scenario. A scenario derived by adjusting the NO _x emissions in a base case scenario so VOC and NO _x reductions are equally effective in reducing O ₃ .
Averaged Conditions Scenario	A scenario whose inputs represent the average of those of the base case scenarios

Measures of Reactivity

Incremental Reactivity	Change in ozone formed caused by adding a VOC to the initial and emitted base ROG in a scenario, divided by the amount of VOC added.
Relative Reactivity	The Incremental reactivity of the VOC divided by the incremental reactivity of the base ROG mixture.
Kinetic Reactivity	Fraction of the VOC which reacts in the scenario.
Mechanistic Reactivity	Change in ozone formed caused by adding a VOC to the initial and emitted base ROG in a scenario, divided by the amount of VOC which reacted.
O ₃ Yield Reactivity	Incremental or relative reactivity based on the effect of the VOC on the maximum amount of ozone formed.
IntO ₃ Reactivity	Incremental or relative reactivity based on the effect of the VOC on the O ₃ concentration integrated over time.
IntO ₃ >90 Reactivity	Reactivity based on the effect of the VOC on the sum of the O ₃ concentrations for each hour when O ₃ ≥ 90 ppb.

Table I. (continued)

<u>Reactivity Scales</u>	
Reactivity Scale	A numerical ranking system where each VOC is assigned a number giving a measure of how its emissions affect ozone formation.
Adjusted NO _x Scales	Reactivity scales derived from incremental reactivities in scenarios with a specified condition of NO _x availability.
MIR, MOIR, or EBIR Scales	The adjusted NO _x scales consisting of the average of ozone yield reactivities in the MIR, MOR, or EBIR scenarios, respectively.
Base Case Scales	Relative reactivity scales based on incremental reactivities in scenarios where NO _x inputs were not adjusted.
Base (AR) Scales	Base case scales derived using the averaged ratio method. Averages of the relative reactivities in the base case scenarios.
Base (L1) Scales	Base case scales derived using the least squares error method which minimizes the change in ozone caused by substituting the base ROG for the VOC using reactivity weighting factors which the scale predicts has zero effect on ozone.
Base (L2) Scales	Base case scales derived using the least squares error method which minimizes the change in ozone caused by substituting the VOC for the Base ROG using reactivity weighting factors which the scale predicts has zero effect on ozone.
<u>Other</u>	
VOC	Volatile Organic Compound. In this paper CO is also referred to as a VOC, but strictly speaking it is not.
ROG	Reactive Organic Gas. VOCs which react in the atmosphere to a significant extent, i.e., VOCs other than CO, methane, chlorofluorocarbons, or other unreactive compounds.
NMOG	Non Methane Organic Gases. VOCs excluding methane and CO.
EKMA	Empirical Kinetic Modeling Approach. A method to estimate effects of ROG or NO _x controls on ozone based on box model calculations of one day episodes using a particular computer program. In the context of this work, it refers to the box model scenarios developed for this type of modeling analysis.
Null test	A model simulation where one VOC or mixture of VOCs is replaced by another in a proportion which a reactivity scale predicts would have no effect on ozone. The resulting change in ozone is a way of measuring the error of a reactivity scale.

1986-88 data¹⁸. The initial NMOG and NO_x concentrations, the aloft O₃ concentrations, and the mixing height inputs were based on measurement data for the various areas, the hourly emissions in the scenarios were obtained from the National Acid Precipitation Assessment Program (NAPAP) emissions inventory,¹⁸ and biogenic emissions were also included. Table II gives a summary of the urban areas represented and other selected characteristics of the scenarios.

Note that the initial NMOG and NO_x concentrations are based on air quality data, so they are not affected by uncertainties and possible errors in the emissions inventory. Errors in the inventory would affect amounts of hourly emissions after the beginning of the simulation, which usually have less of an effect on the ozone than the amounts of NMOG and NO_x present initially. Thus if the NMOG inventory were too low, then the base case ROG/NO_x ratio would also be low, but to a lesser extent. However, this would not significantly affect the ROG/NO_x ratio in the adjusted NO_x scenarios (discussed below.)

Several changes to the scenario inputs were made based on discussions with the California ARB staff and others.^{13,21} Two percent of the initial NO_x and 0.1% of the emitted NO_x in all the scenarios was assumed to be in the form of HONO. The photolysis rates were calculated using solar light intensities and spectra calculated by Jeffries²² for 640 meters, the approximate mid-point of the mixed layer during daylight hours. The composition of the NMOGs entrained from aloft was based on the analysis of Jeffries et al. of aircraft data from a number of urban areas²³. The composition of the initial and emitted ROG_s was derived as discussed below. Complete listings of the input data for the scenarios are given elsewhere.²⁰

This set of 39 EKMA scenarios are referred to as "base case" to distinguish them from the scenarios derived from them by adjusting NO_x inputs to yield standard conditions of NO_x availability as discussed below. No claim is made as to the accuracy of these scenarios in representing any real episode, but they are a result of an effort to represent, as accurately as possible given the available data and the limitations of the formulation of the EKMA model, the range of conditions occurring in urban areas throughout the United States. When developing general reactivity scales it is more important that the scenarios employed represent a realistic distribution of chemical conditions than any one accurately representing the details of any particular episode.

Base ROG Mixture. The Base ROG mixture is the mixture of reactive organic gases used to represent the chemical composition of the initial and emitted anthropogenic reactive organic gases from all sources in the scenarios. It is referred to as the "base" mixture because it is used in the simulations

Table II. Summary of conditions of the EPA base case scenarios.

City, State	Calc. Max O ₃ (ppb)	ROG /NO _x	NO _x /NO _x ^{MOR}	Final Height (km)	Init.+Emit Base ROG (mmol m ⁻²)	Aloft O ₃ (ppb)
Atlanta, GA	163	7.3	0.8	2.1	12	63
Austin, TX	162	9.3	0.6	2.1	11	85
Baltimore, MD	275	5.2	1.2	1.2	17	84
Baton Rouge, LA	211	6.8	1.0	1.0	11	62
Birmingham, AL	223	6.9	0.6	1.8	13	81
Boston, MA	182	6.5	0.7	2.6	14	105
Charlotte, NC	137	7.8	0.4	3.0	7	92
Chicago, IL	251	11.6	0.6	1.4	25	40
Cincinnati, OH	183	6.4	0.8	2.8	17	70
Cleveland, OH	220	6.6	1.1	1.7	16	89
Dallas, TX	167	4.7	1.4	2.3	18	75
Denver, CO	172	6.3	1.3	3.4	29	57
Detroit, MI	217	6.8	0.9	1.8	17	68
El Paso, TX	162	6.6	1.1	2.0	12	65
Hartford, CT	160	8.4	0.5	2.3	11	78
Houston, TX	266	6.1	1.1	1.7	25	65
Indianapolis, IN	187	6.6	1.0	1.7	12	52
Jacksonville, FL	141	7.6	0.7	1.5	8	40
Kansas City, MO	146	7.1	0.7	2.2	9	65
Lake Charles, LA	257	7.4	0.7	0.5	7	40
Los Angeles, CA	483	7.6	1.1	0.5	23	100
Louisville, KY	191	5.5	0.9	2.5	14	75
Memphis, TN	205	6.8	0.8	1.8	15	58
Miami, FL	125	9.6	0.5	2.7	9	57
Nashville, TN	155	8.1	0.5	1.6	7	50
New York, NY	317	8.1	0.8	1.5	39	103
Philadelphia, PA	212	6.2	1.0	1.8	19	53
Phoenix, AZ	242	7.6	1.1	3.3	40	60
Portland, OR	152	6.5	0.8	1.6	6	66
Richmond, VA	212	6.2	0.9	1.9	16	64
Sacramento, CA	184	6.6	0.9	1.1	7	60
St Louis, MO	269	6.1	1.2	1.6	26	82
Salt Lake City, UT	173	8.5	0.7	2.2	11	85
San Antonio, TX	119	3.9	1.2	2.3	6	60
San Diego, CA	169	7.1	1.1	0.9	8	90
San Francisco, CA	167	4.8	2.0	0.7	25	70
Tampa, FL	192	4.4	1.3	1.0	8	68
Tulsa, OK	201	5.3	1.0	1.8	15	70
Washington, DC	250	5.3	0.9	1.4	13	99
Avg. Conditions	206	6.6	0.9	1.8	15	70

without the added test VOC in the reactivity calculations. (When the reactivity of a VOC is assessed, that VOC is added to this base ROG mixture in the simulation.) Consistent with the approach used in the original EPA scenarios, the same mixture was used for all scenarios — except for the calculations where the effects of changing this mixture are assessed. The speciation for this mixture was derived by Croes²⁴ based on an analysis of the EPA database²³ for the hydrocarbons and the 1987 Southern California Air Quality Study (SCAQS) database for the oxygenates.^{25,26} This mixture consists of 52% (by carbon) alkanes, 15% alkenes, 27% aromatics, 1% formaldehyde, 2% higher aldehydes, 1% ketones, and 2% acetylene. The detailed composition of this mixture is given elsewhere.²⁰

Adjusted NO_x Scenarios. Since incremental reactivities are highly dependent on NO_x^{5,9,11}, and since the NO_x conditions of the base case scenarios are variable (as indicated by the ROG/NO_x ratios on Table II), one would expect the incremental reactivities to also be highly variable. But if the NO_x inputs to these scenarios were adjusted to yield consistent NO_x conditions, one might expect the incremental reactivities, or at least the ratios of incremental reactivities, to be much less variable. In this case, the set of incremental reactivities so obtained may provide a general reactivity scale which is at least applicable to that particular condition of NO_x availability. Comparing different reactivity scales for different NO_x conditions would provide a systematic means to assess how reactivity scales, and control strategies based on them, would vary with NO_x levels.

To develop a set of scenarios for this purpose, one needs a means to assess NO_x availability, or to establish equivalency of NO_x conditions, which is applicable to a variety of scenarios. NO_x availability is determined both by the amount of NO_x input and the rate at which it is removed. The latter is affected not only by the reactivity and amount of ROG which are present, but also by factors such as light intensity, temperature, and dilution, which in general will vary from scenario to scenario. Therefore the amount of NO_x present or the ROG/NO_x ratio are not necessarily reliable indicators of NO_x availability.

However, if one examines how changes in ROG and NO_x affect ozone formation as a function of NO_x inputs, essentially the same pattern is observed for all scenarios. This is shown on Figure 1, which plots, against total NO_x input, the changes in ozone caused by 1% increases in ROG or NO_x inputs for a typical scenario. The figure also includes a plot of the peak daily ozone concentration against NO_x input. Note that in all cases there is a NO_x input level (designated "MIR" on the plot) where the ROG input has the highest and most positive effect on ozone which is near or the same as the point where the effect of NO_x is the most negative; there is a lower NO_x level ("MOR") which yields the maximum ozone concentration and where the effect of NO_x on ozone changes sign; and there is a yet lower NO_x level

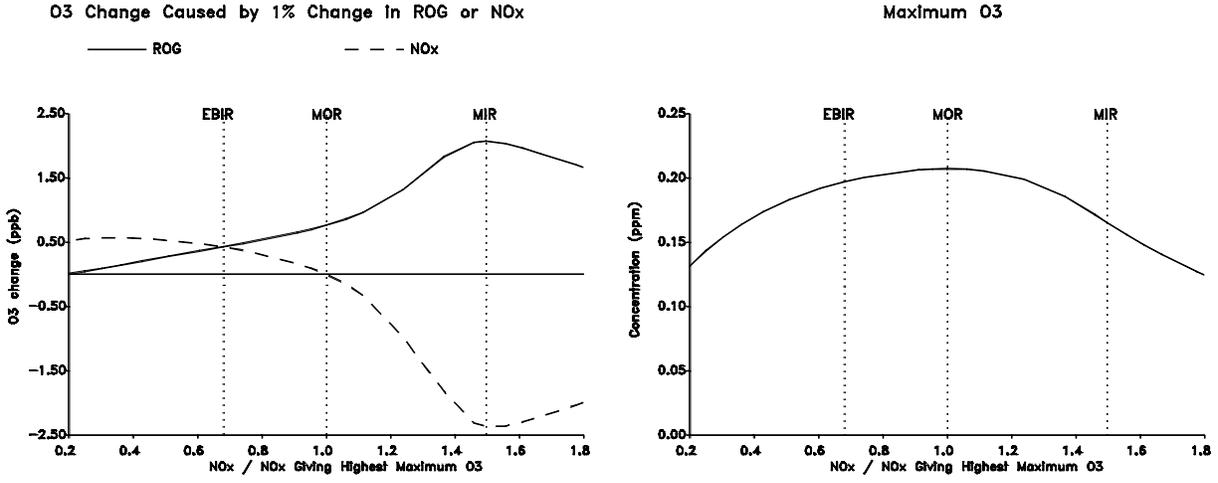


Figure 1. Qualitative dependencies on NO_x inputs of maximum ozone and of relative changes in ozone caused by 1% increases in total ROG or total NO_x emissions for the "Averaged Conditions" Scenarios. NO_x inputs are shown relative to NO_x inputs which give maximum ozone yields.

("EBIR") where the effects of fractional changes of ROG and NO_x on ozone formation are equal. Although these three points in general occur at different NO_x inputs or ROG/ NO_x ratios for conditions of different scenarios, they represent consistent NO_x conditions in terms of how ozone formation is affected by ROG and NO_x changes. Thus, these can be used to define three conditions of consistent NO_x availability, which yield three sets of adjusted NO_x scenarios. These are as follows:

Maximum Incremental Reactivity (MIR) Scenarios. In these scenarios the NO_x inputs are adjusted so that the base ROG mixture had the highest incremental reactivity. The NO_x adjustment was done by varying both the initial NO_x and the emitted NO_x by the same factor.²⁰ These MIR scenarios represent NO_x conditions where emissions of ROG have the greatest effect on ozone formation, and where NO_x has the strongest ozone inhibiting effect. Thus they represent conditions where ROG control has the greatest effect on ozone. They can also be thought of representing approximately the highest NO_x levels which are relevant in considering control strategies for ozone, because ozone is suppressed to low levels if NO_x inputs are increased significantly above this level.

Maximum Ozone Reactivity (MOR) Scenarios. In these scenarios the NO_x inputs are adjusted to yield the highest peak ozone concentration. This represents the dividing line between conditions where NO_x is in excess and where ozone is NO_x limited, or the "ridgeline" on ozone isopleth plots.²⁷ MOR scenarios represent NO_x conditions which are optimum for ozone formation.

Equal Benefit Incremental Reactivity (EBIR) Scenarios. In these scenarios the NO_x inputs are adjusted so that the effect on ozone of a given percentage incremental change in ROG input is the same as the effect of an equal percentage change in NO_x . In other words, this is the point where the incremental reactivity of the base ROG mixture, multiplied by the total amount of ROG input (excluding aloft or biogenic ROGs), equals the incremental reactivity of NO_x , multiplied by the amount of NO_x input. The EBIR scenarios represent the lowest NO_x conditions where ROG control is of equal or greater effectiveness for reducing ozone as NO_x control. Thus they represent the lowest NO_x conditions which are of relevance to ROG control, since at lower NO_x levels NO_x control becomes much more effective in reducing ozone.

Averaged Conditions Scenarios. It is useful for sensitivity studies and example calculations to have a single scenario or set of scenario conditions which can be taken as being representative of the larger set. For this purpose, we derived an "averaged conditions" scenario from the averages of the relevant inputs of the 39 base case scenarios. This was then used as the basis for developing scenarios with some input modified, such as the base ROG composition or the initial HONO. The MIR, MOR, or EBIR versions of this scenario are determined as discussed above for the base case scenarios. Note that when conducting sensitivity calculations on varied scenario conditions, the NO_x adjustments to determine MIR, MOR or EBIR conditions were done after the scenario condition was varied, so the effect of the variation can be assessed on an equal NO_x availability basis. Otherwise, the effect of the variation on NO_x availability may dominate the result.

Calculation of Reactivities in a Scenario

Incremental Reactivities. Incremental reactivities in a given scenario are calculated by conducting model simulations of ozone formation in the scenario, and then repeating the calculations with a small amount of the test VOC added. The amount of test VOC added depended on how rapidly it reacted in the scenario, being determined such that the amount added is sufficiently large so that numerical errors in the computer simulation do not significantly affect the results, yet is sufficiently small that the

effect of adding the VOC is within the linear range where the change in ozone is proportional to the amount added.²⁰ The incremental reactivities are then the change in ozone formed in the two calculations, divided by the amount of test VOC added. The detailed methodology used for calculating incremental reactivities in a scenario is given elsewhere.²⁰

Incremental reactivities depend on how the amounts of VOC added and how the amounts of ozone formed are quantified. In this work, incremental reactivities are based on VOCs quantified on a mass basis, i.e., by the amount of ozone formed per gram of VOC added. This is most relevant for control strategy applications because VOC emissions are quantified by mass. Alternative quantifications, which have a closer correspondence to the chemical processes, are mole basis or carbon basis, where the latter is more frequently used. Note that the VOC quantification affects relative reactivities of VOCs with different molecular weights per carbon, such as oxygenates compared to hydrocarbons.

The way the amount of ozone formed is quantified will also affect incremental reactivities. The following ozone quantifications are used:

Ozone Yield Reactivities. These are based on the maximum number of moles or grams of ozone formed in the scenario, i.e., the moles or grams per unit area in the mixed layer at the time of the maximum ozone concentration. This gives the same ratios of incremental reactivities as reactivities calculated from peak ozone concentrations, but is preferred because it permits magnitudes of reactivities in scenarios with differing dilutions to be compared on the same basis. Most previous recent studies of incremental reactivity^{2,3,5,9,28} have been based on ozone yield or peak ozone concentration reactivities.

Integrated Ozone (IntO₃) Reactivities. These are based on the ozone concentrations integrated over time throughout the simulated day. Note that if two VOCs give the same maximum ozone concentration when added in equal amounts in the scenarios, but one causes ozone to be formed earlier, their IntO₃ incremental reactivities would be different, even though the ozone yield reactivities would be the same.

Integrated Ozone Over 90 ppb (IntO₃>90) Reactivities. These are based on the extent to which the ozone exceeds the California ambient air quality standard of 90 ppb, and the length of time of the exceedence. In this work, this is quantified by the sum of the hourly ozone concentrations for the hours when the ozone exceeds the standard in the calculations without the added VOC. (The hours when

the standard is exceeded in the calculations with the added VOC would be the same if the amount of VOC added were sufficiently small.)

Relative Reactivities. For control strategy purposes, the ratios of incremental reactivities for one VOC relative to others are of greater relevance than the incremental reactivities themselves. To define a relative reactivity scale, one needs to select a VOC to use as the standard. For example, Chameides et al.²⁹ used propene, Russell and co-workers³⁰ used carbon monoxide, and Derwent and Jenkins³¹ used ethylene for this purpose. In this work, the standard we will use is the base case ROG mixture, i.e., the mixture used in the model simulations to represent the initially present and emitted anthropogenic reactive organic gases in the scenarios. Thus, the relative reactivity of a VOC is the ratio of the incremental reactivity of the VOC to the incremental reactivity of the base ROG mixture. When defined in this way, the VOC's relative reactivity measures the effect on ozone of changing the emissions of this VOC compared to the effect changing the emissions of all VOCs equally.

Kinetic and Mechanistic Reactivities. To provide a basis for examining in more detail how differing aspects of VOC reaction mechanisms and scenario conditions affect reactivity, it is useful to consider incremental reactivity as being the product of the "kinetic" and the "mechanistic" reactivities.⁹ The kinetic reactivity is the fraction of the emitted VOC which reacts in the scenario, and depends on the VOC's relevant rate constants and the levels of the radicals and species in the scenarios which react with the VOCs. Mechanistic reactivity is the change in ozone formed caused by adding the VOC, divided by the amount which reacts — or the incremental reactivity divided by the kinetic reactivity. The mechanistic reactivities are independent (to a first approximation) on how rapidly the VOC reacts, but are affected by factors such as the as number of conversions of NO to NO₂ which occur when the VOC reacts, whether the VOC's reactions enhance or inhibit radical or NO_x levels, the reactivities of the products they form, and conditions of the scenario such as NO_x availability and other factors which affect the overall efficiency of ozone formation.⁹ These two components of incremental reactivity are affected by different aspects of the VOC reaction mechanism and of the scenario conditions. Thus they are useful when explaining factors which affect reactivity, and why reactivity can vary from scenario to scenario.

Derivation of Multi-Scenario Reactivity Scales

A total of 18 different general or multi-scenario reactivity scales were derived in this work, depending on which type of ozone quantification, scenarios, or aggregation method was used. These are discussed below.

Adjusted NO_x Scales. Adjusted NO_x reactivity scales are scales derived from incremental or relative reactivities in the adjusted NO_x scenarios. A total of 9 such scales were derived based on the three conditions of NO_x availability (MIR, MOR, and EBIR) and the three methods for quantifying ozone (O₃ yield, IntO₃, and IntO₃>90). Incremental reactivities in these scales were derived by averaging the kinetic and mechanistic reactivities in the MIR, MOR or EBIR scenarios, and combining them to yield aggregate incremental reactivities for these three NO_x conditions. This gives essentially the same result as simply averaging the incremental reactivities, but this approach was used because it also gives kinetic and mechanistic reactivities characteristic of the adjusted NO_x conditions. This is useful for analyzing reactivity trends. Incremental reactivities were computed only for the ozone yield scales; for the IntO₃ and IntO₃>90 scales only relative reactivities were computed. Relative reactivities for the 9 adjusted NO_x scales were derived by averaging the relative reactivities in the adjusted NO_x scenarios.

In the remainder of this paper the terms "MIR scale", "MOIR scale" or "EBIR scale" will be used to refer to the *ozone yield* adjusted NO_x scales. (MOIR stands for "maximum ozone incremental reactivity.") The IntO₃ or IntO₃>90 adjusted NO_x scales will be referenced explicitly as such when they are discussed. This conforms to the terminology used elsewhere for the MIR and MOIR scales.^{12,13}

Base Case Scales. Base case relative reactivity scales are derived from incremental reactivities in the base case scenarios. Only relative reactivities are derived because the varying NO_x conditions in the base scenarios caused incremental reactivities to vary widely. For many VOCs relative reactivities also varied widely in the base case scenarios, and different scales can be obtained depending on the methods used to derive a single scale from the distribution of values among the scenarios. Three different methods, discussed below, were employed. Combined with the three methods for quantifying ozone, these yielded 9 different base case relative reactivity scales.

The "Average Ratio" (AR) Method. This consists of simply averaging the relative reactivities in the base case scenarios, with each scenario being weighed equally. This is the method used to derive the relative reactivities in the adjusted NO_x scales. However in this case, unlike the adjusted

NO_x scales, the quantities being averaged are quite variable. The fact that this method weighs the relative reactivities in all scenarios equally, despite the fact that ozone is much more sensitive to VOC changes in some scenarios than in others, suggests that this may not give an optimum scale for control applications. A more optimum scale should give greater weight to scenarios which are more sensitive to the quantities being regulated.

The "Least Squares Error" Methods. These are based on minimizing the calculated sum-of-squares change in ozone which would result if a substitution which the scale predicts would have zero effect on ozone were applied throughout the set of scenarios. Model calculations of substitutions which a reactivity scale predicts has no effect on ozone are referred to as "null tests" of the scale. For example, if the relative reactivity of a compound in a scale were 0.5, then the scale predicts that substitution of 2 units of the compound for one unit of the base ROG would result in no net change in ozone. A null test calculation would be a simulation of the effect of this substitution. Since in general relative reactivities vary from scenario to scenario, a null test substitution would cause a change in ozone in at least some of the scenarios no matter what relative reactivity were used. This change can then be thought of as a measure of the "error" of the reactivity scale for the scenario. The least squares error relative reactivity is the value which minimizes the sum of squares of this error, or change in ozone, resulting from this null test. Note that this method gives greater weight to scenarios where ozone is more sensitive to VOCs.

Since relative reactivity is defined as reactivities relative to the base ROG, the relevant substitution strategies for deriving these scales would involve either (1) reducing emissions of the VOC and offsetting it by an increase in the emissions of all ROG_s, or (2) reducing all ROG_s and offsetting it by an increase in the VOC. Least squares error method "L1" is based on minimizing the errors in null tests of ROG for VOC substitutions, while least squares error "L2" is based on minimizing errors in null tests of VOC for ROG substitutions. It can be shown²⁰ that the Base (L1) relative reactivities are the same as the weighted average of the relative reactivities in the individual base case scenario, where the weighting factor is the square of the incremental reactivity of the base ROG mixture. On the other hand, the Base (L2) relative reactivities are the reciprocals of the weighed averages of the reciprocals of the relative reactivities in the scenarios, where the weighting factor is the square of the incremental reactivity of the VOC.

Method L2 may seem preferable from a control strategy perspective because most substitutions of interest involve replacing current emissions with some less reactive VOC, which is the basis of the null test the L2 method is designed to optimize. However, method L1 is more tractable mathematically

because method L2 does not give well defined results for VOCs whose incremental reactivities vary around zero, and because the relative reactivities of mixtures in the Base (L1) scales can be derived by linear summations of relative reactivities of their components — which is not the case for the Base (L2) scales.

Chemical Mechanism

The chemical mechanism used in this study is that of Carter,³² with updates for several VOCs as indicated in footnotes to the reactivity results tabulations, below. A complete listing of the updated mechanism is given elsewhere.²⁰ This mechanism contains rate constant and product yield assignments for almost 120 separate VOCs. It was evaluated by simulating results of a variety of environmental chamber experiments, and was found to be able to simulate maximum ozone concentrations and rates of NO oxidation and ozone formation to within $\pm 30\%$ for 63% of the experiments³³. However, it had a slight bias ($\sim 15\%$) towards overpredicting maximum ozone concentrations in the experiments designed to represent ambient mixtures.³³ This is comparable to or slightly better than the performance of the RADM-II^{34,35} and Carbon Bond IV³⁶ mechanisms in simulating the same³⁵ or a similar³⁶ database. This is as good as can be reasonably expected given our current state of knowledge of atmospheric chemistry and characterization of chamber artifacts.^{33,35}

This mechanism is considered appropriate for reactivity calculations because it is at least as up to date as the other available comprehensive mechanisms^{34,36,37} and it is the only one designed to represent large numbers of VOCs which has been extensively tested against chamber data. However, its limitations and uncertainties must be recognized. Most of the mechanism represents the state of knowledge as of 1989-1990 and is out of date in some respects. At the time it was developed, the available chamber data were sufficient to test the representation of ~ 20 representative VOCs, and the reactions for most of the others were derived by extrapolation or estimations.³² It has not been updated to take into account results of recent experimental studies of incremental reactivities of a variety of VOCs.¹⁰ The uncertainties in the reaction mechanism obviously must be taken into account when the results of model calculations of reactivities are used to assess ozone control strategies. To aid in such assessments, the master listing of reactivity results given in the following section includes footnotes indicating levels of uncertainty in the mechanisms for the various VOCs, based on the amount of experimental data available to test the mechanisms at the time they were developed.

Results and Discussion

Table III gives the incremental reactivities in the MIR scale and the relative reactivities in all 9 adjusted NO_x scales for all the types of VOCs in the mechanism. Comparisons of relative reactivities in the base case scales are shown for selected VOCs in figures given later in this paper. These data are discussed below, first in terms of the variability and differences of incremental reactivities and its components, and then in terms of the differences and variabilities of the relative reactivities. Finally, reactivity adjustment factors for selected vehicle exhaust mixtures calculated using these various scales are compared.

Distributions of NO_x and Reactivity in the Scenarios

Figure 2 shows the distribution plots of the maximum ozone concentrations, two measures of the NO_x levels, and the base ROG incremental reactivities for the various scenarios. Note that the wide distributions of ROG/ NO_x ratios in the adjusted NO_x scenarios indicate that the ROG/ NO_x ratios are, by themselves, poor predictors of NO_x availability. A much better predictor is the ratio of the NO_x input to the NO_x yielding maximum ozone concentrations, or the $\text{NO}_x/\text{NO}_x^{\text{MOR}}$ ratio. This ratio, which is 1 by definition for the MOR scenarios, was found to be narrowly distributed around 1.5 for the MIR scenarios, and 0.7 for the EBIR scenarios. On the other hand, as expected it varies widely among the base scenarios. By this measure, most of the EPA base scenarios used in this work are between MOR and EBIR conditions.

The distribution of maximum ozone levels is very similar in all the scenarios, being only slightly lower in the MIR scenarios relative to the others. Thus, while MIR conditions are not optimum for ozone formation, levels of ozone which exceed air quality standards are still formed. On the other hand, the distribution of base ROG incremental reactivities are significantly higher in the MIR scenarios than in the lower NO_x MOR or EBIR scenarios. The wide distribution of base ROG reactivities in the base scenarios is expected given their distribution of NO_x conditions.

Note that in a previous derivation of general VOC reactivity scales,¹¹ a different set of scenarios, obtained from the studies of Gery et al.¹⁷ and Whitten³⁸ were used. To show how the distribution of NO_x conditions from these scenarios compare with the EPA-derived scenarios used in this work, Figure 2 also shows plots of $\text{NO}_x/\text{NO}_x^{\text{MOR}}$ for the Gery et al.¹⁷ and Whitten³⁸ scenarios. These are designated as "base

Table III. Tabulation of incremental reactivities in the MIR scale and relative reactivities in the adjusted NO_x scales, with notes concerning the uncertainty of the VOCs' mechanisms.

Compound	MIR	Ozone Yield			Relative Reactivity [b]			Int'd Ozone >90 ppb			Unc. Notes [c]
	Inc.Rct. [a]				Integrated Ozone						
		MIR	MOIR	EBIR	MIR	MOIR	EBIR	MIR	MOIR	EBIR	
<u>Carbon Monoxide</u>	0.054	0.018	0.032	0.044	0.016	0.023	0.029	0.017	0.025	0.034	1
<u>Alkanes</u>											
Methane	0.015	0.005	0.008	0.010	0.004	0.005	0.006	0.004	0.006	0.008	2
Ethane	0.25	0.079	0.140	0.18	0.061	0.078	0.088	0.069	0.091	0.109	2
Propane	0.48	0.16	0.27	0.33	0.128	0.17	0.19	0.139	0.19	0.23	2
n-Butane	1.02	0.33	0.57	0.70	0.26	0.33	0.36	0.29	0.38	0.44	1
n-Pentane	1.04	0.33	0.58	0.71	0.29	0.37	0.42	0.31	0.41	0.48	5
n-Hexane	0.98	0.31	0.55	0.65	0.28	0.35	0.38	0.29	0.39	0.44	5
n-Heptane	0.81	0.26	0.45	0.49	0.22	0.26	0.25	0.24	0.30	0.30	5
n-Octane	0.60	0.19	0.34	0.33	0.15	0.17	0.137	0.17	0.21	0.18	5
n-Nonane	0.54	0.17	0.30	0.27	0.132	0.125	0.063	0.150	0.16	0.113	5
n-Decane	0.46	0.146	0.26	0.22	0.109	0.091	0.021	0.128	0.130	0.070	7
n-Undecane	0.42	0.132	0.23	0.19	0.095	0.072	-0.002	0.114	0.110	0.046	8
n-Dodecane	0.38	0.118	0.21	0.16	0.082	0.058	-0.016	0.101	0.094	0.028	8
n-Tridecane	0.35	0.110	0.19	0.15	0.074	0.049	-0.025	0.093	0.082	0.018	8
n-Tetradecane	0.32	0.100	0.17	0.136	0.067	0.041	-0.031	0.085	0.073	0.011	8
Isobutane	1.21	0.39	0.63	0.80	0.33	0.43	0.51	0.36	0.48	0.60	7
Neopentane	0.37	0.117	0.18	0.21	0.092	0.105	0.104	0.104	0.123	0.126	7
Iso-Pentane	1.38	0.44	0.74	0.93	0.38	0.48	0.55	0.41	0.54	0.63	7
2,2-Dimethylbutane	0.82	0.26	0.43	0.51	0.21	0.26	0.27	0.23	0.30	0.33	7
2,3-Dimethylbutane	1.07	0.34	0.57	0.72	0.32	0.43	0.51	0.33	0.45	0.56	5
2-Methylpentane	1.5	0.48	0.76	0.90	0.42	0.49	0.52	0.45	0.55	0.60	7
3-Methylpentane	1.5	0.48	0.80	0.99	0.42	0.52	0.58	0.45	0.58	0.67	7
2,2,3-Trimethylbutane	1.32	0.42	0.68	0.84	0.38	0.49	0.57	0.40	0.53	0.65	7
2,3-Dimethylpentane	1.31	0.41	0.67	0.79	0.37	0.44	0.48	0.39	0.49	0.55	7
2,4-Dimethylpentane	1.5	0.48	0.73	0.86	0.42	0.48	0.50	0.44	0.53	0.58	7
3,3-Dimethylpentane	0.71	0.22	0.39	0.44	0.18	0.22	0.22	0.20	0.26	0.27	7
2-Methylhexane	1.08	0.34	0.57	0.69	0.30	0.37	0.40	0.32	0.41	0.46	7
3-Methylhexane	1.40	0.44	0.71	0.82	0.38	0.44	0.46	0.41	0.49	0.53	7
2,2,4-Trimethylpentane	0.93	0.29	0.46	0.49	0.24	0.27	0.24	0.27	0.31	0.29	7
2,3,4-Trimethylpentane	1.6	0.51	0.78	0.94	0.47	0.55	0.61	0.49	0.60	0.69	7
2,3-Dimethylhexane	1.31	0.41	0.67	0.79	0.37	0.44	0.48	0.39	0.49	0.55	7
2,4-Dimethylhexane	1.5	0.48	0.73	0.86	0.42	0.48	0.50	0.44	0.53	0.58	7
2,5-Dimethylhexane	1.6	0.52	0.79	0.96	0.49	0.59	0.67	0.51	0.63	0.74	7
2-Methylheptane	0.96	0.30	0.51	0.57	0.26	0.30	0.29	0.28	0.34	0.35	7
3-Methylheptane	0.99	0.31	0.53	0.60	0.27	0.32	0.32	0.29	0.36	0.38	7
4-Methylheptane	1.20	0.38	0.59	0.65	0.32	0.35	0.33	0.35	0.40	0.40	7
2,4-Dimethylheptane	1.33	0.43	0.63	0.72	0.37	0.41	0.40	0.40	0.45	0.47	7
2,2,5-Trimethylhexane	0.97	0.30	0.49	0.54	0.26	0.29	0.27	0.28	0.33	0.33	7
4-Ethylheptane	1.13	0.36	0.54	0.59	0.30	0.31	0.28	0.33	0.36	0.35	7
3,4-Propylheptane	1.01	0.31	0.47	0.50	0.26	0.26	0.22	0.29	0.31	0.28	8
3,5-Diethylheptane	1.33	0.43	0.63	0.72	0.37	0.41	0.40	0.40	0.45	0.47	8
2,6-Diethyloctane	1.23	0.39	0.58	0.68	0.35	0.37	0.38	0.37	0.42	0.45	8
Cyclopentane	2.4	0.76	1.19	1.46	0.67	0.80	0.89	0.71	0.89	1.01	7
Methylcyclopentane	2.8	0.90	1.32	1.5	0.82	0.96	1.05	0.86	1.03	1.17	7
Cyclohexane	1.28	0.41	0.63	0.69	0.35	0.38	0.37	0.38	0.43	0.43	7
1,3-Dimethylcyclohexane	2.5	0.81	1.18	1.43	0.76	0.89	1.00	0.78	0.95	1.10	8
Methylcyclohexane	1.8	0.59	0.84	0.96	0.51	0.56	0.55	0.55	0.62	0.64	5
Ethylcyclopentane	2.3	0.73	1.10	1.31	0.66	0.74	0.78	0.69	0.81	0.90	8
Ethylcyclohexane	1.9	0.62	0.86	0.97	0.55	0.57	0.56	0.59	0.64	0.65	8
1-Ethyl-4-Methylcyclohexane	2.3	0.73	1.00	1.15	0.66	0.70	0.71	0.70	0.76	0.81	8
1,3-Diethylcyclohexane	1.8	0.57	0.79	0.92	0.51	0.55	0.56	0.55	0.60	0.64	8
1,3-Diethyl-5-Methylcyclohexane	1.9	0.61	0.84	1.00	0.57	0.61	0.65	0.59	0.65	0.73	8
1,3,5-Triethylcyclohexane	1.7	0.54	0.74	0.86	0.49	0.53	0.55	0.51	0.57	0.62	8

Table III (continued)

Compound	MIR Inc.Rct. [a]	Ozone Yield			Relative Reactivity [b]			Int'd Ozone >90 ppb			Unc. Notes [c]
					Integrated Ozone						
		MIR	MOIR	EBIR	MIR	MOIR	EBIR	MIR	MOIR	EBIR	
<u>Alkenes</u>											
Ethene	7.4	2.4	2.8	3.2	2.2	2.4	2.7	2.3	2.6	2.9	1
Propene	9.4	3.0	3.2	3.7	3.0	3.0	3.2	3.0	3.1	3.4	4
1-Butene	8.9	2.9	3.0	3.4	2.8	2.7	2.8	2.8	2.8	2.9	4
1-Pentene	6.2	2.0	2.1	2.3	2.0	1.9	1.7	2.0	1.9	1.9	7
3-Methyl-1-Butene	6.2	2.0	2.1	2.3	2.0	1.9	1.7	2.0	1.9	1.9	7
1-Hexene	4.4	1.40	1.46	1.5	1.32	1.17	1.00	1.38	1.27	1.14	4
1-Heptene	3.5	1.10	1.15	1.18	1.02	0.88	0.69	1.08	0.97	0.82	8
1-Octene	2.7	0.85	0.90	0.89	0.76	0.62	0.41	0.82	0.71	0.55	8
1-Nonene	2.2	0.71	0.74	0.72	0.62	0.48	0.28	0.68	0.58	0.41	8
Isobutene	5.3	1.7	1.6	1.9	2.0	2.1	2.5	1.9	2.0	2.3	5
2-Methyl-1-Butene	4.9	1.5	1.6	1.9	1.7	1.9	2.2	1.6	1.7	2.0	7
trans-2-Butene	10.0	3.2	3.2	3.6	3.5	3.6	4.0	3.3	3.3	3.6	5
cis-2-Butene	10.0	3.2	3.2	3.6	3.5	3.6	4.0	3.3	3.3	3.6	5
2-Pentenes	8.8	2.8	2.8	3.1	3.0	3.1	3.2	2.9	2.8	2.9	7
2-Methyl-2-Butene	6.4	2.1	2.0	2.2	2.4	2.7	3.1	2.2	2.3	2.5	7
2-Hexenes	6.7	2.2	2.2	2.3	2.3	2.3	2.3	2.2	2.1	2.1	8
2-Heptenes	5.5	1.8	1.8	1.9	1.9	1.9	1.9	1.8	1.8	1.8	8
3-Octenes	5.3	1.6	1.6	1.7	1.7	1.6	1.5	1.6	1.5	1.5	8
3-Nonenes	4.6	1.46	1.45	1.5	1.48	1.40	1.32	1.46	1.37	1.29	8
1,3-Butadiene	10.9	3.5	3.5	4.1	3.6	3.5	3.6	3.5	3.4	3.6	8
Isoprene	9.1	2.9	2.9	3.3	3.2	3.1	3.2	3.0	2.9	3.1	6
Cyclopentene	7.7	2.4	2.3	2.5	2.9	3.1	3.5	2.5	2.6	2.8	8
Cyclohexene	5.7	1.8	1.9	2.1	2.0	2.0	2.1	1.8	1.8	1.9	8
α-Pinene	3.3	1.04	1.08	1.23	1.11	1.11	1.17	1.06	1.05	1.09	5
β-Pinene	4.4	1.40	1.42	1.6	1.5	1.47	1.5	1.44	1.41	1.46	8
<u>Acetylenes</u>											
Acetylene	0.50	0.16	0.28	0.38	0.140	0.19	0.23	0.15	0.21	0.27	5
Methylacetylene	4.1	1.31	1.8	2.2	1.14	1.24	1.28	1.21	1.36	1.45	9
<u>Aromatics</u>											
Benzene	0.42	0.135	0.114	0.051	0.112	0.113	0.097	0.123	0.122	0.101	4
Toluene	2.7	0.88	0.53	-0.023	0.77	0.71	0.54	0.82	0.72	0.48	4
Ethylbenzene	2.7	0.86	0.52	0.007	0.77	0.72	0.54	0.82	0.72	0.49	7
n-Propylbenzene	2.1	0.68	0.41	-0.016	0.59	0.55	0.41	0.64	0.56	0.37	7
Isopropylbenzene	2.2	0.71	0.43	-0.007	0.64	0.59	0.44	0.68	0.59	0.40	7
s-Butylbenzene	1.9	0.60	0.37	-0.014	0.54	0.49	0.38	0.57	0.51	0.33	7
o-Xylene	6.5	2.1	1.6	1.26	2.0	2.0	1.8	2.1	2.0	1.7	4
p-Xylene	6.6	2.1	1.7	1.29	2.1	2.0	1.8	2.1	2.0	1.8	7
m-Xylene	8.2	2.6	2.1	1.7	2.7	2.7	2.6	2.7	2.6	2.5	4
1,3,5-Trimethylbenzene	10.1	3.2	2.6	2.4	3.8	3.8	4.0	3.5	3.5	3.5	4
1,2,3-Trimethylbenzene	8.9	2.8	2.3	1.9	3.0	3.0	3.0	2.9	2.9	2.8	7
1,2,4-Trimethylbenzene	8.8	2.8	2.3	1.9	3.0	3.0	3.0	2.9	2.9	2.8	7
Tetralin	0.94	0.31	0.103	-0.23	0.33	0.26	0.147	0.31	0.23	0.076	5
Naphthalene	1.17	0.37	0.066	-0.43	0.36	0.26	0.064	0.36	0.24	-0.009	5
Methylnaphthalenes	3.3	1.05	0.65	0.21	1.11	0.96	0.75	1.07	0.90	0.65	8
2,3-Dimethylnaphthalene	5.1	1.6	1.16	0.79	1.8	1.7	1.48	1.8	1.5	1.31	5
Styrene	2.2	0.71	-0.26	-1.8	0.82	0.54	0.043	0.73	0.32	-0.40	8
<u>Alcohols and Ethers</u>											
Methanol	0.56	0.18	0.23	0.28	0.149	0.18	0.19	0.17	0.20	0.23	1
Ethanol	1.34	0.43	0.61	0.72	0.33	0.36	0.37	0.38	0.43	0.45	1
n-Propyl Alcohol	2.3	0.72	0.95	1.07	0.60	0.63	0.61	0.66	0.71	0.70	7
Isopropyl Alcohol	0.54	0.17	0.27	0.35	0.17	0.22	0.27	0.17	0.23	0.30	7

Table III (continued)

Compound	MIR Inc.Rct. [a]	Ozone Yield			Relative Reactivity [b]			Int'd Ozone >90 ppb			Unc. Notes [c]
					Integrated Ozone						
		MIR	MOIR	EBIR	MIR	MOIR	EBIR	MIR	MOIR	EBIR	
n-Butyl Alcohol	2.7	0.86	1.09	1.25	0.74	0.77	0.76	0.79	0.84	0.86	7
Isobutyl Alcohol	1.9	0.62	0.80	0.92	0.54	0.58	0.60	0.58	0.64	0.67	7
t-Butyl Alcohol	0.42	0.132	0.21	0.27	0.114	0.148	0.18	0.125	0.17	0.21	7
Dimethyl Ether	0.77	0.24	0.48	0.68	0.24	0.35	0.47	0.24	0.38	0.53	7
Meth. t-Butyl Ether	0.62	0.20	0.34	0.47	0.18	0.25	0.31	0.19	0.27	0.36	1
Ethyl t-Butyl Ether	2.0	0.64	0.88	1.11	0.62	0.77	0.92	0.63	0.80	0.98	7
<u>Aldehydes</u>											
Formaldehyde	7.2	2.3	1.8	1.7	2.8	2.9	3.2	2.5	2.5	2.6	1
Acetaldehyde	5.5	1.8	1.8	2.2	1.7	1.5	1.31	1.8	1.6	1.6	4
C3 Aldehydes	6.5	2.1	2.1	2.4	2.1	1.8	1.49	2.1	1.9	1.7	5
Glyoxal	2.2	0.71	0.61	0.63	0.90	0.90	0.95	0.75	0.80	0.85	3
Methyl Glyoxal	14.8	4.7	4.0	3.9	6.5	7.1	8.2	5.3	5.5	6.1	3
<u>Ketones</u>											
Acetone	0.56	0.18	0.17	0.18	0.16	0.142	0.134	0.16	0.16	0.149	5
C4 Ketones	1.18	0.38	0.46	0.53	0.32	0.30	0.29	0.34	0.34	0.34	5
<u>Aromatic Oxygenates</u>											
Benzaldehyde	-0.57	-0.18	-1.08	-2.7	-0.31	-0.74	-1.5	-0.25	-0.74	-1.7	5
Phenol	1.12	0.36	-0.45	-1.7	0.32	0.091	-0.42	0.33	0.0147-0.65	7	
Alkyl Phenols	2.3	0.74	-0.53	-2.6	0.69	0.33	-0.53	0.70	0.20	-0.92	5
<u>Others</u>											
Methyl Nitrite	9.5	3.1	3.5	5.2	5.2	6.9	10.2	3.5	4.7	6.9	3
Base ROG Mixture	3.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

[a] Incremental reactivities in units of grams ozone formed per gram VOC emitted for the ozone yield reactivity scale for the MIR scale. Note that there are small differences in the last digit in the tabulated values compared to those used in the California ARB Regulations¹² for some VOCs. This is within the numerical uncertainties of these calculations, and is because of minor changes in the software used²⁰.

[b] Incremental reactivities of the VOCs (in units of ozone per gram of VOC) divided by incremental reactivities of the base ROG mixture.

[c] Notes concerning the uncertainty of the mechanism are as follows:

- 1 Least uncertain mechanism, and tested against chamber data.
- 2 Mechanism probably not uncertain, but was not tested.
- 3 Laboratory data are available for the major reactions in the mechanism, but the mechanism was not tested.
- 4 Uncertain portions of the mechanism are adjusted or parameterized to fit chamber data.
- 5 The mechanism is uncertain, and only limited or uncertain data were available to test it.
- 6 The mechanism was not optimized to fit existing chamber data.
- 7 The mechanism was estimated and was not tested.
- 8 The mechanism was estimated and was not tested, and must be considered to be highly uncertain.
- 9 The mechanism was estimated and was not tested, and is likely to be incorrect. Suitable only for estimating reactivities of mixtures where this is a component.

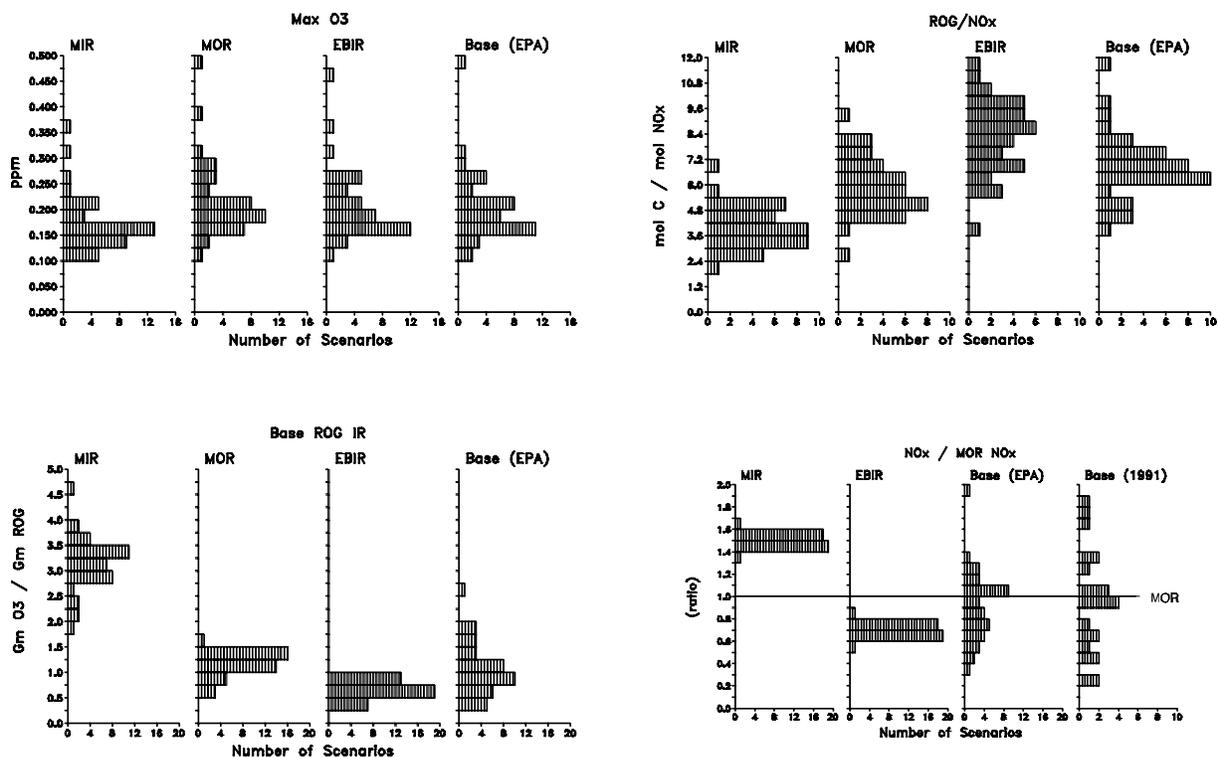


Figure 2. Distribution plots of maximum ozone, the base ROG incremental reactivity, the ROG/NO_x ratio, and the ratio of NO_x inputs to MOR NO_x inputs for the MIR, MOR, EBIR and base case scenarios. Base scenarios used previously¹¹ are shown on the NO_x/MOR NO_x plot.

(1991)" on the figure. This shows that these scenarios have a much wider distribution of NO_x conditions than those used in this work. The implications of this on reactivity scales are discussed later.

Factors Affecting Reactivity

Dependence of Reactivity on Environmental Conditions. Table III shows that as expected the incremental reactivities of a given VOC vary significantly with NO_x conditions. However, it does not show the extent to which the reactivities or their components vary among the individual adjusted NO_x and base case scenarios. An illustration of this is shown on Figure 3, which shows distribution plots of kinetic, mechanistic, incremental, and relative ozone yield reactivities for carbon monoxide and toluene. Although these are only two of the many types of VOCs, together they illustrate the trends which are characteristic of most other VOCs to varying degrees.

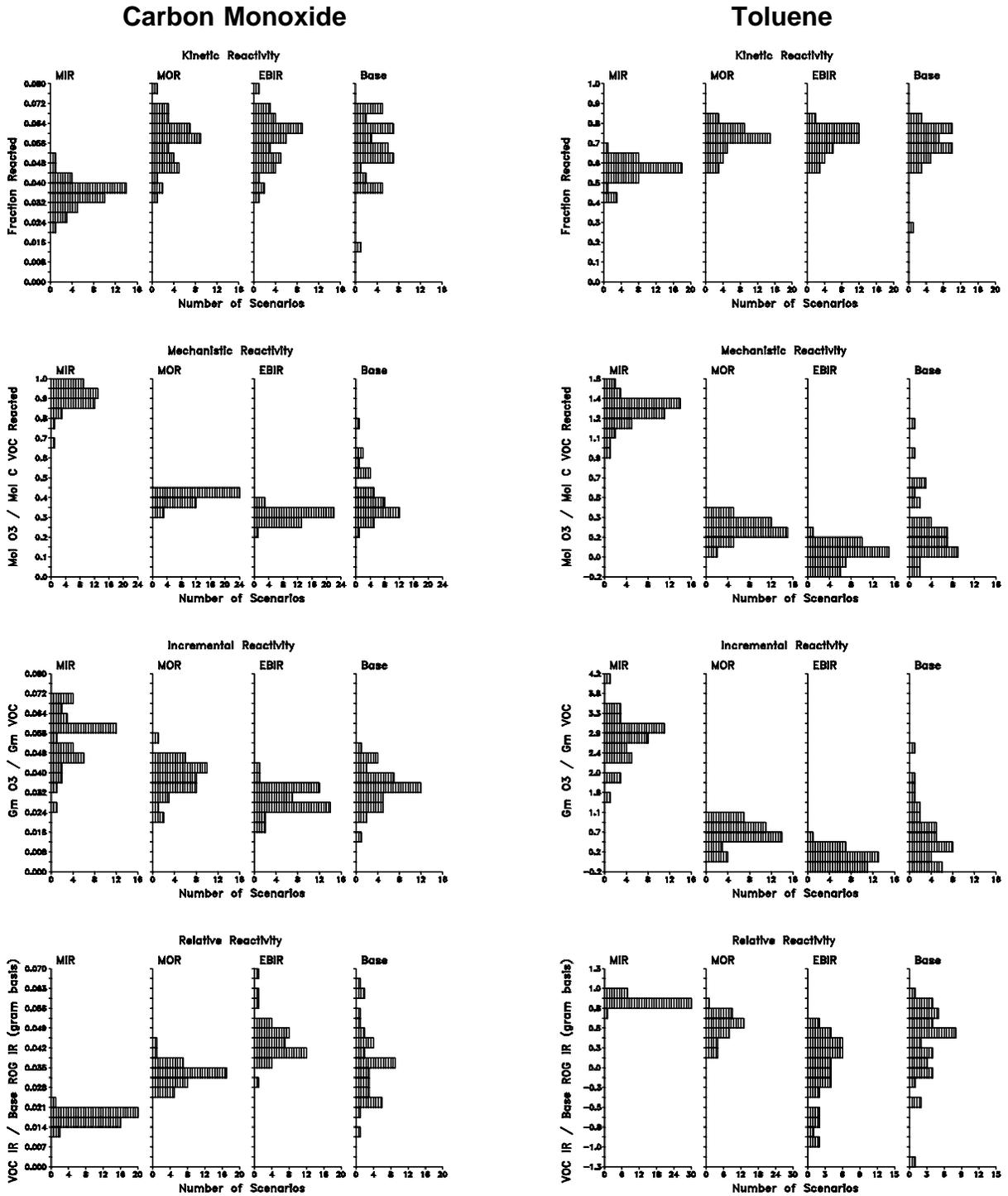


Figure 3. Distribution plots of kinetic, mechanistic, incremental, and relative reactivities for carbon monoxide and toluene in the MIR, MOR, EBIR and base case scenarios.

The sensitivity of kinetic reactivities to scenario conditions depends on how rapidly the VOC reacts, with slowly reacting compounds being most sensitive, and having kinetic reactivities which are essentially proportional to the integrated levels of species with which the VOC reacts. Rapidly reacting compounds have kinetic reactivities approaching unity. Most slowly reacting compounds react only with OH radicals, so variations in their kinetic reactivities reflect variations in integrated OH radical levels. CO reacts so slowly that its kinetic reactivity is essentially proportional to the integrated OH, and thus the distribution plot of its kinetic reactivities is the same as the distribution plot of integrated OH. The distribution for kinetic reactivities of toluene, which reacts more rapidly, is qualitatively similar but varies over a narrower range.

The distribution plots show that kinetic reactivities, and thus integrated OH radical levels, are lower in the MIR scenarios compared to MOR and EBIR conditions. This is attributed to the fact that NO_x is involved in a number of radical termination reactions. However, the kinetic reactivities apparently do not increase further to a significant extent as NO_x is reduced from MOR to EBIR levels. Apparently reduced termination caused by lower NO_x when going from MOR to EBIR is offset by the increased termination due to $\text{HO}_2 + \text{HO}_2$ and other peroxy + peroxy reactions which become more important once NO_x is consumed. On the other hand, the wide distributions of kinetic reactivities in the adjusted NO_x scenarios indicate that kinetic reactivities are significantly affected by other factors besides NO_x . Factors such as light intensity, temperature and dilution might be of equal or greater significance as NO_x in affecting radical levels and thus kinetic reactivities.

Since the dependence of kinetic reactivity on NO_x is in the opposite direction as that for incremental reactivities, the mechanistic reactivity must be the dominant factor affecting how incremental reactivities vary with NO_x . In contrast to the case with kinetic reactivities, for most VOCs there is also almost no overlap in the distributions of mechanistic reactivities in the MIR and MOR scenarios; the data on Figure 3 are typical in this regard. Thus, at least when NO_x is above MOR levels, NO_x availability dominates over other scenario conditions in affecting mechanistic reactivity. While NO_x is still important in affecting mechanistic reactivities when NO_x is below MOR levels, the other factors become relatively more important, as indicated by the overlap in the distributions of the MOR and EBIR mechanistic reactivities for both CO and toluene.

VOCs form ozone by producing HO_2 and other peroxy radicals which react with NO to shift the NO- NO_2 - O_3 photostationary state towards ozone formation. The mechanistic reactivity of CO provides a direct illustration how much ozone is formed by this process, since the reaction of CO involves only the

formation of a single HO₂ radical. Thus, no more than one molecule of ozone can be formed from each molecule of CO which reacts. This theoretical maximum is almost achieved under MIR conditions, but the yield of O₃ from HO₂ decreases rapidly as NO_x is reduced from MIR to MOR levels. This is because the HO₂+HO₂ reaction, forming H₂O₂, begins to compete with the reaction of HO₂ with NO in the scenarios where all the NO_x is consumed before the end of the simulation. Since essentially all VOCs react to form peroxy radicals, this factor contributes to the NO_x dependencies of mechanistic reactivities of almost all cases.

For most other VOCs, this is not the only factor affecting how their mechanistic reactivities depend on NO_x. If a VOC is a significant radical source, it will have high mechanistic reactivities under high NO_x conditions where final ozone concentrations are determined how rapidly ozone is formed. However, this enhancement would be less important under lower NO_x conditions where ozone yields are determined less by radical levels and more by NO_x availability. On the other hand, if a VOC has NO_x sinks in its mechanism, it will cause low, and even negative, mechanistic reactivities under low NO_x conditions, but will not significantly affect high NO_x (MIR) reactivities. Toluene is an example of a compound where both factors are operative, and consequently its mechanistic reactivity, and thus its incremental reactivity, decreases much more rapidly as NO_x is reduced than is the case for CO and other VOCs. Note that the NO_x sink effect becomes dominant when NO_x is sufficiently low, causing reactivities to become negative. This is despite the fact that toluene is still calculated to form radical-initiating products and radicals that react with NO. For the mechanism used in this work, the crossover for toluene reactivity occurs at some NO_x level around the equal benefit point, though the exact level appears to be highly variable depending on other scenario conditions. (The crossover occurs at higher NO_x levels when the Carbon Bond IV mechanism is used.³⁹)

One would expect relative reactivities to be much less dependent on scenario conditions than incremental reactivities, at least for scenario conditions which affect reactivities of all VOCs in similar qualitative ways. Thus, while decreasing NO_x levels causes decreased incremental reactivities in all compounds, this effect at least to some extent cancels out when considering relative reactivities. However, if a VOC differs significantly in how its incremental reactivities vary with NO_x than is the case for the base ROG mixture, then its relative reactivity will also vary with NO_x. For example, the mechanistic reactivities of CO are less dependent on NO_x than most VOCs so its relative reactivities increase with decreasing NO_x, while the opposite is true for toluene. For similar reasons, one would expect the distribution of relative reactivities in the adjusted NO_x scenarios to be much narrower than the corresponding distribution of incremental reactivities. This is indeed the case for the MIR scenarios, but

the relative reactivities appear to be much more variable in the MOR and (especially) the EBIR scenarios. Thus non-NO_x scenario conditions appear to affect incremental reactivities of different VOCs similarly under high NO_x, MIR conditions, but this is apparently not the case under more NO_x-limited conditions. The variations in relative reactivity are discussed further in the following section.

Relative Reactivities

The relative reactivities of a variety of VOCs in the various scales are compared graphically on Figures 4-6. (To aid in comparisons of the different scales, the dashed and dotted lines show the relative reactivities in the MIR and MOIR scales, respectively.) Figures 7-9 show how well or poorly the relative reactivities of a number of different VOCs compare in different scales by plotting the relative reactivities of the VOCs in one scale against those in the other. The position of the points for the VOCs should be compared to the 1:1 line where they would fall if they had equal relative reactivities in the two scales. The error bars on Figures 4-9 indicate the standard deviations of the averages or the derivations, and thus for the adjusted NO_x scales they indicate the importance of non-NO_x scenario conditions in affecting relative reactivities. These results are discussed in more detail below.

Ozone Yield Relative Reactivities — Adjusted NO_x Scales. The results show that the ozone yield relative reactivities can depend significantly on NO_x for many VOCs, with the trend depending on the type of VOC. Relative reactivities of the aromatics and other compounds with major NO_x sinks decrease significantly as NO_x is reduced, with the effect being largest for the cresols and benzaldehyde, the compounds with the strongest NO_x sinks. The higher alkenes apparently have similar balances of factors in affecting reactivity as the base ROG mixture, since their relative reactivities appear to be almost independent of NO_x, at least in the MIR to MOR regimes. The relative reactivities of compounds which have weaker than average NO_x sinks, such as CO, ethene and methanol, tend to increase with decreasing NO_x because their incremental reactivities are less sensitive to NO_x than that for the base ROG mixture, which includes a significant contribution from aromatics. In addition, relative reactivities of slowly reacting compounds such as CO and ethane tend to increase with decreasing NO_x because kinetic reactivities, which increase as NO_x is reduced, are relatively more important in affecting reactivities of slowly reacting compounds. Because CO is both slowly reacting and has essentially no NO_x sinks, it provides the most extreme case of a compound whose relative reactivity increases with decreasing NO_x.

- O3 Yield
- Int'd O3
- △ Int'd O3 > 90 ppb
- 1 No Oxygenates
- 2 Oxygenates x3
- 3 Aromatics x2
- 4 Alkenes x2
- 5 No HONO
- 6 Aloff ROG x5

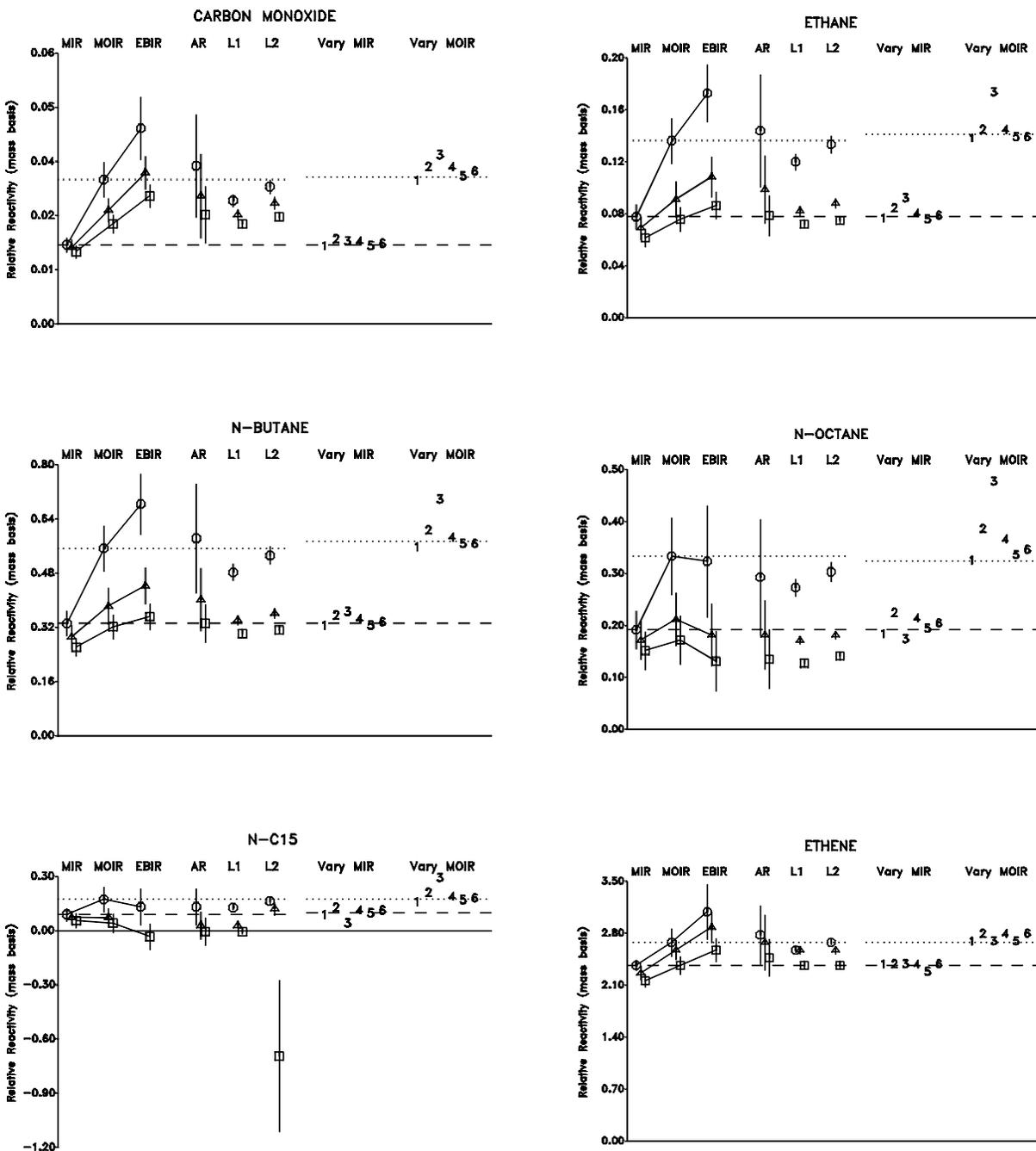


Figure 4. Comparison of relative reactivities of carbon monoxide, ethane, n-butane, n-octane, n-pentadecane, and ethene calculated using various methods. Points on right are ozone yield relative reactivities for the varied averaged conditions scenarios.

○ O3 Yield □ Int'd O3 △ Int'd O3 > 90 ppb
 1 No Oxygenates 2 Oxygenates x3 3 Aromatics x2
 4 Alkenes x2 5 No HONO 6 Aloff ROG x5

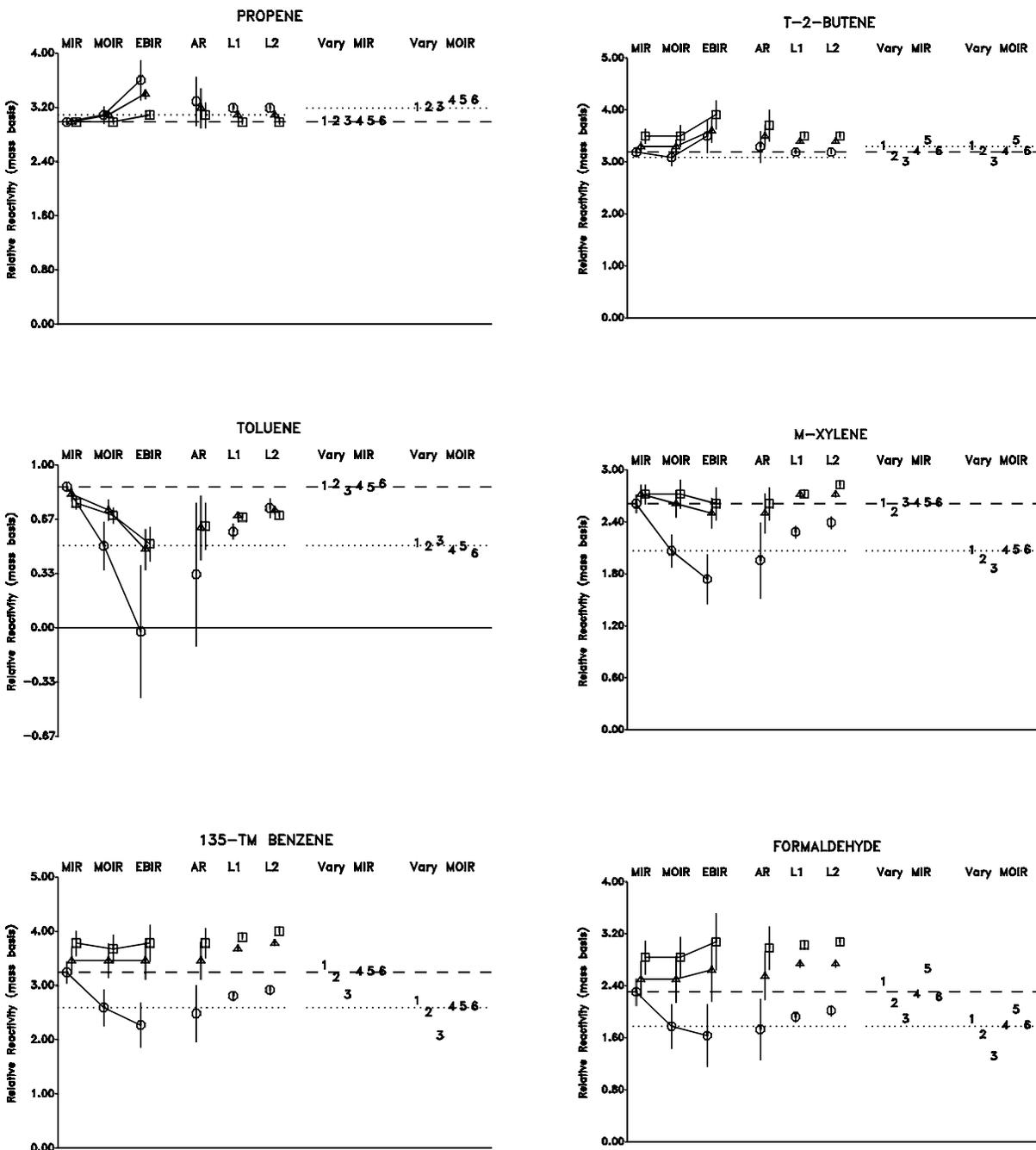


Figure 5. Comparison of relative reactivities of propene, trans-2-butene, toluene, m-xylene, 1,3,5-trimethylbenzene, and formaldehyde calculated using various methods. Points on right are ozone yield relative reactivities for the varied averaged conditions scenarios.

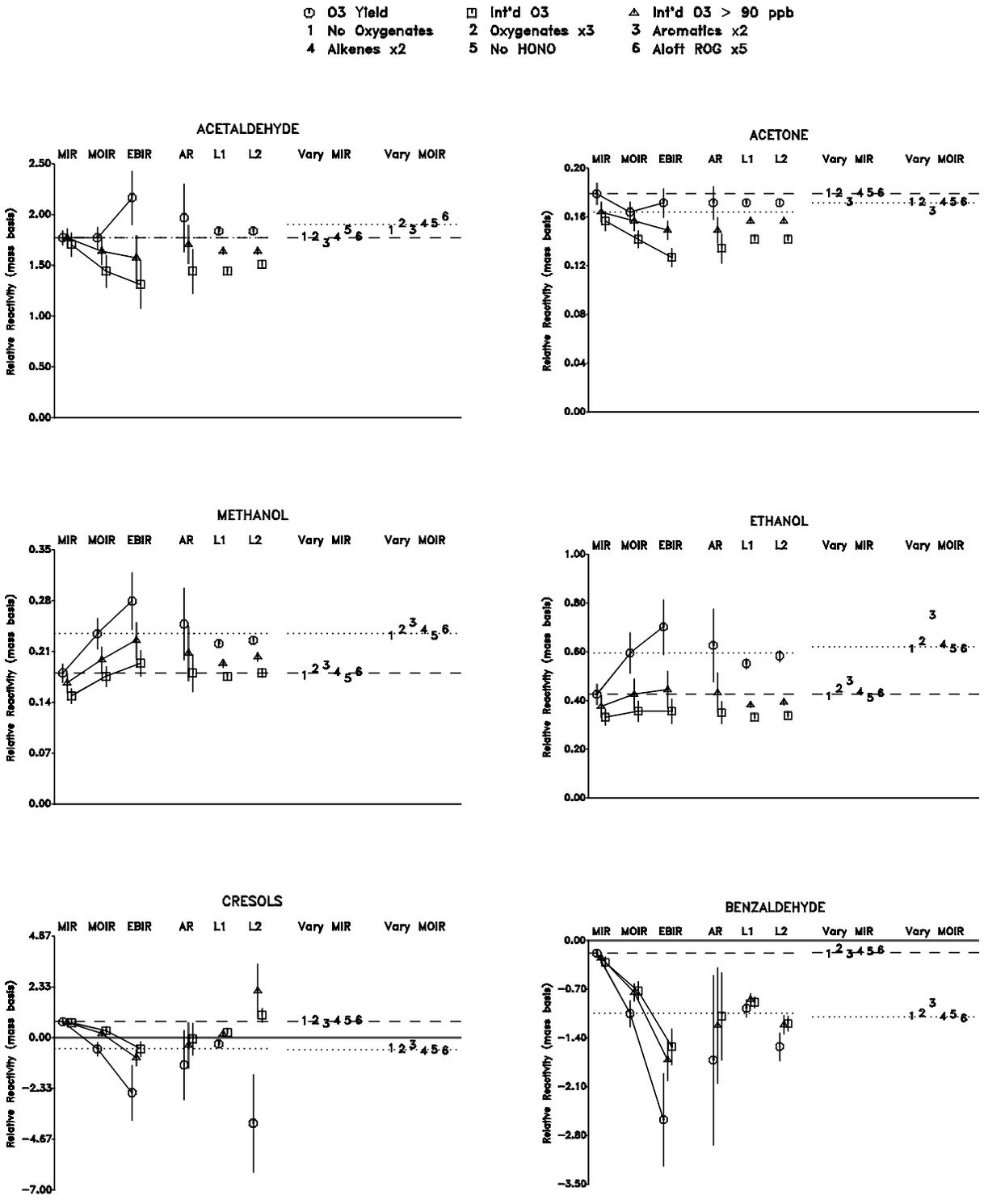


Figure 6. Comparison of relative reactivities of acetaldehyde, acetone, methanol, ethanol, cresols, and benzaldehyde calculated using various methods. Points on right are ozone yield relative reactivities for the varied averaged conditions scenarios.

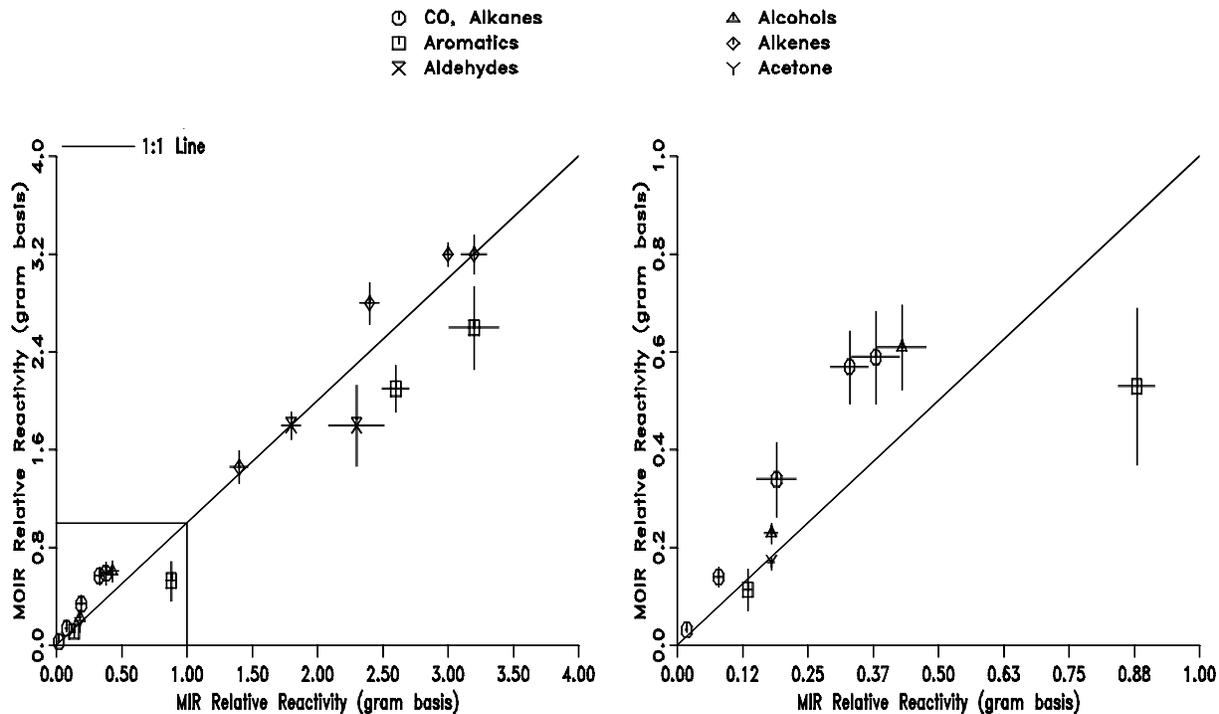


Figure 7. Plots of relative reactivities in the MOR scale against relative reactivities in the MIR scale for selected VOCs. The left plot shows the full range of relative reactivities, while the right plot has an expanded scale to show the less reactive VOCs more clearly.

The distribution plots on Figure 3 and the lengths of the error bars (the standard deviations) on Figures 4-6 provide an indication of how other scenario conditions affect relative reactivities. For most VOCs, the MIR relative reactivities are quite insensitive to scenario conditions, with the distributions shown on Figures 3 being fairly typical. In general, the sensitivities to scenario conditions increase as the NO_x decreases, with the most extreme cases being the compounds, such as toluene, cresols, and benzaldehyde, with the large NO_x sinks in their mechanisms.

Figure 7 shows the extent to which the relative reactivities of positively reactive compounds in the MIR and MOIR scales correspond to each other. Although these relative reactivities are clearly highly correlated, the MIR scale tends to underpredict the MOIR relative reactivities for CO, the alkanes and the alcohols, and overpredict them for the aromatics, on a fairly consistent basis. On the other hand, Figure 8 shows that, except for toluene, the MOIR and EBIR relative reactivities correspond very well. These

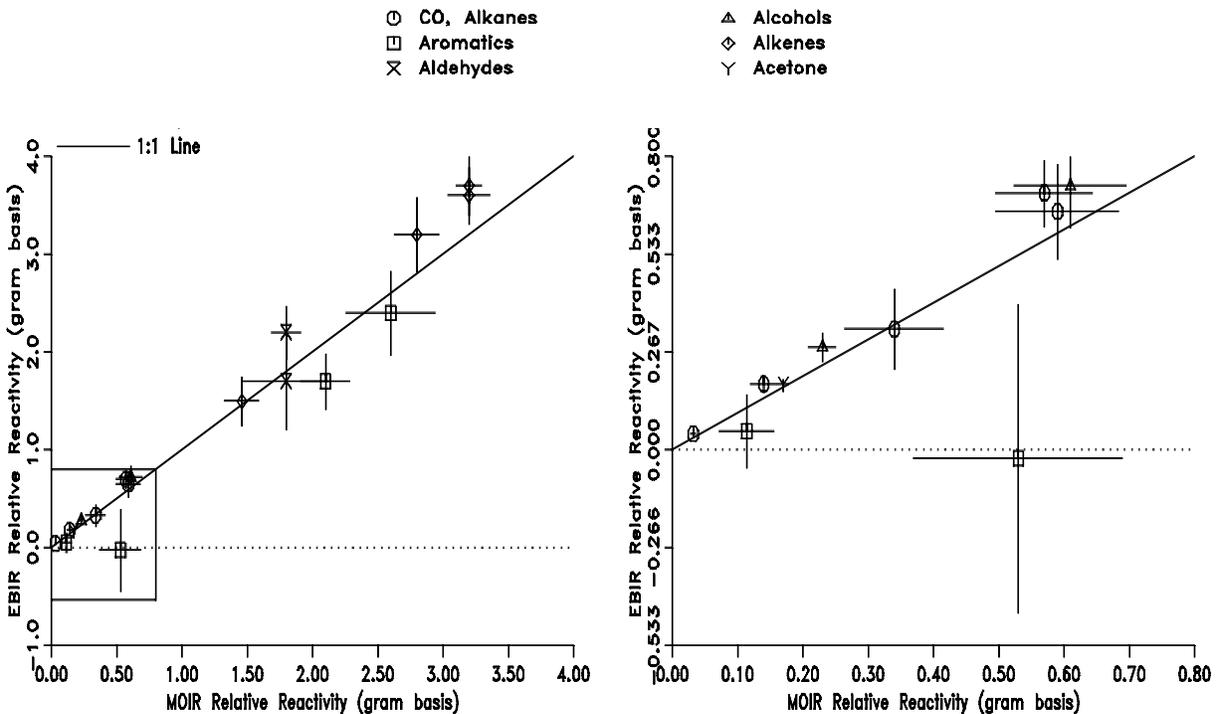


Figure 8. Plots of relative reactivities in the EBIR scale against relative reactivities in the MOIR scale for selected VOCs. The left plot shows the full range of relative reactivities, while the right plot has an expanded scale to show the less reactive VOCs more clearly.

two scales are essentially equivalent to within the uncertainties caused by variabilities in non- NO_x scenario conditions if one considers only compounds which are positively reactive in both scales. These two scales also agree in indicating that phenols and cresols are negatively reactive, while they are positively reactive in the MIR scale. However, the discrepancy in the MOIR and EBIR scales in the relative reactivities of toluene — and by extension the other monoalkylbenzenes, which the current mechanisms^{32,34,36} assume have similar reactivities as toluene — is not insignificant in view of the relatively large emissions of these compounds.

Ozone Yield Relative Reactivities — Base Case Scales. Figures 4-6 show the various base case ozone yield relative reactivities for the representative VOCs, where they can be compared with those for the adjusted NO_x scales. As before, the "error bars" show the standard deviations of the averages or derivations. The average ratio base case [Base (AR)] ozone yield reactivities have high standard

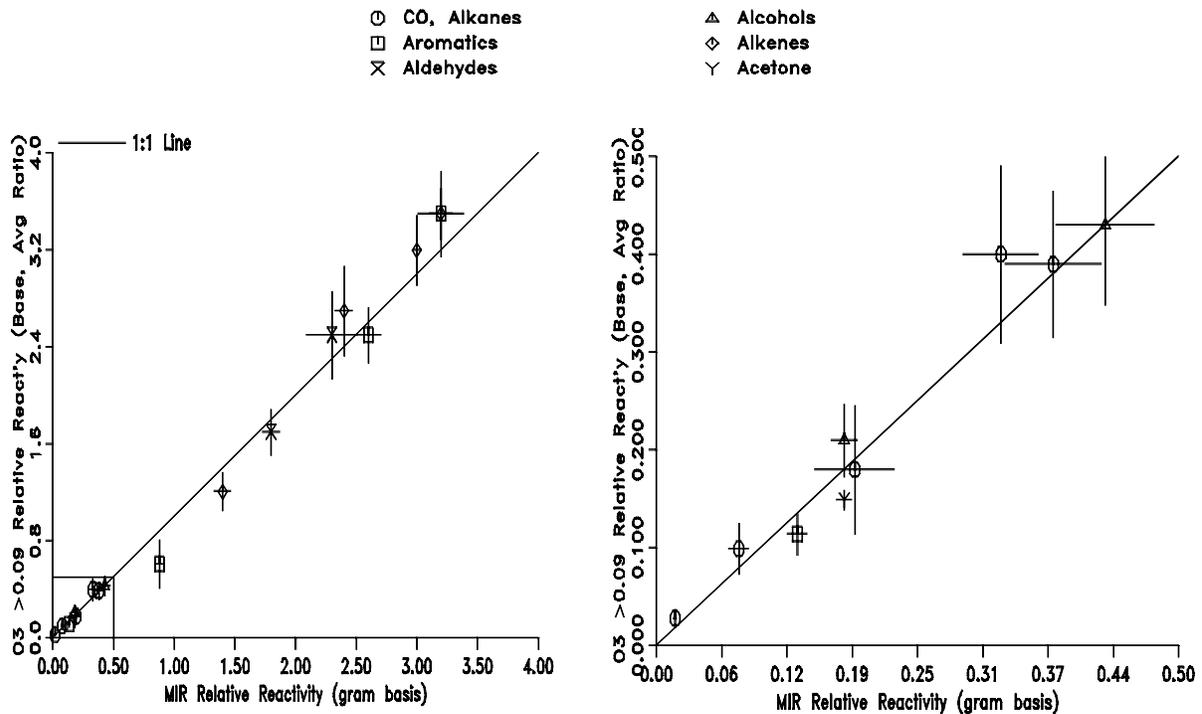


Figure 9. Plots of relative reactivities in the Base (L1), $\text{IntO}_3 > 90$ scale against relative reactivities in the MIR scale for selected VOCs. The left plot shows the full range of relative reactivities, while the right plot has an expanded scale to show the less reactive VOCs more clearly.

deviations because of the variation in relative reactivities in the scenarios due to the variation of NO_x conditions. In most cases the least squares error methods [Base (L1) and Base (L2)] give more well-defined values, having standard deviations which are comparable to or smaller than those for the adjusted NO_x scales. For most VOCs, the Base (L2) relative reactivities are essentially the same as the Base (L1) values. Thus, as one might expect, a reactivity optimized for assessing substitutions involving replacing current emissions with emissions of a less reactive VOC is essentially the same as one optimized for assessing substitutions of highly reactive VOCs for increased emissions of all ROGs.

There are a few apparently anomalous Base (L2) values which can be seen from the data for the cresols and n-pentadecane. These are cases when the incremental reactivities of the VOC are distributed around zero, when the method used to compute the Base (L2) reactivities is most sensitive to the most extreme values in the distribution. Because of the poor performance of this method in these cases, and

the fact that in most other cases it yields essentially the same result as the L1 method, it is concluded that the L1 method is the better method to derive least squares error relative reactivities.

In most cases, the relative reactivities in the Base (AR) case scale tend to fall between those in the MOIR and EBIR scale. This is as one would predict from the distribution of $\text{NO}_x/\text{NO}_x^{\text{MOR}}$ ratios in the base case scenarios. On the other hand, all of the Base (L1) and most of the Base (L2) relative reactivities lie somewhere between the MIR and MOIR values. More MIR-like values for the least squares error scales are expected because the method used to derive them puts more weight on reactivities in scenarios where ozone is more sensitive to VOCs, i.e., which are closer to MIR conditions. However, unlike the least squares error scale given in a previous study,¹¹ where the Base (L1) scale corresponded much better to the MIR scale than MOIR, in this case the Base (L1) reactivities are somewhat closer to the MOIR scale.

The reason for the differences between this result and those given previously¹¹ arises from the fact that the scenarios employed in the previous study represented a more varied set of NO_x conditions. This is apparent from the distribution plots of $\text{NO}_x/\text{NO}_x^{\text{MOR}}$ ratios on Figure 2, which include the distribution for the base scenarios from Gery et al.¹⁷ and Whitten³⁸ used in the previous¹¹ study ("base (1991)"), where they can be compared with distribution for the EPA scenarios used in this work. Although both sets have average $\text{NO}_x/\text{NO}_x^{\text{MOR}}$ ratios near the MOR range, the much wider distribution of NO_x conditions in the base (1991) set results in a larger fraction of scenarios which have near-MIR or higher-than-MIR NO_x conditions. Since reactivities in these high NO_x scenarios are weighed the most heavily in computing the least squares error scales, these scales are highly sensitive to the number of such scenarios in the distribution. In general, the wider the distribution of NO_x conditions in a set, the closer the least squares error reactivity scale derived from it will correspond to an MIR scale.

The appropriateness of base case reactivity scales from this work obviously depends on how well these EPA scenarios represent the distribution of conditions where ozone pollution episodes occur. It should be recognized that MIR conditions probably occur in the atmosphere much more frequently than represented by these EPA episodes. Each of these scenarios is based on the EPA's assessment of the conditions of a near-worst ozone episode in some area, and thus represents a meteorological condition which is near to the most favorable for ozone formation in that area. Thus most other days would have less favorable meteorological conditions for ozone, including many days when unacceptable ozone levels may still be formed. These would include days with lower rates of NO_x removal because lower temperatures or light intensities cause lower rates of photochemical reactions. Slower NO_x removal means

more NO_x availability, and thus more MIR-like conditions. Since, as shown on Figure 2, ozone can still exceed air quality standards under MIR conditions, such meteorological conditions, while not worst case, are not irrelevant to the problem of urban ozone formation. If these conditions were represented in a more comprehensive set of scenarios, the resulting least squares error scales would correspond much more closely to the MIR scale than observed in this work.

Integrated Ozone and $\text{IntO}_3 > 90$ Relative Reactivities. Figures 4-6 show relative reactivities derived from the effects of the selected VOCs on integrated ozone concentrations (the IntO_3 scales) and from the effects of the VOCs on integrated ozone above 90 ppb ($\text{IntO}_3 > 90$), where they can be compared with the ozone yield reactivities discussed above. The IntO_3 , $\text{IntO}_3 > 90$, and ozone yield relative reactivities tend to agree well under MIR conditions, but then they tend to diverge as NO_x is reduced, with the IntO_3 and $\text{IntO}_3 > 90$ values changing less as NO_x is reduced than is the case for ozone yield values. In the cases of a number of the most reactive compounds, such as formaldehyde, m-xylene and trimethylbenzene, the IntO_3 relative reactivities are essentially independent of NO_x , despite the fact that the NO_x dependencies in the ozone yield relative reactivities are significant. The IntO_3 relative reactivities of most other compounds show the same trend with NO_x as the O_3 yield reactivities, except that the change with NO_x is less extreme. This lower sensitivity of IntO_3 reactivities to NO_x means that they are less variable in the base case scenarios. Because of this, the base case relative IntO_3 reactivities are less sensitive to the method used to derive them, except for the few anomalous Base (L2) cases discussed above.

The reason this lower sensitivity of IntO_3 relative reactivities to NO_x — and their tendency to correspond to MIR relative reactivities — is that integrated ozone levels are sensitive to the same mechanistic factors which determine ozone yields under high NO_x , MIR conditions. These are the factors which affect how rapidly O_3 is formed, as opposed to those which affect the ultimate O_3 yield when NO_x is limited. In a high NO_x scenario, both the ozone yield and the integrated ozone would be determined by how rapidly O_3 is formed. In a lower NO_x scenario, the integrated ozone would still be sensitive to the ozone formation rate, but if the O_3 is NO_x limited the maximum ozone yield is more sensitive to the NO_x availability than the ozone formation rate. While NO_x availability has some influence on integrated ozone under low NO_x conditions, it tends to be less important a factor than the amount of time that the highest levels of ozone were present in the scenario. Thus, since IntO_3 reactivities and MIR reactivities are both sensitive to the same aspects of the VOCs' mechanisms, the relative reactivities tend to correspond to each other. NO_x sinks in the VOCs' mechanisms, which become the dominant factor affecting MOIR and EBIR reactivities, are only of secondary importance in affecting IntO_3 reactivities.

One would expect the $\text{IntO}_3>90$ reactivity scales to have characteristics somewhere between those for the IntO_3 and the ozone yield scales, and this is indeed what is observed. However, the $\text{IntO}_3>90$ scales are closer to IntO_3 scales than the ozone yield scales, and all the discussion above for the IntO_3 scales are applicable to $\text{IntO}_3>90$. There are a few cases, such as formaldehyde, trimethylbenzenes, and (to a lesser extent) acetone, ethanol, and methanol, where there is a non-negligible difference between the ozone yield and the integrated ozone reactivities under maximum reactivity conditions. In those cases, the $\text{IntO}_3>90$ reactivities tend to be closer to the MIR reactivities.

Because of this, MIR reactivities tend to give very good predictions of $\text{IntO}_3>90$ reactivities in the base case scenarios. This is shown on Figure 9, which gives plots of base case $\text{IntO}_3>90$ relative reactivities computed using the average ratio method against the values predicted by the MIR scale for selected representative positively reactive VOCs. It can be seen that agreement to within the standard deviations are attained for all but two VOCs, and for those the agreement is within 1.5 standard deviations. This is much better than the correspondence of the base case $\text{IntO}_3>90$ reactivities with the MOIR or EBIR scales.

Effects of Variations of Other Scenario Conditions

The comparisons of reactivities in the adjusted NO_x scenarios provide direct information on their dependencies on NO_x availabilities, and also, through the standard deviations of the averages, provide indirect information on the importance of other conditions which were variable in the scenarios. However, the composition of the base ROG mixture, the level and compositions of ROG aloft, and the initial nitrous acid (HONO) as a fraction of the NO_x inputs were held fixed in all these scenarios, and thus these data provide no information on the sensitivities of reactivities to these inputs. To assess this, modified versions of the averaged conditions scenario were derived by varying these inputs as described below, then the NO_x inputs for each version were adjusted to derive corresponding MIR or MOR scenarios, and then these were used to assess how these variations affect the MIR and MOIR reactivities. Sensitivities of EBIR reactivities to scenario conditions are not discussed here, but they were generally found to be similar to, though often greater than, those for MOIR reactivities.

Four different modifications of the composition of the base ROG were examined, all involving relatively large changes to this mixture. These involved only changes to the ROG associated with anthropogenic emissions, a fraction of which (~60%) were present initially and the remainder emitted

throughout the day. The compositions and amounts of aloft and biogenic ROGs input were not varied. The variations, and the code numbers used to designate them, are as follows: (1) "No Oxygenates": The aldehydes and ketones were removed without modifying the levels of the other components. (2) "Oxygenates x3": The aldehydes and ketones were increased by a factor of 3 without modifying the levels of the other components. (3) "Aromatics x2": The aromatics were increased by a factor of 2, and the alkanes and olefins reduced to keep the total carbon the same. (4) "Alkenes x2": The olefins were increased by a factor of 2 and the alkanes and aromatics reduced to keep the total carbon the same.

One of the changes made to the EPA scenarios was assuming that ~2% of the initial and 0.1% of the emitted NO_x was in the form of nitrous acid (HONO), which is a powerful photoinitiator which could help initiate the photochemical processes early in the day. The EPA scenarios as received from Baugues,⁴⁰ and the scenarios used previously,¹¹ assumed no initial or emitted HONO. The (5) "No HONO" modification, where the initial nitrous acid (HONO) was assumed to be zero and no HONO was subsequently emitted, was used to assess the effect of this change.

The scenarios as received from Baugues all assumed a standard 30 ppb of VOCs aloft, and the same chemical composition was used for this aloft mixture in all scenarios. The (6) "Aloft ROGs x5" modification, where the concentrations of all ROGs aloft were increased by a factor of 5, was used to assess how important aloft ROGs are in affecting reactivity calculations in these scenarios.

The MIR and MOIR relative reactivities calculated using these modified scenarios are shown for the representative VOCs on the right hand side of the plots on Figures 4-6, where they can be compared with the values for the corresponding averaged conditions scenario. The relative reactivities in the varied scenarios are indicated by the code numbers on the plots, while the standard, or averaged conditions, values are indicated by the dashed (for MIR) or dotted (for MOIR) lines.

The data on Figures 4-6 show that these relatively large variations in the base ROG mixture had in most cases had only small effects on the relative reactivities. The variation which had the largest effect was the increase in the aromatics ("3" on the plots), whose twofold increase, for example, caused a ~19% decrease in the relative MIR reactivity of formaldehyde. Removing the oxygenates from the base ROG ("1") increased the relative MIR reactivity of formaldehyde by ~7%. The effects of these variations on the other VOCs were generally smaller.

The removal of initial and emitted HONO from the scenarios ("5") had almost no effect on any of the results except for formaldehyde, whose MIR and MOIR relative reactivities increased by ~15%, and whose integrated ozone relative reactivities (not shown) increased by ~20%. This is a large sensitivity in view of the almost complete insensitivities of the other results to initial HONO. Since both HONO and formaldehyde provide early radical sources in the simulations, this shows that removing one such radical source increases the sensitivity of the scenarios to the other.

The fact that these scenarios have initial HONO while those given previously¹¹ do not might partly explain why the formaldehyde reactivity in these scenarios is less sensitive to changes in aldehyde emissions than calculated previously. In the absence of the initial HONO, we calculate that the relative reactivity of formaldehyde increases by ~11% when the base ROG oxygenates are removed. (This is not shown on the plots.) This is greater than the ~7% effect observed when the HONO is present, and indicates that adding radical initiators such as HONO to the scenario reduces the sensitivity of formaldehyde reactivities on initial aldehydes.

The fivefold increase in the aloft ROGs was found to have an insignificant effect on the relative reactivity results. In view of this, the sensitivity to the composition of the aloft ROG mixture would also be expected to be small.

Examples of Exhaust Reactivity Adjustment Factors

An example of a regulatory application of a reactivity scale is the utilization of reactivity adjustment factors (RAFTs) in the alternative fuel vehicle exhaust standards recently adopted in California.¹² The mass emissions of exhausts from alternatively-fueled vehicles are multiplied by these RAFTs to place them on the same ozone impact basis as emissions from vehicles using conventional gasoline. The RAFTs are calculated from the ratios of incremental reactivities (as ozone per gram) for the exhaust mixtures from alternative-fueled vehicles, relative to that for a mixture characteristic of exhaust from vehicles using industry-average gasoline. The regulations as adopted utilize the MIR scale to calculate these RAFTs,¹³ but it is of interest to see how these would differ if other scales were used. This is shown on Figure 10, which gives RAFTs for selected vehicle exhaust mixtures calculated using the various reactivity scales. The example mixtures, which are based on analysis provided by the CARB,¹³ include exhausts from vehicles fueled with 85% methanol + 15% gasoline (M85), compressed natural gas (CNG), liquified petroleum gas

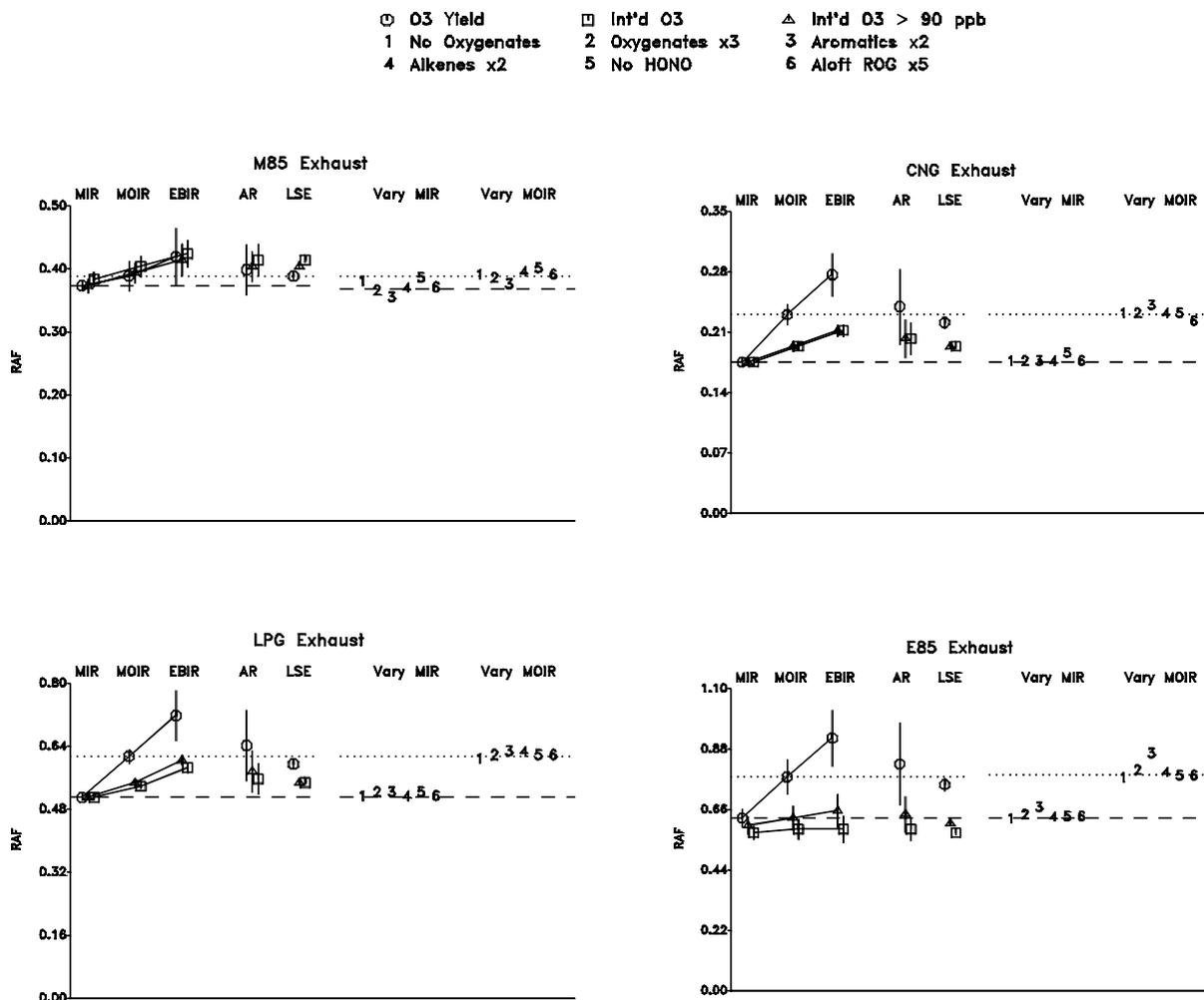


Figure 10. Comparisons of Reactivity Adjustment Factors for selected vehicle exhaust mixtures calculated using various methods. Points on right are calculated from ozone yield RAFs for the varied averaged conditions scenarios.

(LPG), and 85% ethanol + 15% gasoline (E85). The RAFs are calculated relative to the standard exhaust mixture used by the CARB.¹³

The format for the data on Figure 10 is similar to that on Figures 4-6. The MIR, MOIR, EBIR and Base (AR) RAF's are the averages of the RAFs for the individual adjusted NO_x or base case scenarios, calculated from ozone yield, IntO₃ and IntO₃>90 incremental reactivities. The least squares error (LSE) RAF's shown are those which give the least squares error in ozone yield, integrated O₃, or integrated O₃>90 ppb in the null tests where the alternative fuel exhaust is substituted for the standard exhaust.

This is analogous to the Base (L2) method except that the reactivity of the standard exhaust is used in place of that for the base ROG. The points under "Vary MIR" and "Vary MOIR" show the effects of varying the various scenario conditions on the MIR or MOIR RAFs, as discussed in the previous section.

For all four exhausts shown, the RAFs tend to increase with decreasing NO_x conditions, except that the integrated O_3 RAFs for E85 are almost independent of NO_x . The M85 RAF is least sensitive to the scale used, but is somewhat unique in that the integrated ozone and ozone yield RAFs have about the same dependence on NO_x . The RAFs for the other mixtures are more typical of relative reactivities in general in that the integrated O_3 RAFs are less sensitive to NO_x than ozone yield values. The fact that the MIR scale predicts the lowest RAF in all cases (except E85) may suggest to some that the MIR has a bias towards giving undue credits to alternative fuels. This increase in RAF with decreasing NO_x is due to the fact that most alternative exhausts have more slowly reacting compounds whose reactivities are affected by the lower radical levels in MIR scenarios, and by the fact that the alternative exhausts tend to have less species with strong NO_x sinks (e.g., aromatics) than the standard exhausts. However, regardless of this variability, the range of RAFs do not overlap unity except for E85, which overlaps unity only in some extremely NO_x -limited scenarios.

The points on the right hand side of the plots show that the variations in the base ROG mixture, the removal of initial HONO, and the increase in aloft ROGs will not significantly affect the RAFs in these cases. Thus the main issue in affecting RAFs do not relate to these uncertainties, but to what type of scale is most appropriate.

It should be noted that calculating reactivity adjustment factors for exhausts is not the only regulatory application where a reactivity scale might be useful⁴¹. However, this is the only regulation where such a scale has been applied to date. The results of this study should aid in assessing the appropriateness of reactivity scales in other regulatory contexts.

Discussion of Issues and Research Needs

A quantitative reactivity scale which compares the effects of different types of VOCs on ozone formation could be useful for a number of ozone control strategy applications. However, the development of such a scale has a number of difficulties. These can be categorized into three major areas. The first is that the gas-phase chemical mechanisms by which VOCs react in the atmosphere to form ozone are in

many cases highly uncertain. This results in uncertainties in the model predictions of the reactivity of a VOC in any given scenario. The second is that the effects of VOCs on ozone formation — their reactivities — depend on the environment in which they are emitted. This means that even if we are capable of reliably predicting the reactivity of a set of VOCs in a set of scenarios, it is not obvious how these results should be used in developing a single reactivity scale — or even whether a use of a single reactivity scale has any validity. The third is that there are uncertainties in conditions of airsheds and episodes where unacceptable levels of ozone are formed. The uncertainties in conditions of a specific episode affect predictions of VOC reactivities for that episode, and uncertainties in distribution of conditions affect the development of appropriate methods for aggregating scenario-specific reactivities into a generalized reactivity scale.

The focus of this paper has been on the second of these problems, that of deriving a reactivity scale given that reactivities depend on environmental conditions. This has been studied by deriving reactivity scales using several different techniques, given a single chemical mechanism and a single set of representative airshed scenarios. The chemical mechanism employed is uncertain for many VOCs, but it incorporates our current best estimate of their atmospheric reactions, and represents most of the major types of species which need to be incorporated in reactivity scales. The representative environmental scenarios employed are even more uncertain, but they represent their developers' best estimate of the conditions of a wide variety of representative pollution episodes given the limitations in available data and the constraints of the simplified physical formulation of the model used. This is sufficient at least for evaluating methods for deriving reactivity scales.

Consistent with results of previous studies, it was found that the NO_x conditions can significantly affect relative as well as absolute reactivities. In addition, it was also found that relative reactivities can depend on how ozone impacts are quantified, especially under low NO_x conditions. Because of this, different reactivity scales give different reactivity rankings for VOCs and in a few cases different orderings of VOCs in these rankings. However, in most cases the qualitative rankings among the different scales are very similar, and the quantitative differences between them are small compared to the full range of reactivities of those VOCs which are now regulated as ozone precursors. The results of this study do not support the conclusion that reactivities are so strongly dependent on scenario conditions that all VOCs can be considered to be equal to within this variability. Therefore, use of some appropriate type of scale will yield more a more efficient ozone control strategy than regulating all VOCs equally. The more difficult issue is what is the optimum type of scale to use for this purpose.

Although a total of 18 different scales based on various NO_x conditions and methods for quantifying ozone were derived, essentially the choice is between scales which are sensitive to effects of VOCs on how rapidly ozone is formed and scales which are sensitive to effects of VOCs on the maximum amount of ozone which is formed when ozone is NO_x -limited. Scales in the first category are the MIR and the various integrated ozone scales, scales in the second category are the MOIR, EBIR and the average ratio base case ozone yield scales. (Least squares error base case ozone yield scales are in the first category if the base case scenarios represent a varied set of NO_x conditions, but are intermediate between the two if they represent only near-worst-case conditions.) Although there are arguments for each type of scale, it is concluded that if only one scale can be used, a scale like MIR is more appropriate²⁰. While the MOIR and scales like it are most effective at addressing peak ozone levels under conditions which are the most favorable for ozone formation, the scales like MIR it are more optimal when applied to the wide variety of conditions where ozone is sensitive to VOCs, or when one is concerned with reducing exposure to integrated ozone or ozone over the air quality standard.

Although these conclusions are based on reactivities calculated for highly simplified single day scenarios whose accuracies are unknown, the scenarios employed are sufficiently varied that it is not unreasonable to expect that similar results would be obtained if a more detailed and accurate scenarios were employed. This is supported by the results of Russell and co-workers,^{30,41} who calculated integrated ozone reactivities using a much more complex physical model,^{42,43} and obtained results which corresponded very closely to the MIR and integrated ozone scales calculated in this work. The calculations of Russell and co-workers^{30,41} also increased the level of confidence in the validity of the reactivity scale derivation because they showed that a detailed physical model^{42,43} with condensed chemistry⁴⁴ can give essentially the same reactivity scale as a simplified physical model with detailed chemistry. However, it is clear that further work is needed to develop and utilize a more comprehensive and physically realistic set of scenarios for VOC reactivity assessment. All the scenarios used in this work represented the reactions of the VOCs only over a single day, and scenarios involving multi-day episodes and regional models are needed to assess the total impact of VOCs on ozone over their lifetimes. The work of Russell and co-workers^{30,41} is an important start in this regard, but these results need to be further evaluated using physically detailed models of other areas, and using regional models which can assess the impacts of VOCs over longer time periods and in long range transport scenarios.

It should be recognized that regardless of which approach or set of airshed conditions is used for developing a reactivity scale, model calculations of VOC reactivities are no more reliable than the chemical mechanism used to calculate them. Modeling studies may give us an indication of the

magnitudes of the effects of these uncertainties, but will not reduce them. To reduce these uncertainties, experimental data are needed to test the mechanisms used to derive the reactivity factors, or at a minimum to test their predictions of maximum reactivity. Such experiments are underway in our laboratories.¹⁰

Conclusions

Practical implementation of ozone control strategies which take into account differences among VOCs in their effects on ozone require use of some quantitative reactivity ranking scheme. Use of incremental reactivity, or more particularly ratios of incremental reactivities or relative reactivities, is an appropriate means to do this. However, relative reactivities can vary depending on environmental conditions, how ozone impacts are quantified, and on what approaches are used to derive single scales from reactivities under a variety of conditions. Although these variations can in some cases be significant, in most cases they are smaller than the ranges of reactivity among non-exempt VOCs. Thus, despite the variabilities, use of any appropriate reactivity ranking scheme would yield a more efficient ozone control strategy than ignoring reactivity altogether.

The availability of NO_x in the environment is the most important single factor affecting reactivity rankings. This is often measured by the ROG/NO_x ratio, though this is not always a good predictor of reactivity characteristics because of variability of factors affecting rates of NO_x removal. The ratio of NO_x to NO_x levels giving maximum ozone concentrations is a better measure of this. Variations in the composition of the base ROG mixture, the amount of initial HONO , and level of aloft VOCs are relatively unimportant in affecting reactivity when compared to the NO_x effect. However, the effect of NO_x is less when ozone impacts are quantified by integrated ozone concentrations, or by integrated ozone above air quality standards, than is the case when ozone is quantified by peak ozone concentrations or ozone yields. Under high NO_x conditions where VOCs have their greatest effect on ozone, which is the basis for deriving the Maximum Incremental Reactivity (MIR) scale, the relative reactivities are not strongly affected by how ozone is quantified, and are also relatively insensitive to other scenario conditions. Under lower NO_x conditions, relative reactivities tend to become more sensitive to other scenario conditions, and tend to differ depending on how ozone is quantified.

Thus the MIR scale is relatively well defined in the sense that it is fairly insensitive to the choices of scenarios used to derive it, and in most cases it gives a reasonably good approximations to scales based on integrated ozone under lower NO_x conditions. The MOIR scale gives better predictions of effects of

VOCs on peak ozone yields in base case scenarios, but gave poor predictions of effects on integrated ozone or integrated ozone above the standard. It is also more sensitive to the set of scenarios used to derive it. Based on these considerations, and the fact that the MIR scale is based on environmental conditions where VOC control is most important for affecting ozone, we conclude that the MIR scale (or a scale similar to it, such as one based on integrated ozone over the standard) is appropriate for regulatory applications which a reactivity scale is required. Airshed model calculations using a much more detailed physical scenario (but a simpler chemical mechanism) lead to similar conclusions^{30,41}.

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