STATUS OF RESEARCH ON VOC REACTIVITY IN THE UNITED STATES

by

William P. L. Carter

Statewide Air Pollution Research Center and
College of Engineering, Center for Environmental Research and Technology
University of California
Riverside, CA 92521

For Presentation at the
Fifth US-German Workshop on the Photochemical Ozone Problem and its Control
Berlin, Germany
September 24-27, 1996

Abstract

An overview of VOC reactivity with respect to ground level ozone formation, and the mechanistic and environmental factors affecting it, are discussed. Methods of quantifying reactivity are described, and the roles of chemical mechanisms and environmental chamber data in reactivity quantification are discussed. A brief summary of ongoing reactivity-related research is presented, which can be classified as basic kinetic and mechanistic studies, environmental chamber studies, and chemical mechanism development. The current status of the reactivity-related environmental chamber and mechanism development research being carried out by the author is summarized, and illustrative examples of recent research results are presented. The development of an updated SAPRC mechanism for VOC reactivity assessment calculations is summarized.

1

VOC Reactivity

Tropospheric ozone is formed from the gas-phase reactions of oxides of nitrogen (NO_x) in the presence of volatile organic compounds (VOCs). Although NO_x is required for ozone formation in the lower troposphere, and is the major limiting factor affecting the ultimate amount of ozone formed given sufficient reaction time), VOCs affect the rate of ozone formation from NO_x, and is believed to a major factor affecting ozone levels in most U.S. urban areas where exceedence of the ozone air quality standard is a problem. Because of this, control of emissions of VOCs has been, and will continue to be, one of the focal points of U.S. regulatory policy to reduce tropospheric ozone.

In developing effective strategies for VOC control to reduce ozone, it is important to recognize that not all VOCs are equal in their effects on ozone formation. First, VOCs can differ significantly in how rapidly they react in the atmosphere. Clearly if they do not react at all they cannot contribute to ozone, and if they react so slowly that the air mass is highly diluted or the NO_x is consumed before a significant portion reacts, then their contribution will be minimal. However, experimental (e.g., Carter and Atkinson, 1987; Carter et al, 1993a, 1995a) and modeling (e.g., Dodge, 1984; Carter and Atkinson, 1989a; Carter, 1994) studies have shown that other mechanistic factors are also significant, and become the dominant factor affecting reactivity differences among rapidly reacting VOCs. These include not only how much O_3 is formed from the VOC's direct reactions and those of its major oxidation products, but also the effects of the VOCs reactions (and those of its products) on overall radical levels and on rates of NO_x removal. The effects on radical levels can be a major factor since it influences the rates of O_3 formation caused by the reactions of all other VOCs present. Indeed, if a VOC has a sufficiently large effect in inhibiting radical levels, its emissions would result in less O_3 formation than would be the case were it not emitted, even if its direct reactions caused O_3 formation. In addition, if a VOC is unusually reactive, it is almost always because its reactions have large, positive effects on radicals. Finally, if the reactions of a VOC tend to increase the rates of NO_x removal from the system (such as by forming relatively stable organic nitrate products), it will have an inhibiting effect on ozone formation when NO_x levels are low and ozone formation is NO_x limited.

The nature of the environment where the VOC reacts is also a major factor affecting a VOC's impact on ozone formation. The availability of NO_x is perhaps the most important factor. Since NO_x is required for O_3 formation, if NO_x were absent then no O_3 could be formed regardless of the VOC emissions, i.e., all VOCs would have an ozone reactivity if zero. On the other hand, if NO_x levels are relatively high then ozone sensitive to VOC, which means that all VOCs have much higher O_3 impacts. Indeed, the NO_x levels where VOCs have the highest ozone impact in terms of amount of additional ozone formed per amount of VOC added to the emissions is higher than the NO_x, i.e., where VOCs have their "maximum reactivity", is higher than the NO_x level which is most favorable for ozone formation.

2

Other environmental factors, such as light intensity, temperature, amount of dilution, and nature of the other VOCs present will also affect a VOC's ozone impact for various reasons. The most important would be those affecting the rate of removal of NO_x, which would determine the extent to which ozone formation were NO_x limited or VOC limited. In addition, the radical levels or amounts of radical sources in the environment (such as the relative levels of radical initiators such as formaldehyde or aged pollutants entrained from aloft or the background) will be important in determining how sensitive O_3 formation is to the emissions of other radical initiating VOCs. For example, the relative reactivity of a radical initiating VOC such as formaldehyde would be less in an environment with abundant radical initiators from other sources than in an environment poor is such sources, even if differences in relative NO_x levels were factored out. Radical levels and the duration of the ozone pollution episode are also important in affecting ozone impacts of slowly reacting species, since the higher the radical levels or the greater the duration of the episode, the more of the slowly reacting will react to contribute to O_3 formation.

From the perspective of developing ozone control strategies which take VOC reactivity into account, it is *ratios* of reactivities among different VOCs which is more important than absolute ozone impacts. Environmental conditions also affect ratios of reactivities because the relative importances of the various aspects of aspects VOC reaction mechanisms are different under differing conditions. For example, aspects of a mechanism affecting rates of NO_x removal have no effect on a VOCs ozone impact in environments where NO_x is abundant, but become a major factor when NO_x is limited. Also radical initiating or inhibiting effects are relatively more important when NO_x is abundant because under those conditions ozone levels are primarily determined by its formation rate. For this reason, relative reactivities of aromatics, which form radical initiating products but also have strong NO_x sinks in their mechanisms, have much lower reactivities relative to other VOCs under NO_x-limited conditions than when NO_x is abundant. Also, differences in ozone impacts of slowly reacting VOCs compared to more rapidly reacting compounds becomes less if radical levels or the duration of the episode increases.

Reactivity Scales

A reactivity scale is any scheme which assigns numbers to a VOC in some manner that is intended to relate to its ozone impact. One relatively simple but still useful scale which has been proposed a number of years ago, and has been used in observational analyses of relative roles of different VOCs from ambient air monitoring (Chameides, et. al., 1988) is the OH radical rate constant, or kOH scale. This gives a measurement of how rapidly a VOC reacts in the atmosphere, since for many VOCs reaction with OH radicals is the only important atmospheric loss process, and other VOCs with other loss processes (such as alkenes or aldehydes) also have high OH radical rate constants. This has the obvious advantages of simplicity since it is known or can be estimated for most VOCs, and is not dependent on environmental conditions. It is also a good predictor of relative ozone impacts for very slowly reacting VOCs, and can be used as a means for estimating upper limit ozone impacts for the purpose of determining VOC exemption on the basis of "negligible" reactivity. However, because of the other mechanistic factors

discussed above, it is a poor predictor of relative ozone impacts for rapidly reacting VOCs, or for comparing ozone impacts of VOCs with similar OH radical rate constants.

From a regulatory perspective, the relevant measure of ozone impact (or reactivity) is the actual change in ozone formation caused by changing emissions of the VOC. This can be measured by *incremental reactivity*, which is defied as the change in ozone formation caused by the addition of a small amount of a VOC to the emissions in an ozone pollution scenario, divided by the amount added (Carter and Atkinson, 1989a). An alternative measure is what Derwent and Co-workers (e.g., Derwent and Jenkin, 1991) termed *Photochemical Ozone Creation Potential* (POCP), which is defined as the change in mid-day ozone caused by removing a VOC from the emissions, divided by the amount emitted. Although the incremental reactivity concept has the advantage of being independent (to a first order approximation at least) of the amount of test VOC emitted (being mathematically equivalent to a derivative), incremental reactivities and POCP measure essentially the same thing, the actual change in O_3 caused by changing the VOC emissions by a given amount.

Note that incremental reactivity (or POCP) is *not* the same as what Bowman and Seinfeld (1994a,b) call "ozone productivity" or what Jeffries and co-workers call "contribution to ozone". The latter measure the amount of ozone formation directly attributable to the radicals formed from the reactions of the VOC and its reaction products. As such, this does not take into account the facts that, as discussed above, reactions of some VOCs enhance or inhibit radical levels, thus affecting how much all the other VOCs react, or enhance the rate of NO_x removal, thus affecting the efficiency of O_3 formation from all the other VOCs. These effects of VOCs on the amounts of ozone formed (or "productivity") of the other VOCs are not taken into account by this analysis, but are taken into account in derivations of incremental reactivity or POCP.

The main problems with incremental reactivity (or POCP) scales are that they depend on environmental conditions, and that they must be calculated using computer airshed models and chemical mechanisms, which have uncertainties. The dependence on environmental conditions was assessed by Carter (1994), who derived a number of different scales representing differing environmental conditions, as well as using different methods for quantifying ozone impacts. In terms of NO_x effects, the major Carter (1994) scales are the *Maximum Incremental Reactivity* (MIR) scale, which represents relatively high NO_x conditions which where O_3 is most sensitive to VOC emissions, and the *Maximum Ozone Incremental Reactivity* (MOIR) scale, which represents the lower NO_x conditions which are most favorable for peak ozone formation.

Figure 1 shows a comparison of incremental reactivities in the MIR and MOIR scales calculated by Carter (1994) and the averages of the POCP scales calculated by Harwell mechanism (Derwent and
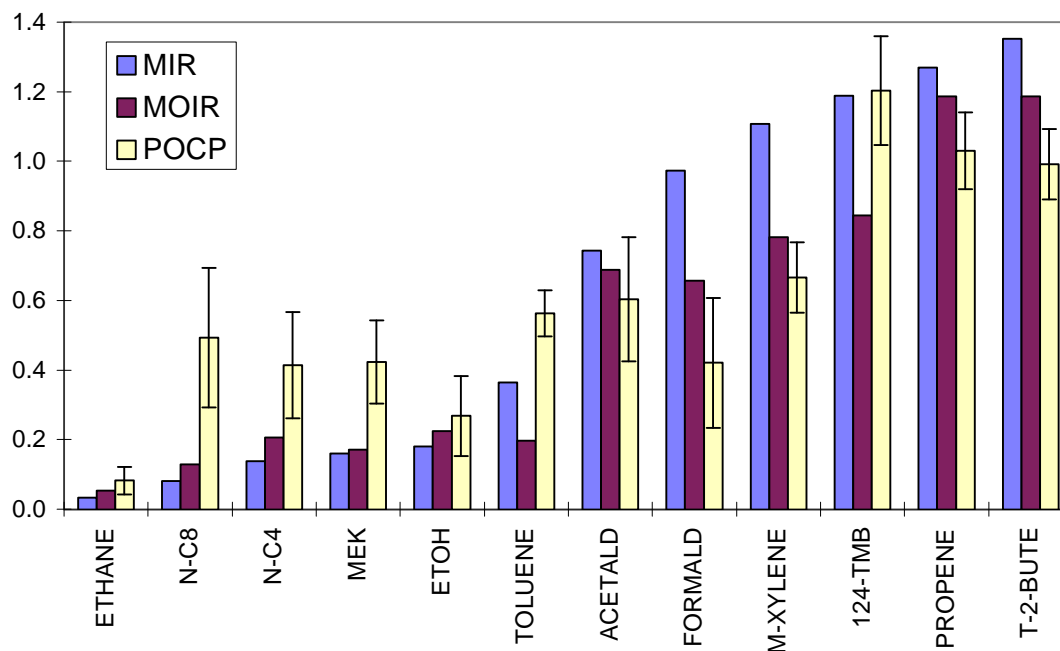
Figure 1.   Comparison of MIR, MOIR, and POCP Reactivities relative to Ethane. [Reactivities are
             given as ozone formed per unit mass VOC emitted. MIR and MOIR reactivities from
             Carter (1994). POCP reactivities are from Derwent and Jenkin (1991). Error bars on the
             POCP reactivities show standard deviations of the averages for different scenarios or days.

Hov, 1979). The MIR and MOIR scales were calculated using the using the SAPRC-90 chemical mechanism (Carter, 1994) and one-day EKMA scenarios derived by the EPA to represent various urban areas around the United States (Baugues 1990), with NO_x inputs adjusted to yield either maximum incremental reactivities of VOCs (for MIR) or maximum ozone yields (for MOIR). The POCP scales were calculated using the Harwell mechanism for scenarios representing multi-day trajectories across Europe (Derwent and Jenkin, 1991). All scales are normalized to ethylene, which was chosen because this was how the POCP results were presented. The results show reasonably fair correlation between relative MIR and MOIR reactivities, except that the aromatics have lower relative MOIR reactivities because the NO_x sinks in their mechanisms are important in reducing reactivities in the lower NO_x MOIR conditions, and formaldehyde has lower MOIR reactivity because radical initiation is relatively more important in the higher NO_x MIR scenarios. Generally the two scales give reasonably good agreement in reactivity rankings, which is the most important factor to consider from a regulatory perspective.

The agreement between the POCP and the Carter (1994) scales is not quite as good. However, the greatest discrepancies, the higher alkanes and MEK, can be attributed to differences between the

COMPARISON OF MIR, MOIR, and POCP
REACTIVITIES RELATIVE TO ETHENE.

- Reactivities given on ozone per mass VOC emitted

- MIR and MOIR reactivities from Carter (1994)

- POCP reactivities from Derwent and Jenkin (1991). Error bars show standard
deviations of the averages of different scenarios or days.

SAPRC and the Harwell mechanisms, and not to fundamental differences between the Carter and POCP approaches. The Harwell mechanism neglects organic nitrate formation in the reactions of the higher alkenes, which environmental chamber data has verified is an important factor affecting their reactivity (Carter et al, 1993a; 1995a). Also the Harwell mechanism assumes much higher photolysis rates for MEK than does the SAPRC mechanism, which is inconsistent with environmental chamber data (Carter and Lurmann, 1991; unpublished results from this laboratory). The Harwell mechanism also does not represent the strong NO_x sink from aromatics to the same extent as does the SAPRC mechanism, which may contribute to the relatively high reactivity for toluene. However, the mechanisms for the other compounds are more similar, and the consequently the reactivity results correspond much better. The difference for formaldehyde is probably due to scenario differences, since the scenarios used in the POCP calculations are believed to be somewhat richer in radical sources than those used by Carter (1994).

Figure 2 shows the correspondence between the kOH scale and the MIR incremental reactivity scale. Since MIR is quantified in terms of ozone impacts per unit mass, the kOH scale is also placed on a mass basis by dividing the OH radical rate constants by the molecular weight. (Thus, the kOH scale is proportional to the mass flux of the reacting VOCs at a given OH radical level.) It can be seen that, when considering VOCs whose reaction rates vary over orders of magnitude, a fair correlation is obtained. However, Figure 2 shows that for a given kOH the incremental reactivities can vary by over an order of magnitude, and that the kOH scale is not a particularly useful for ranking ozone contributions of the more reactive VOCs. For that reason, in the subsequent discussion, we will focus on measurement and calculation of incremental reactivities.

Measurement or Calculation of Atmospheric Reactivity

A VOC's ozone impact, or its incremental reactivity, can be measured in environmental chamber experiments or can be calculated for atmospheric conditions using computer airshed models. Chamber experiments have the obvious advantage that they do not depend on uncertain models. However, as discussed above, incremental reactivities depend on environmental conditions, and it is not practical to experimentally duplicate in the laboratory all the conditions which affect incremental reactivity in the atmosphere. Chamber experiments have wall effects, usually higher levels of NO_x and VOCs to overcome background effects, static conditions, etc. In addition, higher amounts of test VOCs have to be added in incremental reactivity experiments to obtain a measurable effect. Even if it were practical to duplicate all relevant atmospheric conditions, separate experiments would have to be carried out for conditions of different scenarios to obtain incremental reactivities representative of those scenarios. This is usually not practical for regulatory applications.

For example, Figures 3 and 4 show plots of incremental reactivities calculated for conditions of chamber experiments against those calculated for the atmosphere for similar NO_x conditions, for VOCs whose reactivities have been experimentally studied, and for which the experimental data has verified the

Figure 2.   Correspondence between the OH radical rate constant and an incremental reactivity scale.

predictions of the chemical mechanism (Carter et al, 1993a, Carter, 1995).   Figure 3 shows the correspondence between relatively high NO_x experiments with the MIR reactivity scale. It can be seen that there is a correlation, though it not precise, and that the reactivities for certain VOCs, such as acetaldehyde, are much lower in the chamber than they are calculated for the atmosphere. Therefore, high NO_x experiments can give an indication of the approximate MIR reactivities, but will not serve as a very precise measure.

On the other hand, Figure 4, which shows plots of incremental reactivities for lower NO_x experiments with those calculated for the MOIR scale, shows that for lower NO_x conditions there is almost no correlation between incremental reactivities measured in the chamber and those calculated for the atmosphere. This can be attributed to ozone formation in low NO_x chamber experiments being much more

7

CORRESPONDENCE BETWEEN THE OH RADICAL RATE CONSTANT
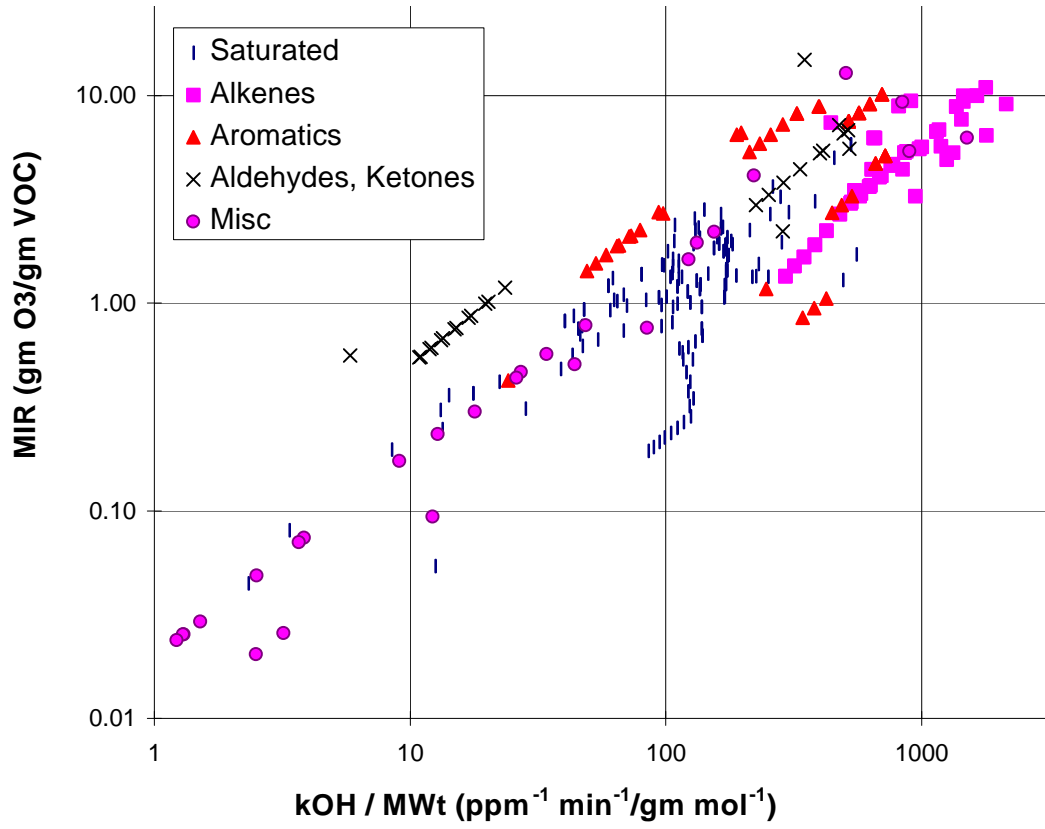# AND AN INCREMENTAL REACTIVITY SCALE

Figure 3.   Correspondence between environmental chamber and calculated atmospheric reactivities for high NO$_x$ conditions.

CORRESPONDENCE BETWEEN ENVIRONMENTAL CHAMBER AND CALCULATED ATMOSPHERIC REACTIVITIES.
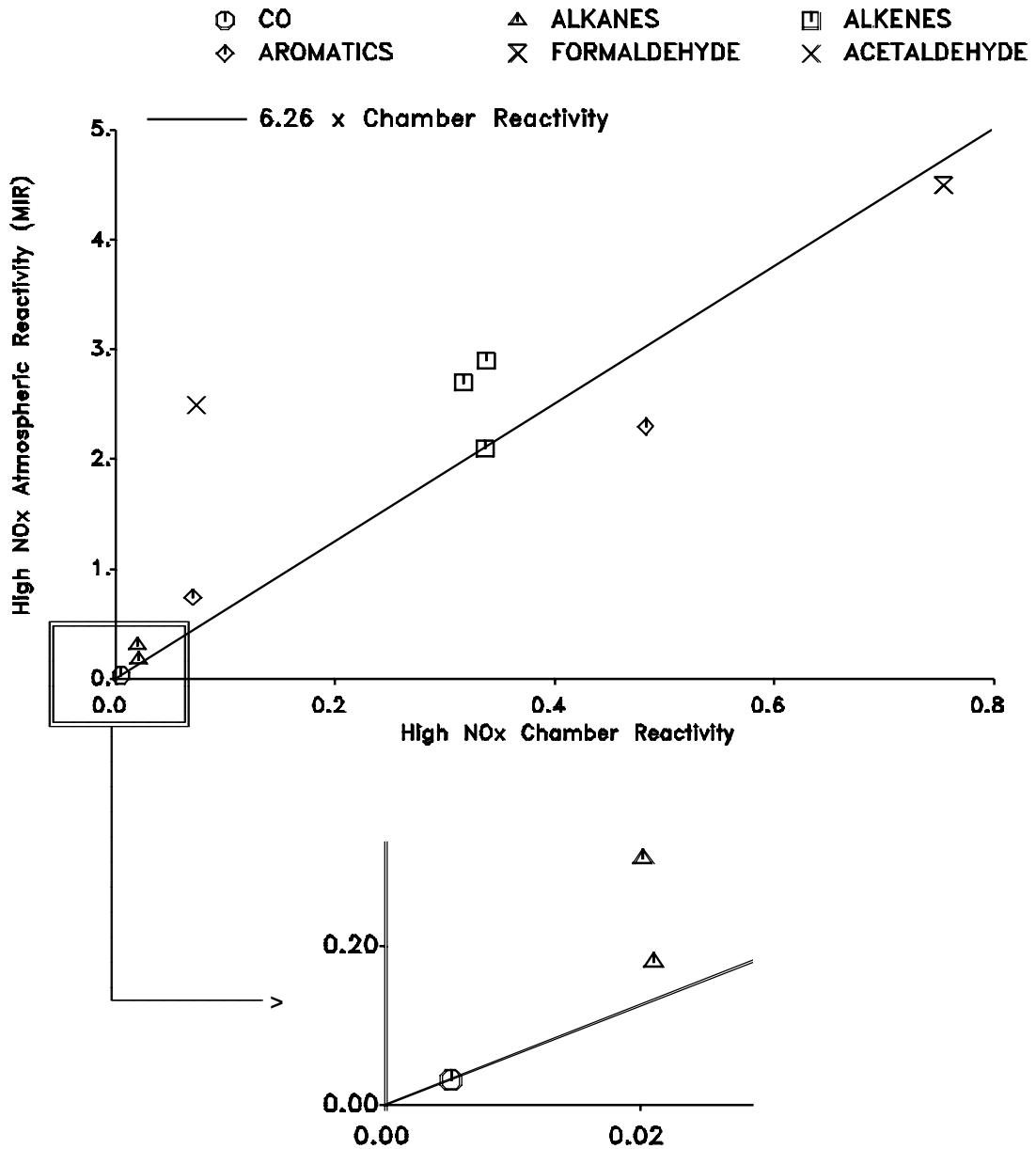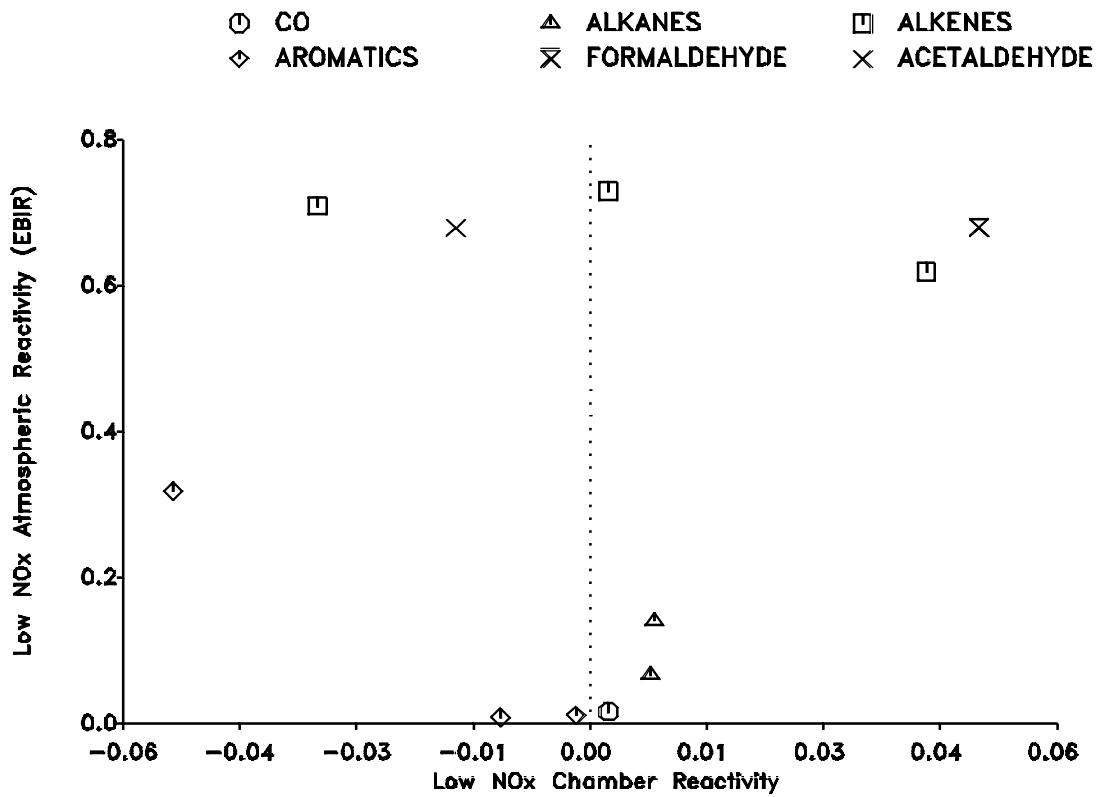
HIGH NO$_x$ CONDITIONS

Figure 4.   Correspondence between environmental chamber and calculated atmospheric reactivities for low NO_x conditions.

sensitive to NO_x sinks in VOCs mechanisms than ozone formation in the atmosphere, as indicated by the fact that many VOCs which are calculated to have positive ozone impacts in the atmosphere under low NO_x conditions are found to inhibit O_3 in the low NO_x chamber experiments. From this it is clear that results of low NO_x chamber experiments cannot be used to predict ozone reactivities in the atmosphere, even for low NO_x environments

Therefore, the only practical way to predict ozone impacts of VOCs for the atmosphere is to calculate them with computer airshed models. This requires both a model for airshed conditions and a chemical mechanism for the VOC. The problem of adequately representing airshed conditions will not be discussed further here, except to note that, for general VOC reactivity assessment, it is more important that a variety of scenarios be employed to represent the appropriate range of atmospheric conditions of relevance to ozone control, than that any scenario represent any particular episode with a high degree of

CORRESPONDENCE BETWEEN ENVIRONMENTAL CHAMBER AND CALCULATED ATMOSPHERIC REACTIVITIES.

LOW NO$_x$ CONDITIONS

⊙ CO   △ ALKANES   ⊡ ALKENES
◇ AROMATICS   ⊠ FORMALDEHYDE   ✕ ACETALDEHYDE

Low NOx Atmospheric Reactivity (EBIR) vs Low NOx Chamber Reactivity

accuracy. The most critical factor is the chemical mechanism for the VOC, since reactivity is a chemical effect. Reactivity predictions are no more reliable than the chemical mechanism employed.

Mechanism Evaluation

Because of the complexity and uncertainties in the atmospheric reaction mechanisms of most VOCs, no model calculation of reactivity can be considered to be reliable unless it has been shown that can accurately predict ozone impacts under a variety of conditions. The only practical way to do this is to carry out environmental chamber experiments, and then model the experiments to determine if the mechanism can accurately predict the ozone impacts that were observed. Although as discussed above ozone impacts in chambers will not be quantitatively the same as they are in the atmosphere, in appropriately designed experiments they will be affected by the aspects of the chemical mechanisms that affect reactivities in the atmospheres. If the mechanism cannot correctly predict the ozone impacts observed in the chamber, it is because it is representing one (or more) of these effects incorrectly, and thus would not be expected to correctly predict ozone formation in the atmosphere. If the mechanism correctly predicts the ozone impacts in a variety of experiments designed to encompass conditions sensitive to all these effects, then one would have greater confidence in its ability to predict ozone reactivity in the atmosphere.

Obviously, the confidence in the ozone predictions of the mechanism would also be greater for mechanisms developed based on detailed understanding of the underlying processes occurring, as opposed to mechanisms containing significant portions which are parameterized and adjusted to fit chamber data. However, even if the major processes appear to be well characterized and all the products identified, experience has shown that in some cases relatively minor processes in a VOCs overall mechanism can significantly affect its reactivity, and more often than not currently available analytical methods are not adequate to identify all the products which are formed. In addition, there is often no data on the subsequent reactions of the products, which might significantly affect reactivity. For these reasons, while detailed laboratory studies and improved mechanistic understanding are critical to the development of improved mechanisms overall, there is no avoiding the need for environmental chamber data to verify the predictive capability of the mechanisms for any particular VOC. Certainly, regulatory decisions should not be made on the basis of predictions of models employing mechanisms which have not been evaluated.

There are basically three types of chamber experiments which can be used to evaluate chemical mechanisms for airshed models. Single VOC NO_x - air experiments provide the most straightforward test of a VOC's mechanism because interpretation of the results are not complicated by mechanisms of other VOCs. For that reason, previous mechanism development and evaluation (e.g., Gery et al, 1988; Carter, 1990; Stockwell et al, 1990; Carter and Lurmann, 1990, 1991) have focused primarily on modeling such experiments, and they have served as the basis of the development of the parameterized aromatics mechanisms currently in use. However, modeling such experiments have proven to be almost useless for

VOCs, such as alkanes, which do not have significant radical sources in their mechanisms, or are radical terminators. That is because if the VOC's reactions involve no significant radical sources, the oxidation processes in such experiments are driven by the chamber radical source, which can be quantified only by adjustment of chamber-dependent parameters in model simulations, and which can vary from run to run (Carter et al, 1982; Carter and Lurmann, 1990, 1991). Therefore, poor fits of model simulations to results of such experiments can be rationalized by uncertainties in chamber effects, and models using erroneous mechanisms can be made to fit such experiments by adjusting uncertain chamber effects parameters. Finally, single mixture - NO_x experiments do not provide a realistic representation of atmospheric conditions, where many different types of VOCs are reacting together.

Figure 5 shows the current status of model performance of the most updated currently available SAPRC detailed mechanism (see below) in simulating ozone formed plus NO oxidized [$\Delta([O_3]-[NO])$, or $d(O_3-NO)$] in single VOC - NO_x experiments in a variety of environmental chambers with differing light sources. In most cases the fit is to within $\pm 30\%$; this represents the current state of the art in simulations of such runs. Cases of poorer performance can be attributed to uncertainties in chamber characterization and variable chamber effects, though obviously mechanism inaccuracies cannot be ruled out.

Mixture NO_x - air experiments have the advantages that, with appropriately chosen mixtures, they can provide a more realistic simulation of the chemical environment present in polluted atmospheres, and ale also much less sensitive to chamber effects to single compound runs which do not have radical initiators. They are essential for evaluating the performance of mechanisms as a whole, and this has been their role in previous mechanism evaluations (Carter and Lurmann, 1990, 1991; Gery et al, 1988). However, they are obviously not particularly useful for evaluating mechanisms of single VOCs because it is difficult to identify the source of cases of poor model performance, and because compensation of errors can sometimes make erroneous mechanisms appear to give good model performance. Because the relative importances of the compensating factors may be different in the atmosphere than in the chamber experiment, such a mechanism would likely give erroneous predictions in simulations of the atmosphere.

Incremental reactivity experiments, which consists of determining the effects of adding a test compound to a standard (base case) reactive organic gas (ROG) - NO_x - air mixture, combines the advantages of both single VOC and mixture - NO_x experiments. Like mixture - NO_x experiments, with an appropriate choice of the base case ROG "surrogate" mixture, they can present a realistic representation of the chemical environment in the atmosphere. In addition, they are relatively insensitive to chamber effects, and to the extent that chamber effects influence the results, they would affect both the added VOC and base case experiments to a similar extent, and thus, to a first order approximation, tend to be cancelled out when looking at the difference. Like single compound experiments, they isolate out the effect of the single compound, and provide direct data on its impact on ozone [and other measures, such as overall radical levels (Carter et al, 1993a, 1995b)] in a chemically realistic environment. They provide the best

Figure 5.   Plot of experimental <u>vs</u> calculated ozone formed + NO oxidized in selected single compound - NO$_x$ experiments.

available means for evaluating the mechanisms for low-reactivity compounds such as alkanes (and many of the VOC exemption candidates) without the complications of chamber effects which plague use of low reactivity VOC - NO$_x$ experiments for mechanism evaluation. Varying the NO$_x$ levels or the composition of the base case ROG surrogate in the experiments provide a means for evaluating the mechanism under varying chemical conditions, which is necessary to assure satisfactory performance in varying atmospheric simulations. Because of these advantages, incremental reactivity experiments have become the method of choice of evaluating mechanisms for VOC reactivity assessment, for cases where resources limit the number of experiments which can be carried out.

Figure 6 shows an example of data obtained from an incremental reactivity experiment, and its use for mechanism evaluation. This particular run looks at the effects of adding m-xylene to a relatively high ROG/NO$_x$ experiment using an 8-component ROG surrogate to represent the various classes of

PLOT OF EXPERIMENTAL <u>VS</u> CALCULATED
OZONE FORMED + NO OXIDIZED IN
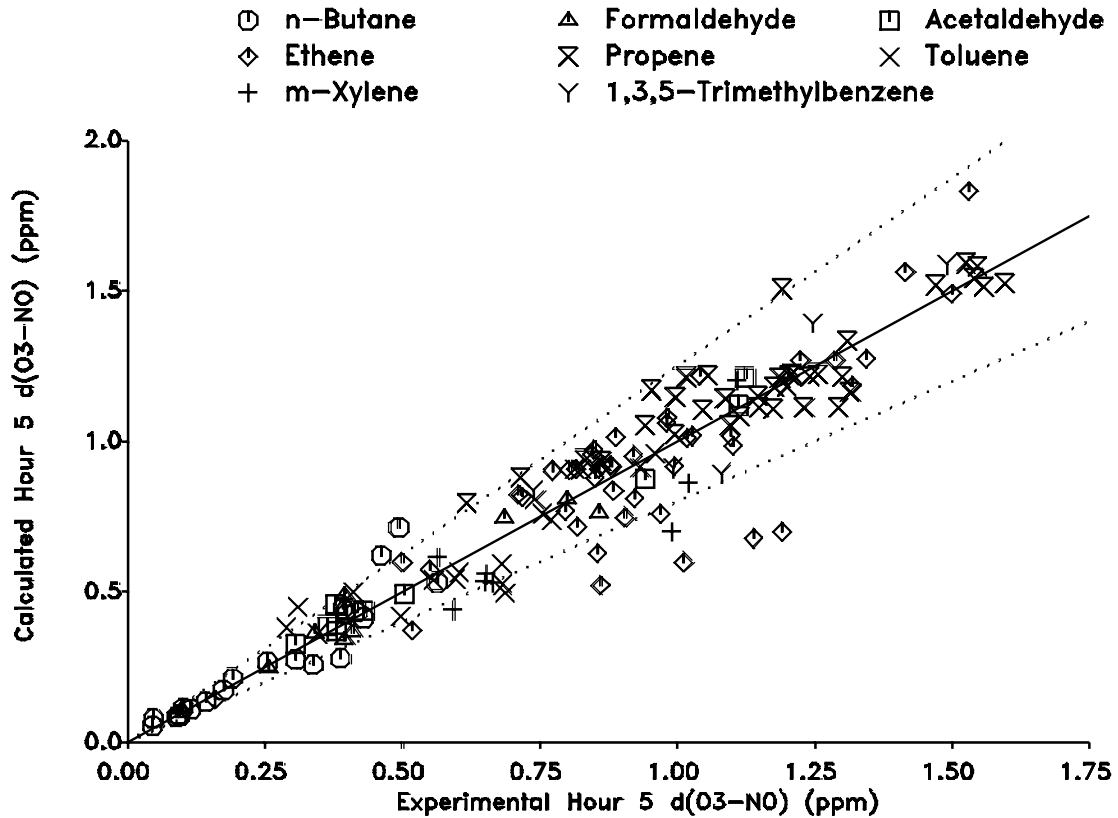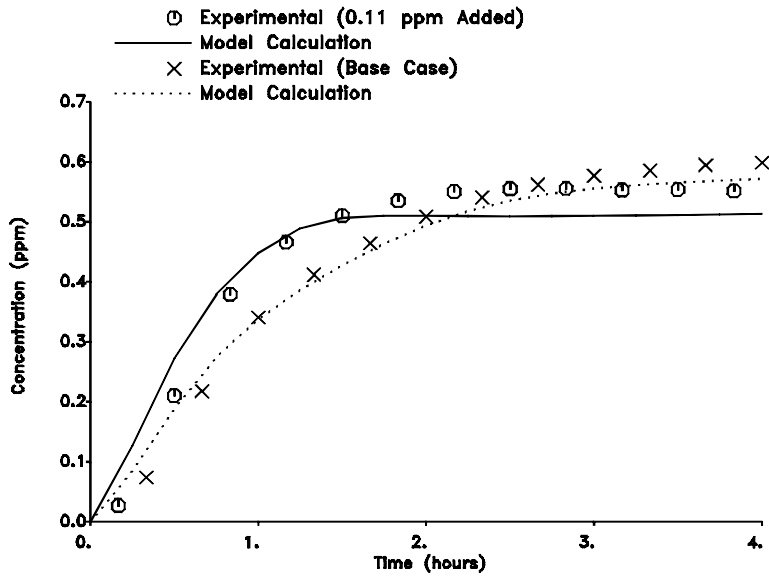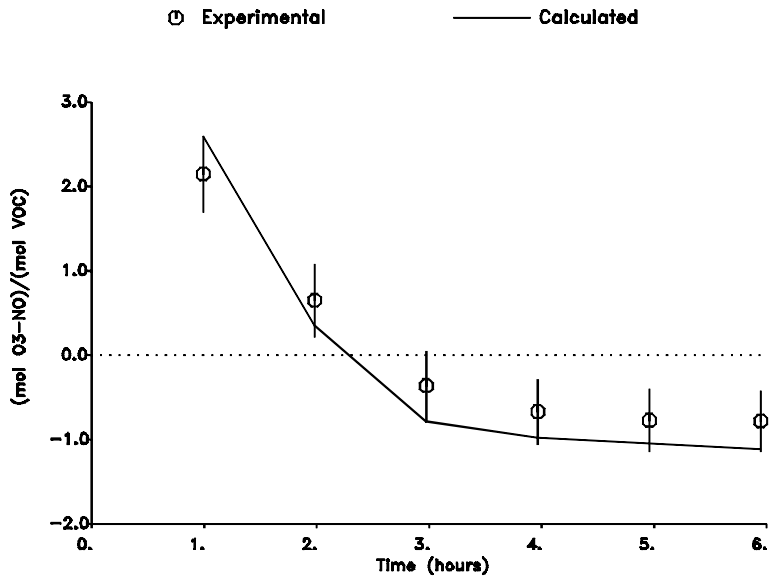## SELECTED SINGLE COMPOUND - NO$_x$ EXPERIMENTS

Figure 6.   Example of an incremental reactivity experiment: Effect of m-xylene under high ROG/NO$_x$ conditions.

EXAMPLE OF AN INCREMENTAL REACTIVITY EXPERIMENT: EFFECT OF M-XYLENE UNDER HIGH ROG/NO$_x$ CONDITIONS

$\Delta([O_3]-[NO])$ vs TIME

{CHANGE IN $\Delta([O_3]-[NO])$} / (XYLENE REACTED) vs TIME

reactive VOCs present in the atmosphere. The top plot shows the effect of the m-xylene on the O_3 formed + NO oxidized [$d(O_3$-NO)], and the bottom plot shows the incremental reactivity (change in $d(O_3$-NO), divided by amount of m-xylene added) as a function of time. The figure shows that m-xylene addition accelerates the initial rate of NO oxidation and O_3 formation, but causes a decline in the final O_3 yield in this low NO_x experiment, due to the NO_x sinks in the mechanism, as discussed above. The lines show the model calculations, which perform reasonably well in simulating this behavior.

Summary of Ongoing Reactivity-Related Research

Reactivity-related research can be categorized into three general areas, basic kinetic and mechanistic studies, environmental chamber studies, and mechanism development. Basic kinetic and mechanistic studies are obviously critical, since they are necessary to provide the underlying scientific basis for the mechanisms. This consists of measuring the elementary rate constants for the VOC's atmospheric relevant reactions and reactive intermediates, identifying the products formed, and using the product yield information to derive the intermediate processes involved. The atmospherically relevant rate constants have already been measured for a large number of VOCs (e.g., Atkinson, 1994, 1996, and references therein), though kinetic studies continue to be carried out for new classes of VOCs for the purposes of determining atmospheric lifetimes. From the point of view of near-term needs for mechanism development for reactivity assessment, the most valuable data at the present time comes from product studies which elucidate competing processes for the reactions of radical intermediates in aromatic photooxidations. This provides important and necessary input data for development of estimation methods for comparing reactions, such as, for example, the alkoxy radical estimation methods discussed by Atkinson and Carter (1992) and Atkinson (1996). Progress on aromatic mechanisms have been of limited utility for mechanism development in recent years because of lack of quantitative yields and identification of the major products, though this continues to be a priority of research. Major work in this area is being carried out in Europe as well as the United States. Detailed discussion of the ongoing work in this area is beyond the work of this paper.

Environmental Chamber Studies is the second major component of reactivity-related research in the United States. As discussed above, environmental chamber data are essential for verifying that a mechanism can reliably predict the ozone impact of a VOC in the atmosphere, and in recent years this has been a primary focus of reactivity-related research in our laboratories. Previously, this has focused on VOCs which are important in assessing relative ozone impacts for vehicle exhaust mixtures, primarily in the context of evaluating the effects on ozone of alternative fuel use (e.g., Carter et al, 1993a, 1995a,b). However, with data already available concerning the most important compounds affecting reactivities of most vehicle exhausts, the focus has turned more towards other classes of chemicals, usually in the context of assessing if the ozone impact of a compound is low enough for it to be an appropriate candidate for exemption for regulation as an ozone precursor under the criteria used by the EPA. In addition, under funding from the California Air Resources Board, we are conducting chamber experiments to reduce

uncertainties in reactivity estimates in the various classes of compounds present in consumer product emissions which have not been studied previously. The results are providing useful information concerning reactivity and characteristics of classes of compounds which were not previously studied, which will improve our ability to estimate mechanisms for other chemically similar compounds. These studies will be discussed further below.

While our laboratories have focused primarily on chamber studies for mechanism evaluation, Kelly and co-workers at GM (Kelly et al, 1994; Kelly and Wang, 1996) have conducted environmental chamber experiments to directly evaluate reactivity scales. Reasonably good correlation with MIR reactivities were obtained in experiments employing a number of VOCs which are important in exhaust mixtures. However, my understanding is that additional work in this area is not planed for the near term.

Several laboratories are conducting environmental chamber experiments to directly evaluate vehicle exhaust reactivities. We have begun work in this area in our laboratories, with the focus being on evaluating (1) whether we have identified all the compounds present in exhaust which contributes significantly to their reactivity, and (2) whether current chemical mechanisms can simulate the results of experiments with real exhaust mixtures. Part of the approach is to compare experiments using synthetic surrogates containing the compounds identified in the real exhaust mixtures with the experiments using the actual exhaust. If the results are significantly different, it would mean that there is something in the exhaust affecting the results which we are not accounting for. This will not be discussed further here, except to note that experiments have been concluded with LPG exhaust which indicate no significant problems either with the mechanism or our identifying the reactive compounds present in the LPG exhaust which accounts for its reactivity, which are primarily ethylene and propene, along with the propane and small contribution from the other $C_{\leq 4}$ alkanes.

Mechanism development is the third component of reactivity-related research in the United States. In our laboratories, much of this is being carried out in conjunction with the environmental chamber studies of individual VOCs. This consists primarily of developing and evaluating the mechanisms for the individual compound(s) being studied, and then adding them to the current version of the SAPRC detailed mechanisms. In addition, we are also working on updating this mechanism to incorporate recent kinetic and mechanistic laboratory data results of recent evaluations, to reduce uncertainties in VOC reactivity assessments in general, and to evaluate the effects of chemical mechanism uncertainties on reactivity assessments and other airshed model results. The SAPRC mechanisms, and our ongoing work in this area, are discussed further below.

Another major mechanism development effort being carried out in the United States is the development of a chemical mechanism for Models 3. In this case, new approaches are being developed to represent greater chemical detail in comprehensive airshed models than previously been the case. To

my knowledge, this work has not evolved to the point where it can be used for VOC reactivity assessment. A discussion of the status of this effort is beyond the scope of this paper.

A third major mechanism development effort is enhancing existing gas-phase mechanisms so they can be used to predict secondary particulate formation. This important effort also will not be discussed further here because it is not strictly applicable to ozone reactivity assessment. However, eventually it may allow for the development of VOC reactivity scales for particulate formation, which might be useful for development of more efficient control strategies for reducing secondary particulate, since VOCs also differ significantly in this regard.

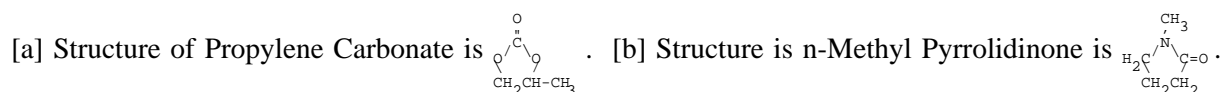**Environmental Chamber and Reactivity Studies at CE-CERT**
A number of programs are underway at our environmental chamber laboratories at the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California Riverside which are related to VOC reactivity assessment. Most of these programs are aimed at improving our ability to more reliably estimate atmospheric ozone impacts of individual chemicals which have not been previously studied. Many of these programs are funded by chemical manufacturers or users who are interested in determining if a compound of interest to them might have sufficiently low ozone impact that they can petition the EPA to exempt it from regulation as an ozone precursor. In addition, the California Air Resources Board, which is considering development of reactivity-based control strategies in consumer products regulations, is funding us to study some of the more reactive compounds present in the consumer product emissions inventory, for which reactivity estimates are currently highly uncertain. A list of the compounds which we have recently studied is given in Table 1.

In most of these studies, the overall objective is to estimate the ozone impact of the compound(s) in the atmosphere, using a mechanism whose predictive capability has been experimentally verified. This involves several steps, which are summarized below.

The first step consists of conducting environmental chamber experiments to measure the incremental reactivities of the compounds under varying conditions. The minimum set of experiments are: (1) experiments with relatively high NO_x/ROG ratios and a simple ROG "mini-surrogate", which have has been shown to be highly sensitive to mechanism differences and radical initiation/inhibition effects (Carter et al, 1995a); (2) high NO_x/ROG experiments using a more realistic ROG surrogate which have been shown to give incremental reactivities which correlate reasonably well with those calculated for the atmosphere (e.g., see Figure 3, above); and (3) low NO_x/ROG experiments using the realistic ROG surrogate which are necessary to determine the effects of varying NO_x, and to evaluate the mechanism under NO_x-limited conditions. If the compound is photoreactive or may form photoreactive products with unknown action spectra, experiments are conducted using both blacklights and xenon arc lights, to determine the effect of varying the light source. [Data on effects of varying the light source have proven

Table 1.　　Summary of compounds whose reactivities have recently been studied in environmental chamber experiments at the University of California at Riverside.

Compounds Studied	Compounds Being Studied
Acetone	Ethyl Acetate
C_{12+} n-alkanes	Butyl Acetate
Methyl Acetate	Methyl Ethyl Ketone
t-Butyl Alcohol	Methyl Isobutyl Ketone
Trichloroethylene	Isopropanol
Chloropicrin (CCl_3NO_2)	Propylene Glycol
Propylene Carbonate [a]	Acetylene
n-Methyl Pyrrolidinone [b]	Alkyl Bromides
	C_{12+} Cycloalkanes

[a] Structure of Propylene Carbonate is . [b] Structure is n-Methyl Pyrrolidinone is .

extremely valuable in evaluating the mechanism for acetone (Carter et al, 1993b).] In addition, single compound - NO_x experiments are conducted if there is reason to believe it will provide useful information for mechanism evaluation, and if the compound is known to have internal radical sources and thus not be highly sensitive to chamber effects. Such experiments were carried out, for example, for acetone, chloropicrin, and trichloroethylene.

Estimated mechanisms for these compounds are then derived based on available kinetic and mechanistic information, and the predictive capabilities of these mechanisms are evaluated by comparing their predictions against chamber data. In many cases, unknown parameters have to be adjusted to yield acceptable fits; often this is the organic nitrate yield from the NO + peroxy reactions, as discussed below. In a number of cases, there are several reasonable alternative mechanisms, and it has to be determined which of these is more consistent with the data. (An example of such a case is also discussed below.) Note that the mechanism predictions are compared not only with the rate of NO oxidation and O_3 formation, but also the overall OH radical levels as indicated by the rate of consumption of the ROG surrogate component m-xylene, the chlorine atom levels for Cl-containing compounds as determined by the rates of consumption of the alkane ROG surrogate components, the formaldehyde and PAN yields, and yields of any other products that might be detected in the routine GC analyses carried out with all reactivity experiments.

The mechanisms developed in this effort are then incorporated in the updated version of the SAPRC detailed mechanism, which is then used to calculate the ozone impacts of the VOC in the

atmosphere. If no single mechanism satisfactorily fits the data, then a set of mechanisms, using alternative assumptions or varying unknown parameters which span the range of uncertainty, are employed to obtain estimates of upper and lower limit reactivity ranges given this uncertainty. The scenarios and reactivity assessment methods are based on those employed previously in developing the MIR, MOIR, and various "base case" incremental reactivity scales, and are based on one-day EKMA scenarios developed by the EPA to represent 39 ozone exceedence areas around the United States. For VOCs being considered for exemption by the EPA, their calculated reactivities are compared with those calculated for ethane, the compound used by the EPA as the standard to establish "negligible" reactivity. The reactivities are compared using multiple scenarios and scales, since in many cases relative reactivities are variable, and regulatory decisions need to be made based on distributions of reactivities, rather than single points.

As indicated above, the <u>Alkyl Nitrate Yields</u> in the VOCs oxidation mechanism is often the major uncertainty affecting predictions of its reactivity. One of the several links in the series of radical chain reactions by which VOCs enhance ozone formation is the reaction of peroxy radicals with NO, yielding NO_2 and alkoxy radicals, e.g., reaction (1), below.

$$VOC + OH \rightarrow H_2O + R\cdot$$
$$R\cdot + O_2 \rightarrow RO_2\cdot$$
$$RO_2 + NO \rightarrow RO\cdot + NO_2 \tag{1}$$

The alkoxy radical then reacts in a number of possible ways, but usually it leads to the regeneration of OH radicals, allowing the chain process to continue. However, for some time it has been known that for the higher alkanes, the competing reaction

$$RO_2 + NO \rightarrow RONO_2 \tag{2}$$

becomes increasingly important as the size of the molecule increases. See, for example, Table 2, which shows some representative examples of measured $k_2/(k_1+k_2)$ ratios derived from alkyl nitrate yield measurements from the reactions of OH radicals with alkanes (Carter and Atkinson, 1989b, and references therein.) This alkyl nitrate formation reaction significantly reduces ozone formation because it is both a radical and NO_x sink, and is the principal reason why the calculated incremental reactivities of alkanes decrease as the size of molecule increases, despite the increase in their OH radical rate constants (Carter and Atkinson, 1989a; Carter, 1994).

Unfortunately, because of analytical limitations and the instability of many organic nitrates, quantitative alkyl nitrate yields have only been determined for $C_{\leq 8}$ peroxy radicals formed from alkanes. Therefore, particularly for larger VOCs, the overall alkyl nitrate yield from peroxy + NO reactions in the VOC's mechanism has to be used as an adjustable parameter in order to obtain acceptable fits to chamber

Table 2.　　　Examples of measured and adjusted organic nitrate yields.

Measured Yields		Adjusted to Fit Chamber Data	
$2\text{-}C_3H_7OO\cdot$	4 %	$C_{\leq 8}$ δ-Hydroxy $RO_2\cdot$ isomers	~0 %
$3\text{-}C_5H_{11}OO\cdot$	14 %	$CH_3(CO)OCH_2OO\cdot$	~0 %
$3\text{-}C_8H_{17}OO\cdot$	35 %	$(CH3)_3COCH_2OO\cdot$	2 %
		$HOC(CH3)_2CH_2OO\cdot$	7 %
		Propylene Carbonate $RO_2\cdot$'s	8 %
		N-Methyl Pyrrolidinone $RO_2\cdot$'s	15 %
		Terpene $RO_2\cdot$'s	25 %
		n-C_{12} RO_2's	42 %

data.　For example, t-butanol is a relatively simple molecule and the only major uncertainty in its mechanism is the alkyl nitrate yield in the reaction of the $(CH_3)_2C(OH)CH_2OO\cdot$ radical with NO. Figure 7 shows plots of incremental reactivities of t-butanol at each hour in a mini-surrogate - NO_x + t-butanol experiment, along with model calculations assuming various nitrate yields. Note the sensitivity of the calculated incremental reactivities to this parameter. The data are best fit by assuming a ~7% alkyl nitrate yield, so this parameter was used when estimating t-butanol's atmospheric reactivity. Note that this is reasonably close to the ~10% nitrate yield which was derived for the same radical when modeling isobutene - NO_x experiments. This agreement is reasonably good, especially considering the uncertainties in radical yields in the isobutene + O_3 reactions.
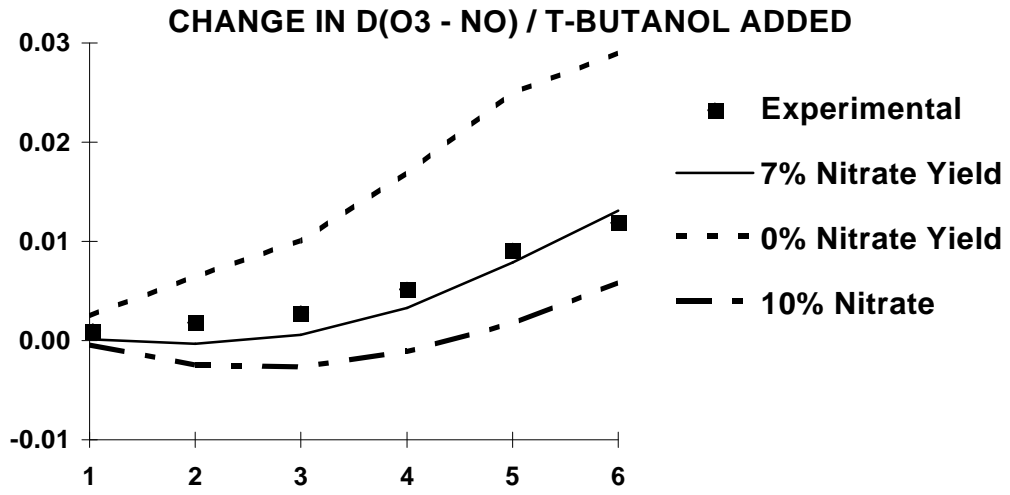
Table 2 gives the adjusted nitrate yields which were derived from model simulation of various VOCs which we have studied. Note that while the nitrate yields generally increase as the size of the molecule increases, there is no obvious method for quantitatively predicting them from the structure of the molecule. It is particularly difficult to understand why it is not possible for model simulations to fit chamber data for the higher n-alkanes unless it is assumed that nitrate formation from the reactions of NO with the Δ-hydroxy peroxy radicals (expected to form following isomerization of long-chain alkoxy radicals) is negligible. Theoretical work in this area would clearly be useful for developing a framework for a workable prediction or even an empirical estimation method. As information for more classes of compounds become available, patterns may become apparent which might allow estimation methods to be developed.
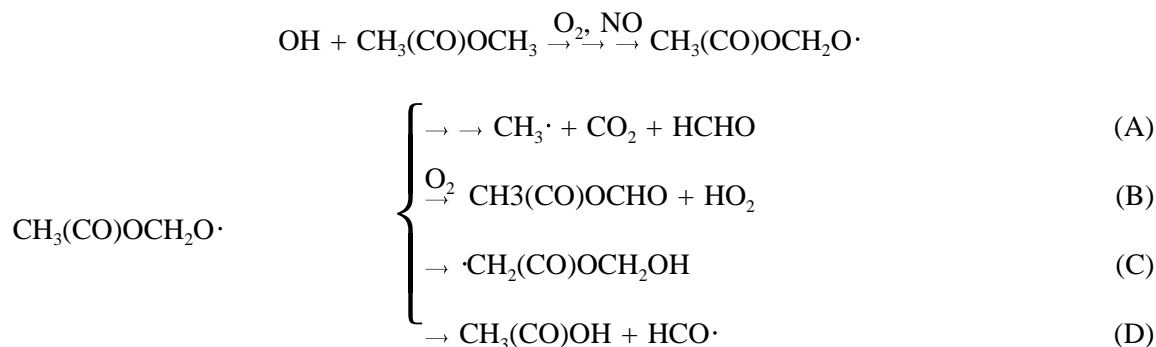
Figure 7.   Example of results of adjusting alkyl nitrate yields to fit environmental chamber data: Experimental and model simulation results for a mini-surrogate - NO_x + 11 ppm t-butanol chamber experiment.

An illustrative example of the <u>use of our environmental chamber data for distinguishing between alternative mechanisms</u> comes from our recently completed and ongoing studies of methyl and ethyl acetates, which form alkoxy radicals which have a number of competing alternative reactions. A summary of possible mechanisms for methyl acetate is shown on Figure 8, and Figure 9 shows model simulations of selected methyl acetate reactivity data using these alternative mechanisms. The results show that the reactivity data are consistent only with mechanisms, such as "Model B" and "Model D", which predict two NO to NO_2 conversions prior to regeneration of OH, and formation of relatively unreactive products [$CH_3(CO)OCHO$ for Model B, and CH_3COOH + CO for Model D]. The possibility of Model D was not considered when we wrote up our report on methyl acetate (Carter et al, 1996a), since no evidence has previously been presented for this type of reaction (involving a shift of the H in the α-position relative to the alkoxy moving, via a 5-member ring transition state, to the carbonyl group, and simultaneous C-O bond re-arrangements or cleavage) in atmospheric photooxidation systems, and since the more conventional Model B explained the methyl acetate data quite well.

However, in subsequent studies of the reactivity of ethyl acetate, we found the analogue to Mechanism B (O_2 reaction with the alkoxy radical, forming acetic anhydride) significantly overpredicted the reactivity relative to NO oxidation and O_3 formation. This is shown on Figure 10. Furthermore, adjusting the nitrate yields to fit the approximate reactivity in the mini-surrogate experiment did not satisfactorily fit the reactivity observed in the lower NO_x complex, and also significantly underpredicted the PAN yield. The observed relatively low reactivity and formation of relatively high PAN yields

20

CHANGE IN D(O3 - NO) / T-BUTANOL ADDED

Experimental
7% Nitrate Yield
0% Nitrate Yield
10% Nitrate

$$OH + CH_3(CO)OCH_3 \xrightarrow{} \xrightarrow{O_2, NO} \xrightarrow{} CH_3(CO)OCH_2O\cdot$$

$$CH_3(CO)OCH_2O\cdot \begin{cases} \rightarrow \rightarrow CH_3\cdot + CO_2 + HCHO & \text{(A)} \\[2mm] \xrightarrow{O_2} CH3(CO)OCHO + HO_2 & \text{(B)} \\[2mm] \rightarrow \cdot CH_2(CO)OCH_2OH & \text{(C)} \\[2mm] \rightarrow CH_3(CO)OH + HCO\cdot & \text{(D)} \end{cases}$$

MODEL A: β-SCISSION DECOMPOSITION
- THREE NO TO NO_2 CONVERSIONS BEFORE OH IS REGENERATED
- HIGH YIELDS OF FORMALDEHYDE

MODEL B: O_2 ABSTRACTION
- TWO NO TO NO_2 CONVERSIONS
- LOW REACTIVITY PRODUCT NOT DETECTABLE BY GC

MODEL C: H-SHIFT ISOMERIZATION VIA C—O···H—C
- THREE NO TO NO_2 CONVERSIONS
- LOW REACTIVITY PRODUCT NOT DETECTABLE BY GC

MODEL D: H-SHIFT VIA C—H···O=C, DECOMPOSITION
- TWO NO TO NO_2 CONVERSIONS
- LOW REACTIVITY PRODUCTS NOT DETECTABLE BY GC

Figure 8.　　　Summary of mechanisms and models for the atmospheric reactions of methyl acetate.

(together with the lack of formation of acetaldehyde, which might be formed by other possible rearrangements of the intermediates) can only be explained by a rearrangement corresponding to Model D, as shown on Figure 8. That mechanism fits the data reasonably well, without having to adjust the alkyl nitrate yields.

Of course, the definitive determination of which mechanism occurs will come with product studies which can distinguish whether acetic acid or acid anhydrides are in fact formed, and such studies are underway. However, this illustrates how such environmental chamber data can distinguish between alternative reaction mechanisms in cases where definitive product information is not available.
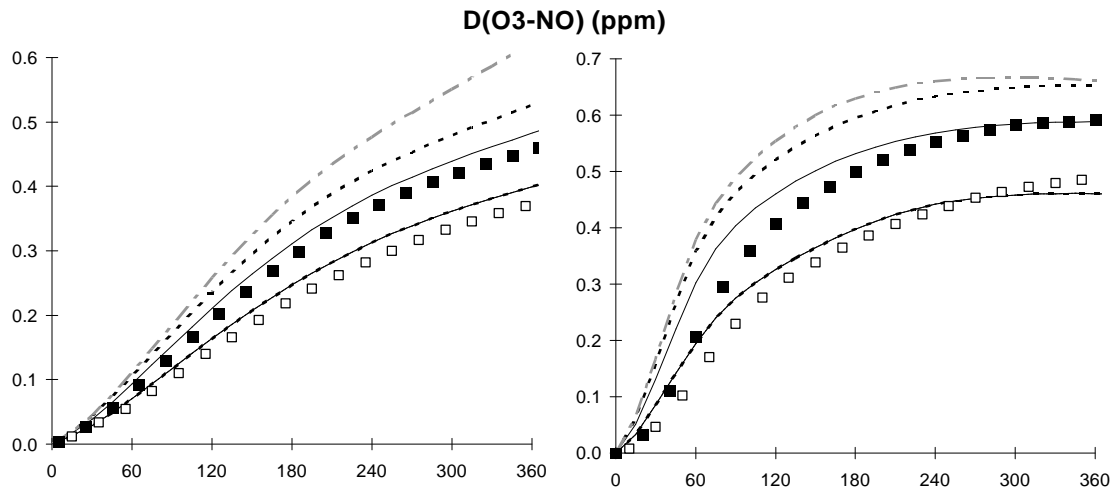
Figure 9.   Results of model simulations of selected methyl acetate incremental reactivity experiments.
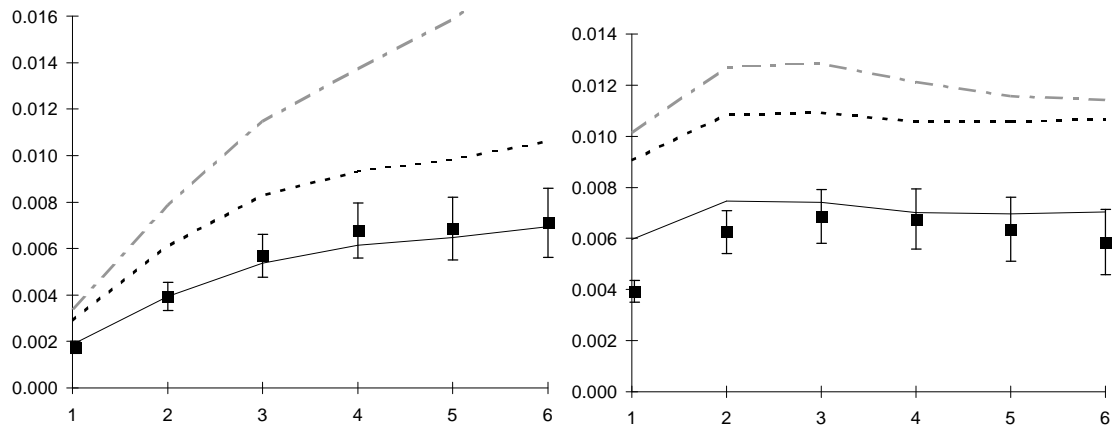
MODEL SIMULATIONS OF METHYL ACETATE
INCREMENTAL REACTIVITY EXPERIMENTS

HIGN NOx MINI-SURROGATE

LOWER NOx FULL SURROGATE

D(O3-NO) (ppm)

[Change in D(O3-NO)] / [Methyl Acetate Added]

- – - – **Model A** ——— **Model B or D** - - - - **Model C**
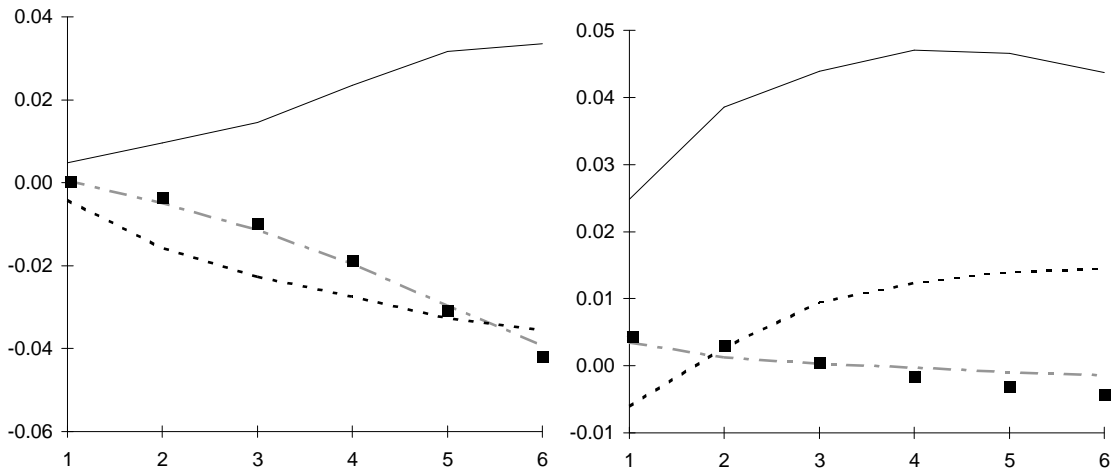 ı **Experimental** □ **Base Case**

Figure 10.   Results of model simulations of selected ethyl acetate incremental reactivity experiments.

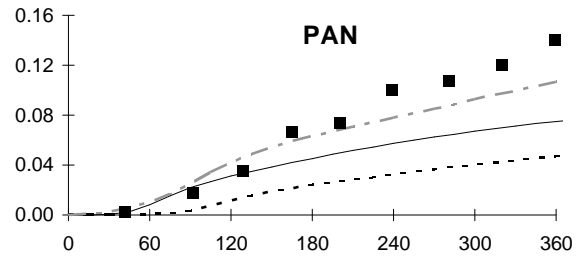# MODEL SIMULATIONS OF ETHYL ACETATE INCREMENTAL REACTIVITY EXPERIMENTS

HIGN NOx MINI-SURROGATE

LOWER NOx FULL SURROGATE

[Change in D(O3-NO)] / [Ethyl Acetate Added]

- ■ **Experimental**
- — **Model B**
- ···· **Model B with 20% Nitrate**
- — · — **Model D**

PAN

SAPRC Mechanism Development

The SAPRC-90 mechanism (Carter, 1990) reflects the state of the science as of 1989, and was developed specifically for the purpose of VOC reactivity assessment. It can explicitly represent a large number of different types of organic compounds, but it lumps together species reacting with similar rate constants and mechanisms in atmospheric simulations, and it uses a condensed representation for many of the reactive organic products. The reactions of inorganics, CO, formaldehyde, acetaldehyde, peroxyacetyl nitrate, propionaldehyde, peroxypropionyl nitrate, glyoxal and its PAN analog, methylglyoxal and several other product compounds are represented explicitly. In addition, the reactions of unknown photoreactive products formed in the reactions of aromatic hydrocarbons are represented by a model species "AFG2", whose yields and photolysis parameters are adjusted based on fits of model simulations to environmental chamber experiments. A chemical operator approach is used to represent peroxy radical reactions, as discussed in detail by Carter (1990). Generalized reactions with variable rate constants and product yields are used to represent the primary emitted alkane, alkene, aromatic and other VOCs (with rate constants and product yields appropriate for the individual compounds being represented in each simulation). Most of the higher molecular weight oxygenated product species are represented using the "surrogate species" approach, where simpler molecules such as propionaldehyde or 2-butanone are used to represent the reactions of higher molecular weight analogues that are assumed to react similarly. This mechanism was extensively evaluated against chamber data employing the major classes of VOCs present in vehicle exhausts and measured in ambient air (Carter and Lurmann, 1991). It was to calculate the MIR, MOIR, and other incremental reactivity scales presented by Carter (1994), and condensed versions of this mechanism have been incorporated in a number of research models.

The SAPRC-93 mechanism incorporates a number of updates to account for new kinetic and mechanistic information, and based on results of environmental chamber data on reactivities of components of vehicle emissions (Carter et al, 1993a,b; Carter, 1995). Changes to the kinetics of PAN formation and decomposition made the mechanism overall somewhat more reactive than SAPRC-90, but this was found to be more consistent with results of environmental chamber data after a re-evaluation of chamber effects characterization data carried out for other reasons (Carter et al, 1995c). The O_3 + alkene mechanisms were modified considerably to be more consistent with data concerning OH radical yields from these reactions, which predicted higher reactivities for internal alkenes and gave much better fits to incremental reactivity experiments for these compounds (Carter et al, 1993a; Carter, 1995b,c). Mechanisms for some other individual VOCs were modified to improve fits to reactivity chamber data, and recently this mechanism was further modified to incorporate the recently-developed condensed version (Carter, 1996) of the updated isoprene mechanism of Carter and Atkinson (1996). This mechanism has recently been implemented into a "Flexible Chemical Mechanism" version of the UAM model (Kumar et al, 1995), and found to give significantly higher ozone predictions in a UAM simulation of a SCAQS episode in the Los Angeles Basin than does the standard UAM with the Carbon Bond Mechanism, which is of similar vintage

(but different design) than SAPRC-90. This mechanism is now available for downloading by anonymous FTP from cert.ucr.edu/pub/carter/mech.

The Updated SAPRC Mechanism is the version currently being used in our VOC reactivity assessment research, though it has not been documented for use by other modeling groups because it is still evolving. The primary changes it incorporates concern a re-parameterization of the representation of the aromatics, the enhancement of mechanisms for the various individual VOCs as data are being generated in our environmental chamber programs, and the addition of ClO_x chemistry to represent the reactions of Cl-containing compounds (Carter et al, 1996b). The re-parameterization of the aromatics mechanisms was necessary because, as shown on Figure 11, the parameterization used in the SAPRC-93 mechanism underpredicted ozone formation in most aromatic - NO_x chamber experiments carried out in our Teflon chamber with a xenon arc light source, despite fitting data runs carried out in similar chambers using blacklights, and also because, as shown on Figure 12, it did not represent reactivity differences among alkylbenzene isomers. The reparameterization consisted of allowing the MGLY yield (which represented methylglyoxal) to be optimized, as well as the AFG2 yield, and also carrying out separate optimizations for each aromatic isomer, for which chamber data using both light sources are now available. (Thus, in effect, MGLY is being used to represent uncharacterized ring-opening products with similar action spectra, as well as just methylglyoxal itself, as was the case with SAPRC-93.) Figures 11 and 12 show that much better fits are obtained with this reparameterization. Unfortunately, there is still insufficient quantitative product information from aromatic reactions to permit the development of non-parameterized aromatic mechanisms which have predictive capabilities.

Table 3 shows a summary of the effects of mechanism changes on calculated MIR incremental reactivities of the ambient mixture (Jeffries et al, 1989; Carter, 1994), and reactivities of selected compounds relative to the ambient mixture. It can be seen that each update resulted in an increase in the reactivity of the ambient mixture. In the case of SAPRC-93, the increase is probably due primarily to the changes in PAN kinetics, with some contribution due to the increase in the internal alkenes, whose relative reactivities increased because of the use of higher OH yields in the O_3 + alkene mechanisms. In the case of the updated mechanism, the increase is probably due to the reparameterization of the aromatics mechanisms, which resulted in significant reactivity increases for some isomers. Note that the relative reactivities for most non-aromatic compounds decreased in the updated mechanism, though the increase for the aromatics in the ambient mixture is probably the main reason. Note also the significant differences in reactivities of aromatic isomers in the updated mechanisms, indicating the effects of optimizing the parameters for each separately.

The SAPRC mechanism is still evolving, and major additional updates are expected by the end of the year. We are in the process of completely updating the core reactions to be consistent with the latest evaluations; most of these have not changed since the development of SAPRC-90. Most changes

Figure 11.   Effects of SAPRC Mechanism Update on results of model simulations of m-xylene - NO$_x$
                 chamber experiments.

EFFECTS OF MECHANISM UPDATE ON RESULTS OF MODEL SIMULATIONS OF M-XYLENE - NOx CHAMBER EXPERIMENTS

USGFIGS.XLS
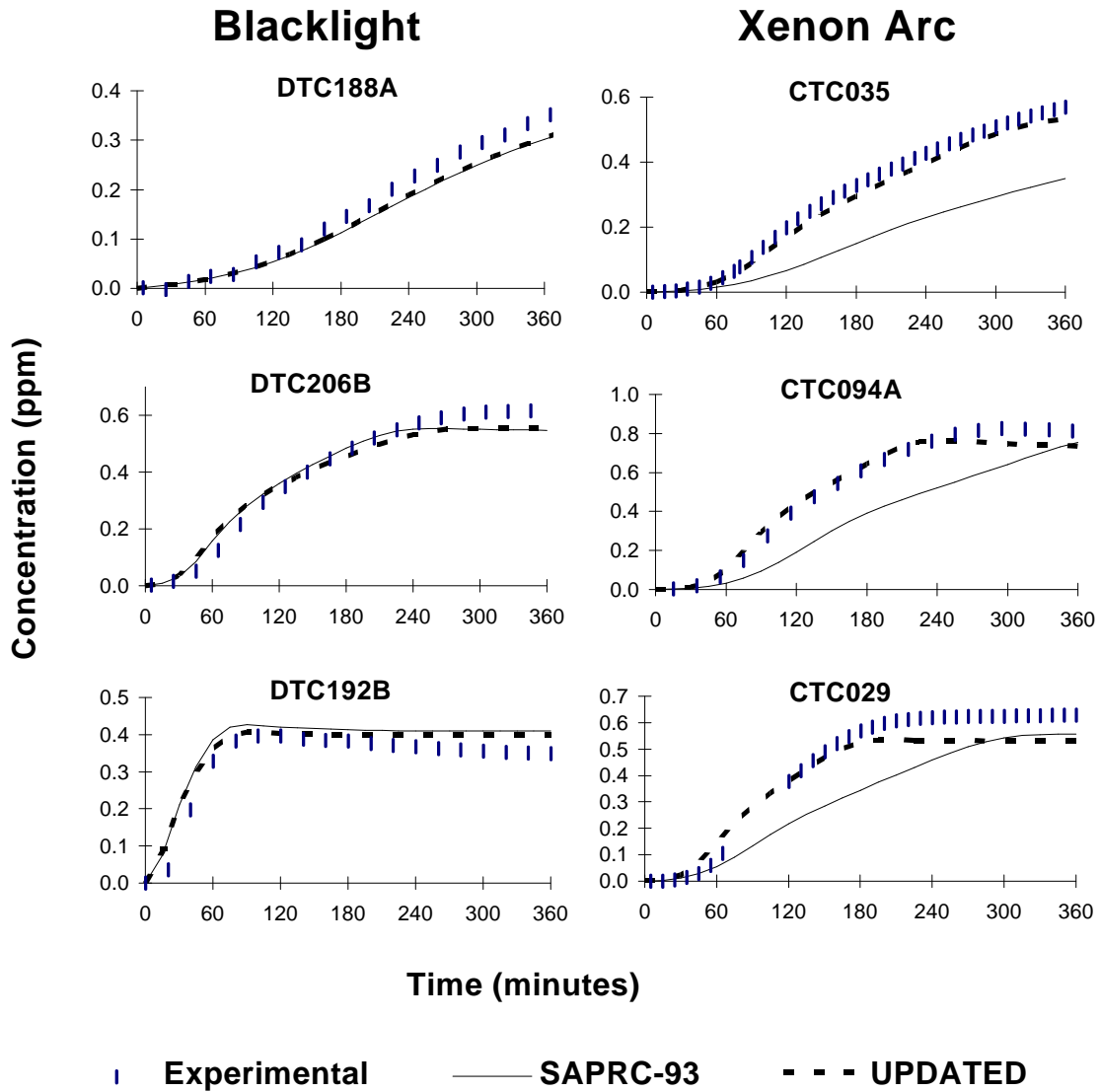
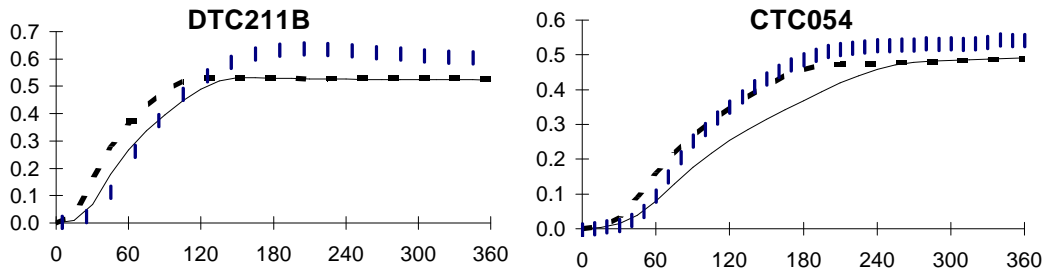10/4/96

Figure 12.   Effects of SAPRC Mechanism Update on results of model simulations of trimethylbenzene
               - NO$_x$ chamber experiments.

EFFECTS OF MECHANISM UPDATE ON
RESULTS OF MODEL SIMULATIONS OF
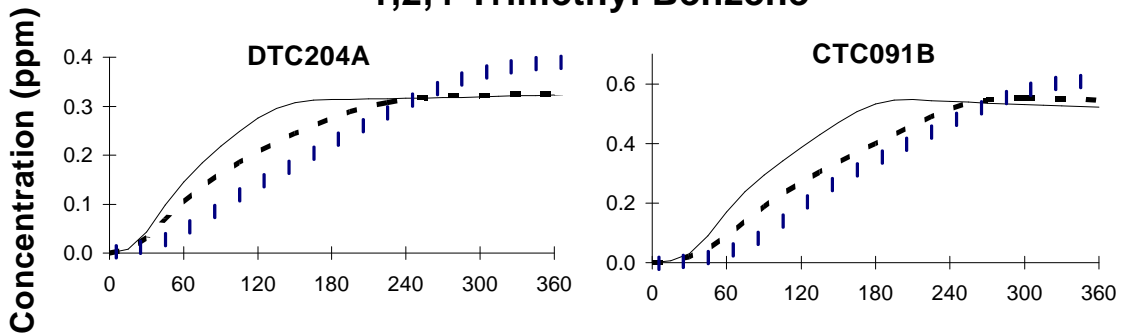# TRIMETHYLBENZENE - NOx CHAMBER EXPERIMENTS

Blacklight   Xenon Arc

1,2,3-Trimethyl Benzene

DTC211B   CTC054

1,2,4-Trimethyl Benzene

DTC204A   CTC091B

Concentration (ppm)

1,3,5-Trimethyl Benzene

DTC206A   CTC071

Time (minutes)

ı **Experimental**   —— **SAPRC-93**   - - - **UPDATED**

Table 3.   Effects of Mechanism Changes in Calculated MIR Reactivities.

found thus far probably will only have minor effects on reactivity predictions. However, the latest IUPAC (Atkinson, 1996) recommended rate constant for the critical OH + NO$_2$ reaction is ~33% higher than that recommended in previous evaluations, and incorporated in the existing SAPRC and other mechanisms. The consequences of this and other changes have not yet been assessed.

We are also working on extending our procedures for estimating complex mechanisms beyond alkanes to broader classes of VOCs, including alcohols, ethers, esters, glycols, etc. The computer program written to generate alkane mechanisms for deriving product yield parameters for SAPRC-90 and SAPRC-93 has been re-written to allowed for broader ranges of VOCs, and to incorporate updated alkoxy radical estimation methods developed by Atkinson (Atkinson and Carter, 1992; Atkinson, 1996). The work on developing estimation methods is still in progress, and the results have not yet been incorporated into the working mechanism.

EFFECTS OF MECHANISM CHANGES
ON CALCULATED MIR REACTIVITIES

VOC or MIX	SAPRC-90	SAPRC-93	Updated
Incremental Reactivity (gm O3 / GM VOC)			
Ambient Mix	3.2	3.8	4.1
Reactivity Relative to Ambient Mix (gram basis)			
Ethane	0.1	0.1	0.1
Iso-Octane	0.28	0.32	0.30
n-Octane	0.20	0.22	0.21
Ethene	2.4	2.3	2.1
Propene	3.0	3.1	2.7
trans-2-Butene	3.2	3.7	3.3
Toluene	0.87	0.87	1.19
o-Xylene	2.1	1.9	1.9
m-Xylene	2.6	2.4	3.5
p-Xylene	2.1	2.0	0.6
123-Trimethyl Benzene	2.8	2.7	3.0
124-Trimethyl Benzene	2.8	2.7	1.3
135-Trimethyl Benzene	3.2	3.1	3.1
Formaldehyde	2.3	1.9	1.6
Acetaldehyde	1.8	1.7	1.6

References

Atkinson, R. (1989): "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," J. Phys. Chem. Ref. Data, Monograph no 1.

Atkinson, R. (1991): "Kinetics and Mechanisms of the Gas-Phase Reactions of the NO_3 Radical with Organic Compounds," J. Phys. Chem. Ref. Data, 20, 459-507.

Atkinson, R. (1996), work in preparation.

Atkinson, R. and W. P. L. Carter (1992): "Reactions of Alkoxy Radicals under Atmospheric Conditions: The Relative Importance of Decomposition versus Reaction with O_2," J. Atm. Chem., 13, 195-210.

Atkinson, R. and W. P. L. Carter (1984): "Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions," Chem. Rev. 1984, 437-470.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe (1996): "Evaluated Kinetic, Photochemical and Heterogenious Data for Atmospheric Chemistry: Supplement V., IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry," J. Phys. Chem. Ref. Data, in press.

Bowman, F. M. and J. H. Seinfeld (1994a): "Ozone Productivity of Atmospheric Organics," J. Geophys. Res. 99, 5309.

Bowman, F. M. and J. H. Seinfeld (1994b): "Fundamental Basis of Incremental Reactivities of Organics in Ozone Formation in VOC/NO_x Mixtures," Atmos. Environ. 28, 3369-3385.

Baugues, K. (1990): "Preliminary Planning Information for Updating the Ozone Regulatory Impact Analysis Version of EKMA," Draft Document, Source Receptor Analysis Branch, Technical Support Division, U. S. Environmental Protection Agency, Research Triangle Park, NC, January.

Carter, W. P. L., R. Atkinson, A. M. Winer, and J. N. Pitts, Jr. (1982): "Experimental Investigation of Chamber-Dependent Radical Sources," Int. J. Chem. Kinet., 14, 1071.

Carter, W. P. L. (1990): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," Atmos. Environ., 24A, 481-518.

Carter, W. P. L. (1994): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," J. Air & Waste Manage. Assoc., 44, 881-899.

Carter, W. P. L. (1995): "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds," Atmos. Environ., 29, 2513-2517.

Carter, W. P. L. (1996): "Condensed Atmospheric Photoxidation Mechanisms for Isoprene", Atmospheric Environment, in press.

Carter, W. P. L. and R. Atkinson (1989a): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environ. Sci. Technol., $\underline{23}$, 864.

Carter, W. P. L. and R. Atkinson (1989b): "Alkyl Nitrate Formation from the Atmospheric Photooxidation of Alkanes; a Revised Estimation Method," J. Atm. Chem. $\underline{8}$, 165-173.

Carter, W. P. L., and F. W. Lurmann (1990): "Evaluation of the RADM Gas-Phase Chemical Mechanism," Final Report, EPA-600/3-90-001.

Carter, W. P. L. and F. W. Lurmann (1991): "Evaluation of a Detailed Gas-Phase Atmospheric Reaction Mechanism using Environmental Chamber Data," Atm. Environ. $\underline{25A}$, 2771-2806.

Carter, W. P. L, D. Luo, I. L. Malkina, and J. A. Pierce (1993a): "An Experimental and Modeling Study of the Photochemical Ozone Reactivity of Acetone," Final Report to Chemical Manufacturers Association Contract No. KET-ACE-CRC-2.0. December 10.

Carter, W. P. L., J. A. Pierce, I. L. Malkina, D. Luo and W. D. Long (1993b): "Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Report to Coordinating Research Council, Project No. ME-9, California Air Resources Board Contract No. A032-0692; South Coast Air Quality Management District Contract No. C91323, United States Environmental Protection Agency Cooperative Agreement No. CR-814396-01-0, University Corporation for Atmospheric Research Contract No. 59166, and Dow Corning Corporation. April 1.

Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995a): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO$_x$," Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323. March 24.

Carter, W. P. L., J. A. Pierce, D. Luo, and I. L. Malkina (1995c): "Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds," Atmos. Environ. $\underline{29}$, 2499-2511.

Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995d): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source," Final report to National Renewable Energy Laboratory, Contract XZ-2-12075, Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March 26.

Carter, W. P. L. and R. Atkinson (1996): "Development and Evaluation of a Detailed Mechanism for the Atmospheric Reactions of Isoprene and NO$_x$," International Journal of Chemical Kinetics, $\underline{28}$, 497-530.

Carter, W. P. L., D. Luo, and I. L. Malkina (1996): "Investigation of the Atmospheric Ozone Formation Potential of Methyl Acetate," Report to Eastman Chemical Co., July 17.

Carter, W. P. L., D. Luo, and I. L. Malkina (1996): "Investigation of the Atmospheric Reactions of Chloropicrin," submitted to Atmos. Environ., May, 1996.

Chameides, W. L., R. W. Lindsay, J. Richardson, and C. S. Kiang (1988): "The Role of Biogenic Hydrocarbons in Urban Photochemical Smog: Atlanta as a Case Study," Science, 241, 1473-1475.

Derwent, R. G. and Hov, Ö (1979): "Computer Modelling Studies of Photochemical Air Pollution Formation in North West Europe," AERE R 9434, Harwell Laboratory, Oxfordshire, England.

Derwent, R. G. and M. E. Jenkin (1991): "Hydrocarbons and the Long-Range Transport of Ozone and PAN Across Europe," Atmos. Environ., 25A, 1661-1678.

Dodge, M. C. (1984): "Combined effects of organic reactivity and NMHC/NOx ratio on photochemical oxidant formation -- a modeling study," Atmos. Environ., 18, 1657.

Gery, M. W., G. Z. Whitten, and J. P. Killus (1988): "Development and Testing of the CBM-IV For Urban and Regional Modeling,", EPA-600/ 3-88-012, January.

Jeffries, H. E., K. G. Sexton, J. R. Arnold, and T. L. Kale (1989): "Validation Testing of New Mechanisms with Outdoor Chamber Data. Volume 2: Analysis of VOC Data for the CB4 and CAL Photochemical Mechanisms," Final Report, EPA-600/3-89-010b.

Jeffries, H. E. and R. Crouse (1991): "Scientific and Technical Issues Related to the Application of Incremental Reactivity. Part II: Explaining Mechanism Differences," Report prepared for Western States Petroleum Association, Glendale, CA, October.

Kelly, N. A., P. Wang, S. M. Japar, M. D. Hurley, and T. J. Wallington (1994): "Measurement of the Atmospheric Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methadologies," final report to Coordinating Research Council, Contract AQ-6-1-92 and NREL Subcontract AF-2-11296-1. June 30.

Kelly, N. A., and P. Wang (1996): "Comparison between Smog Chamber Measurements and Theoretical Predictions of Reactivity," Presented at the 89th Annual Meeting of the Air and Waste Management Association, Nashville, TN, June 23-28.

Kumar, N., F. W. Lurmann, and W. P. L. Carter (1995), "Development of the Flexible Chemical Mechanism Version of the Urban Airshed Model," Report to California Air Resources Board, Agreement no. 93-716. Document No. STI-94470-1508-FR, Sonoma Technology, Inc. Santa Rosa, CA, August.

Stockwell, W. R., P. Middleton, J. S. Chang, and X. Tang (1990): "The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling," J. Geophys. Res. 95, 16343- 16376.