

**ENVIRONMENTAL CHAMBER STUDY
OF MAXIMUM INCREMENTAL REACTIVITIES
OF VOLATILE ORGANIC COMPOUNDS**

by

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ABSTRACT

The effects of 26 individual volatile organic compounds (VOCs) on ozone formation, NO oxidation, and OH radical levels were measured by adding them to reactive organic gas (ROG) - NO_x - air environmental chamber irradiations representing a simplified model photochemical smog system. These experiments had relatively low ROG/NO_x ratios to represent conditions where ozone formation is most sensitive to VOC additions. The compounds studied included representative alkanes, alkenes, aromatic hydrocarbons, aldehydes, alcohols, and CO. The addition of formaldehyde, methylbenzenes, alkenes and methanol all caused increased integrated OH radical concentrations, and caused the most NO oxidation and ozone formation per molecule reacted. The C₆₊ n-alkanes had the most inhibiting effects on OH radicals, and caused reduced NO oxidation and ozone formation in these experiments. The other compounds had smaller negative effects on OH radicals, but moderate positive effects on ozone formed and NO oxidized. The implications of these results in terms of the atmospheric reaction mechanisms of these compounds are discussed.

INTRODUCTION

The formation of ground-level ozone is caused by the gas-phase interactions of emitted volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in the presence of sunlight (NRC, 1991). Individual VOC compounds can differ significantly in their effects on ozone, due not only to differences in their atmospheric reaction rates, but also due to differences in the way in which their reactions affect ozone (Carter and Atkinson, 1987; Carter 1994; Bauman and Seinfeld, 1994a,b). There are a number of ways to quantify a VOC's effect on ozone (e.g., Bauman and Seinfeld, 1994a,b), but probably the most direct quantitative measure for practical air quality impact assessments is its "incremental reactivity" (Carter and Atkinson, 1987; 1989a; Chang and Rudy, 1990; Russell, 1990; Carter, 1991, 1994). This is defined as the amount of additional ozone formation resulting from the addition of a small amount of the compound to the system in which ozone is formed, divided by the amount of compound added. This depends not only on the VOC and its atmospheric reactions, but also on the conditions of the system where the VOC is reacting. For example, incremental reactivities of VOCs under high NO_x conditions can differ from those under conditions where NO_x is limited, not only in terms of absolute magnitude but also (in many cases) in a relative sense (e.g., Carter, 1991, 1994). Model calculations indicate that incremental reactivities measured in environmental chamber experiments can be somewhat different than those in the atmosphere, due to differences in dilution, static conditions, and the "surrogate" mixture of compounds used in the experiment to represent the other VOCs in the atmosphere (Carter and Atkinson, 1989; Carter et al., 1994). Nevertheless, results of incremental reactivities measured in suitably designed chamber experiments should be influenced by the same chemical mechanistic factors which affect incremental reactivities in the atmosphere, and thus can provide insights into these factors. Experimentally measured incremental reactivities also provide the most direct available means to evaluate the ability of the chemical models used in models to predict incremental reactivities in the atmosphere.

This paper describes the results of a series of experiments to measure incremental reactivities of a series of representative VOCs under relatively high NO_x or "maximum reactivity" conditions. Incremental reactivities under high NO_x conditions are referred to as maximum reactivities because VOCs have their highest magnitudes of incremental reactivities (most ozone formed per VOC emitted) under such conditions (Carter and Atkinson, 1989; Carter, 1991, 1994). Although it is clearly of interest to measure reactivities under a variety of conditions, we chose to focus initially on maximum reactivity conditions because those are the conditions where O₃ is most sensitive to VOCs, and because the California Air Resources Board used a maximum incremental reactivity (MIR) scale when implementing reactivity-based standards for motor vehicle emissions (CARB 1990, 1991).

METHODS

Experimental Approach

The reactivities of the representative VOCs were measured by carrying out a series of repeated 6-hour irradiations of a standard mixture representing photochemical smog precursors in an indoor environmental chamber, alternating with irradiations of the same mixture with varying amounts of the test VOC added. The chamber employed consists of a ~3000-liter flexible FEP Teflon reaction bag held in a framework surrounded by blacklights which were used as the light source. Dry purified air for the experiments was provided by an in-house air purification system. The chamber was flushed with purified air overnight, and then the reactants were injected, mixed, and monitored. The chamber contents were then irradiated for six hours. Ozone and NO_x were monitored continuously by commercial continuous analyzers, and the temperature was monitored by a thermocouple probe inside the chamber. The O₃, NO_x, and temperature data were recorded on the data acquisition computer every 15 minutes. Organic reactants were monitored approximately hourly by gas chromatography. After the run the reaction bag chamber was deflated and flushed with pure air to remove the contents and prepare for the next run. The experimental approach and analysis methods are described in detail elsewhere (Carter et al. 1993).

The temperature in the chamber when the lights were on ranged from 298 to 304 K. The light intensity was measured by conducting periodic NO₂ actinometry experiments using a modified version of the quartz tube method of Zafonte et al. (1977). The NO₂ photolysis rate ranged from ~0.4 min⁻¹ initially to ~0.32-0.33 min⁻¹ at the end of the study. The spectral distribution of the blacklight light source was measured using a LiCor LI-1800 spectral radiometer. Characterization and control runs were also carried out as described elsewhere (Carter et al., 1993).

The experiments with the representative photochemical smog precursors but without the added test VOC are referred to as the "base case" experiments. The photochemical smog precursors utilized in the base case experiments consisted of ~3.5 or ~4.5 ppmC of a "mini-surrogate" reactive organic gas (ROG) mixture containing 35% (as carbon) ethene, 50% n-hexane, and 15% m-xylene, along with ~0.5 ppm of

oxides of nitrogen (NO_x) in air. This was designed to represent "maximum reactivity" conditions, i.e., relatively low ROG/NO_x ratios where VOCs have the greatest effects on ozone formation (Carter, 1991, 1994). The 3-component mini-surrogate was designed to be an experimentally simple representative of the reactive organic compounds emitted into the atmosphere. Although this mini-surrogate is a significant oversimplification of the complex mixture of ROGs present in the atmosphere (see, for example, Jeffries et al. 1989), model calculations show that use of this simpler mixture provides a more sensitive measure of reactivities than use of more complex mixtures. The mini-surrogate is also referred to as the "base ROG mixture" (following the terminology used previously [Carter, 1994]), since it is the ROG mixture used in the base case experiments.

The experiments where a test VOC was added to the reactants in the base case experiments are referred to as the "test" experiments. The amount of VOCs added in these experiments varied depending on the observed reactivity of the VOC. Generally the amount added was determined so that it caused at least a 30%, but less than a factor of 2, change in the sum of amount of NO consumed plus the amount of ozone formed in six hours. If the effect of adding the VOC in the first experiment was not in this range, the amount added was adjusted. Usually at least two or three added VOC experiments were conducted for each of the VOCs studied.

Two changes were made in the experimental procedures or conditions during the course of this study, yielding three different sets of base case and test runs. In the Set 1 experiments, 3.5 ppm of the mini-surrogate was employed, and the NO_x was injected using glass syringes. In the Set 2 experiments the NO_x was injected using a vacuum rack preparation to reduce possible formation of nitrous acid (HONO). In the set 3 experiments the amount of mini-surrogate was increased to ~4.5 ppm to increase the ozone yields to levels comparable to Set 1. The reasons for these changes and their effects on the experiments are discussed in the Results section.

Data Analysis Methods

The quantity of interest from a practical perspective is the VOC's *incremental reactivity*, which is defined as the effect of the VOC on some measure of air quality (e.g., ozone), divided by the amount of VOC added. However, from a mechanistic analysis perspective it is more useful to at the components of incremental reactivity. As discussed previously (Carter and Atkinson, 1989a, Carter, 1991, 1994), incremental reactivity can be thought of as being a product of two more fundamental factors: (1) the *kinetic reactivity*, which is defined as the fraction of the emitted VOC which undergoes chemical reaction in the pollution scenario or experiment being considered; and (2) the *mechanistic reactivity*, which is the amount of ozone formed relative to the amount of VOC which has undergone reaction. The utility of this concept is that this provides a means to factor out (at least to a first approximation) the effect of a VOC's reaction rate from all the other mechanistic aspects which affect reactivity. Since the only aspect of the VOC's mechanism which affects kinetic reactivities are the VOC's rate constants, which generally are known, the ability of a mechanism to predict kinetic reactivities are not considered to be particularly

uncertain. On the other hand, the mechanistic reactivities are sensitive to all the other aspects of the VOC's mechanism, many (or all) of which are uncertain. Thus, the mechanistic reactivities are the quantities which are the most difficult to predict *a-priori*. For this reason, in the rest of this paper we will focus primarily on determinations of various measures of mechanistic reactivities.

The results of the experiments were analyzed to yield three measures of VOC reactivity. The first was the effect of the added VOC on the amount of NO reacted plus the amount of ozone formed at hourly intervals in the experiment. This is abbreviated as $d(O_3-NO)$ in the subsequent discussion. As discussed elsewhere (e.g., Johnson, 1983; Carter and Atkinson, 1987; Carter and Lurmann, 1990, 1991) this gives a direct measure of the amount of conversion of NO to NO_2 by peroxy radicals formed in the photooxidation reactions, which is the process that is directly responsible for ozone formation in the atmosphere. (Johnson calls it "smog produces" or "SP".) The incremental reactivity of the test VOC relative to $d(O_3-NO)$ at time t , designated $IR[d(O_3-NO)]_t^{VOC}$, is given by

$$IR[d(O_3-NO)]_t^{VOC} = \frac{d(O_3-NO)_t^{test} - d(O_3-NO)_t^{base}}{[VOC]_0} \quad (I)$$

where $d(O_3-NO)_t^{test}$ is the $d(O_3-NO)$ measured at time t from the experiment where the test VOC was added, $d(O_3-NO)_t^{base}$ is the corresponding value from the "base case" experiments where the test VOC was not present, and $[VOC]_0$ is the amount of test VOC added. In an analogous manner, the mechanistic reactivities, designated $MR[d(O_3-NO)]_t^{VOC}$, is given by

$$MR[d(O_3-NO)]_t^{VOC} = \frac{d(O_3-NO)_t^{test} - d(O_3-NO)_t^{base}}{(VOC \text{ Reacted})_t} \quad (II)$$

where $(VOC \text{ reacted})_t$ is the amount of the test VOC which has undergone reaction up to time= t . (In the subsequent discussion, we will give the derivations only for types of mechanistic reactivities, though the derivations for incremental reactivities are analogous.) These quantities were calculated for each hour of the 6-hour experiments.

The second measure of reactivity obtained in this study is the effect of the VOC on integrated hydroxyl (OH) radical concentrations in the experiment, abbreviated "IntOH" in the subsequent discussion. The effect of a VOC on radicals is an important factor affecting reactivity because radical levels affect how rapidly all VOCs present, including the base ROG components, react to form ozone. If a compound is present in the experiment which reacts primarily with OH radicals, then the IntOH at time t can be estimated from

$$IntOH_t = \int_0^t [OH]_{\tau} d\tau = \frac{\ln\left(\frac{[tracer]_0}{[tracer]_t}\right) - Dt}{k_{OH}^{tracer}} \quad , \quad (III)$$

where $[\text{tracer}]_0$ and $[\text{tracer}]_t$ are the initial and time= t concentrations of the tracer compound, $k_{\text{OH}}^{\text{tracer}}$ its OH rate constant, and D is the dilution rate in the experiments. The latter was found to be 0.5 ± 0.25 %/hr, which is small but non-negligible (Carter et al., 1993). The concentration of tracer at each hourly interval was determined by fitting the experimental $\ln[\text{tracer}]$ data to linear or quadratic curves when plotted against time or $d(\text{O}_3\text{-NO})_t$, as discussed elsewhere (Carter et al., 1993).

For most experiments m-xylene was used as the OH tracer, since as a mini-surrogate component it was present in all experiments, its OH rate constant is known (the value used was $2.36 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ [Atkinson, 1989]), and it reacts relatively rapidly. For some later experiments, particularly those with p-xylene, which we could not monitor simultaneously with m-xylene, trace amounts (~ 2 ppb) of 2-chloromethyl-3-chloropropene, monitored at low levels by GC/ECD, was used as the OH radical tracer. The OH radical rate constant used for it was $3.16 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, which was measured in this work using the relative rate method (Atkinson, 1989) and m-xylene as the reference compound (Carter et al., 1993). This rate constant is in good agreement with the results of Tuazon et al (1988). Although this compound also reacts with ozone, its measured rate constant (Tuazon et al, 1984) is sufficiently low that ozone reaction is calculated to be negligible under the conditions of these experiments.

The effect of the VOC on IntOH was measured by its incremental or mechanistic reactivities relative to IntOH, or $\text{IR}[\text{IntOH}]_t^{\text{voc}}$ and $\text{MR}[\text{IntOH}]_t^{\text{voc}}$. These are defined in a way exactly analogous to the reactivities relative to $d(\text{O}_3\text{-NO})$, e.g.:

$$\text{MR}[\text{IntOH}]_t^{\text{voc}} = \frac{\text{IntOH}_t^{\text{test}} - \text{IntOH}_t^{\text{base}}}{(\text{VOC reacted})_t} \quad (\text{IV})$$

The effects of the test VOC on $d(\text{O}_3\text{-NO})$ and IntOH can also be used to obtain estimates of the direct and indirect components of reactivity. All peroxy radicals which oxidize NO and cause ozone formation in a ROG- NO_x -air photooxidation system can be traced back to an initially present or emitted VOC (Jeffries and Crouse, 1991). Therefore, in an experiment where a test VOC is added to a base ROG mixture, the amount of ozone formed and NO oxidized, $d(\text{O}_3\text{-NO})^{\text{test}}$, is the sum of ozone formed and NO oxidized due to radicals formed from the reactions of the test VOC or its products, $d(\text{O}_3\text{-NO})_{\text{voc}}^{\text{test}}$, plus the ozone formed and NO oxidized from radicals formed from reactions of the components of the base ROG mixture and their products, $d(\text{O}_3\text{-NO})_{\text{base ROG}}^{\text{test}}$. Plugging this into Equation (II) yields

$$\begin{aligned} \text{MR}[d(\text{O}_3\text{-NO})] &= \frac{d(\text{O}_3\text{-NO})_{\text{VOC}}^{\text{test}}}{(\text{VOC rct'd})_t} + \frac{d(\text{O}_3\text{-NO})_{\text{base ROG}}^{\text{test}} - d(\text{O}_3\text{-NO})^{\text{base}}}{(\text{VOC reacted})_t} \\ &= \text{MR}^{\text{direct}} + \text{MR}^{\text{indirect}} \end{aligned} \quad (\text{V})$$

where the first term is the "direct reactivity" and the second is the "indirect reactivity".

Neither $d(O_3-NO)_{voc}^{test}$ nor $d(O_3-NO)_{base\ ROG}^{test}$ are directly measured, but the latter can be estimated if two approximations are made. These are: (1) the amount of base ROG and base ROG products reacting in an experiment (whether base or test) is proportional to IntOH; and (2) the ratio of $d(O_3-NO)_{base\ ROG}^{test}$ to amount of base ROG and base ROG products reacting is unaffected by the addition of the test VOC. From these it follows that

$$\frac{d(O_3-NO)_{base\ ROG}^{test}}{IntOH^{test}} \approx \frac{d(O_3-NO)^{base}}{IntOH^{base}}, \quad (VI)$$

and thus

$$MR^{direct} \approx \frac{d(O_3-NO)^{test} - IntOH^{test} \frac{d(O_3-NO)^{base}}{IntOH^{base}}}{(VOC\ reacted)_t} \quad (VII)$$

and

$$MR^{indirect} \approx MR[IntOH] \frac{d(O_3-NO)^{base}}{IntOH^{base}}. \quad (VIII)$$

Note that these approximations predict that the "indirect" mechanistic reactivity is the same as the mechanistic reactivity with respect to IntOH, except that the $d(O_3-NO)^{base}/IntOH^{base}$ ratio is used to derive the effect on $d(O_3-NO)$ from the effect on IntOH.

The first approximation upon which the above equations is based is only strictly true for VOCs which react relatively slowly and only with OH radicals, but is probably good to within the precision of experimental incremental reactivity data. The second approximation can be applied only if NO_x is in excess and the major fate of peroxy radicals formed from reactions of VOCs is reaction with NO. This is the case for most of the experiments discussed here. Under those conditions the number of peroxy radicals, and thus NO conversions, resulting from the reactions of a given VOC molecule are expected to be unaffected by the presence of other VOCs, since current mechanisms predict that cross reactions of radicals from different VOCs are of negligible importance if sufficient NO_x is present (Atkinson, 1990; Stockwell et al., 1990; Carter, 1990). However, this neglects the fact that the distribution of ROG components which react will change with the extent of reaction, which would be affected by the presence of the VOCs with large effects on radical levels.

Thus, the use of Equations (VII) and (VIII) to estimate direct and indirect reactivities is only applicable in experiments when NO_x is always in excess, and they become increasingly approximate as the IntOH levels in the test experiments deviate from those in the base case runs. Nevertheless, they provide indications of the direct and indirect components of reactivity which are useful for elucidating how

different types of VOCs affect ozone formation, and for evaluating whether chemical mechanisms are accounting for these factors correctly.

The quantities $d(\text{O}_3\text{-NO})^{\text{test}}$, $\text{IntOH}^{\text{test}}$, and $[\text{VOC}]_0$ are obtained from the results of each of the individual test experiments. However, because of run-to-run variability in temperature, light intensity, and initial reactant concentrations, the quantities $d(\text{O}_3\text{-NO})^{\text{base}}$, $\text{IntOH}^{\text{base}}$, and $[d(\text{O}_3\text{-NO})^{\text{base}}/\text{IntOH}^{\text{base}}]$ are not measured in a single experiment. Instead, these are estimates, using the results of many base case runs, of what the result of a base case experiment would be if it were carried out under the conditions of the added test VOC experiment. These are obtained by linear multiple regression analyses on the results of the base case experiments as a function of the variable run conditions which were found to be significant (Carter et al., 1993). The $[d(\text{O}_3\text{-NO})^{\text{base}}/\text{IntOH}^{\text{base}}]$ ratio was derived from separate regressions for $d(\text{O}_3\text{-NO})^{\text{base}}$ and $\text{IntOH}^{\text{base}}$ because the ratio was found to be much less dependent on run conditions than $d(\text{O}_3\text{-NO})$ or IntOH . Separate estimates are made for the three sets of base case experiments.

Determination of mechanistic reactivities requires determining amounts of test compound reacted at the various times in the experiments. These were determined either by direct measurement, after correction for dilution using

$$(\text{VOC reacted})_t = [\text{VOC}]_0 - [\text{VOC}]_t - D \int_0^t [\text{VOC}] dt, \quad (\text{IX})$$

or, if the VOC reacted only with OH radicals, by calculation from the measured IntOH and the $k\text{OH}^{\text{voc}}$, the VOC's OH radical rate constant using

$$(\text{VOC reacted})_t \cong [\text{VOC}]_0 \frac{k\text{OH}^{\text{voc}} \text{IntOH}_t}{k\text{OH}^{\text{voc}} \text{IntOH}_t + Dt} \left(1 - e^{-k\text{OH}^{\text{voc}} \text{IntOH}_t - Dt} \right) \quad (\text{X})$$

The concentration of VOC at each hourly interval was determined in the same manner as used for the tracer data when computing IntOH (Carter et al., 1993). The approach which gave the least uncertainty in estimated $(\text{VOC reacted})_t$ was used. A 20% uncertainty in $k\text{OH}^{\text{voc}}$ was used in determining which approach gave the least uncertainty, but was not used in computing the reported uncertainty in the amounts reacted and the mechanistic reactivities. The tabulations of the results indicate which approach was used.

RESULTS

Results of Base Case Experiments

Concentration-time plots for a representative base case experiment from each of the three run sets are shown on Figure 1. Results of model calculations, discussed elsewhere (Carter, 1995), are also shown. A typical Set 1 base case run in this set produced 0.22 ppm O_3 in six hours. Note that ozone formation

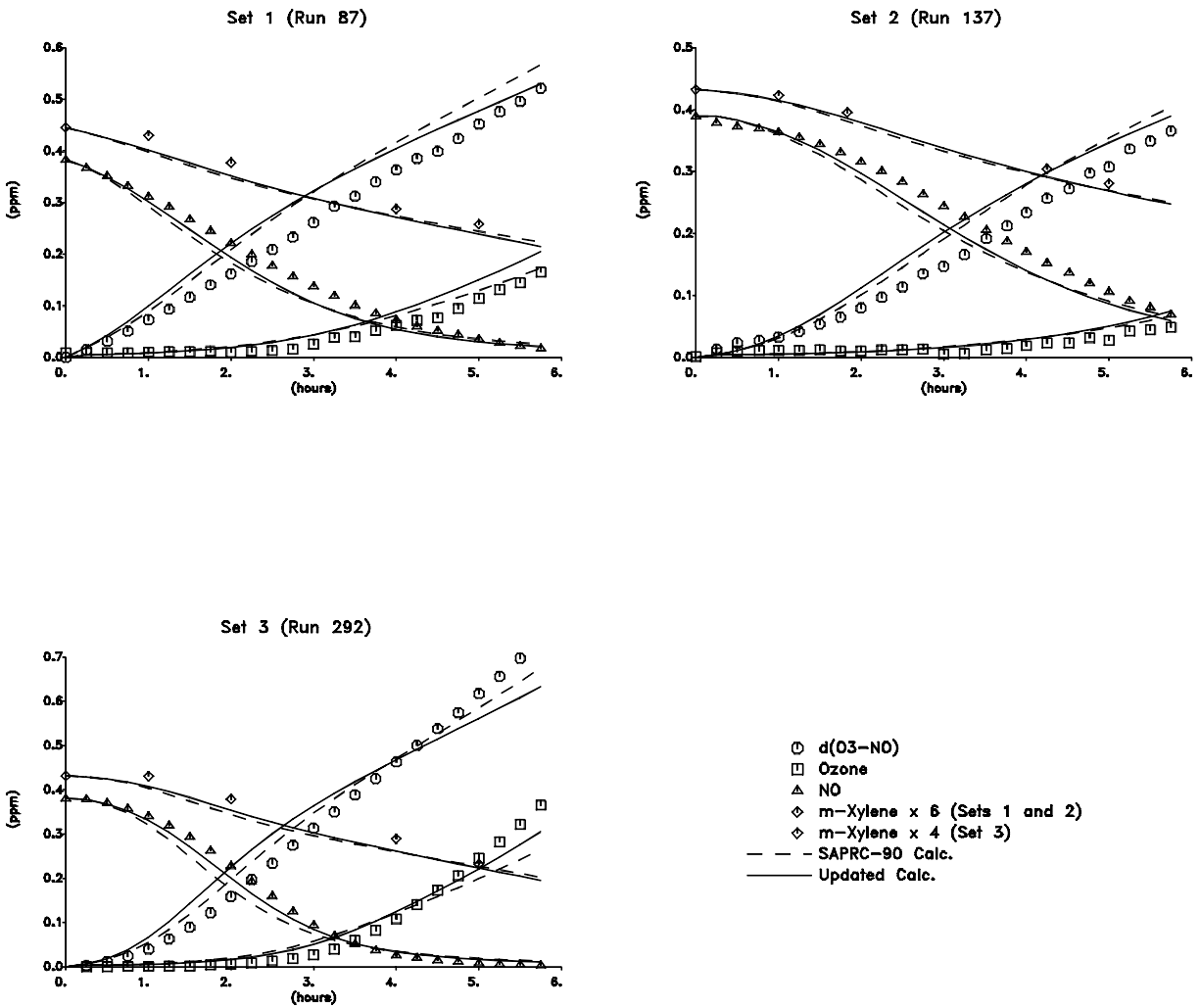


Figure 1. Concentration - time plots of selected species in representative base case runs. Results of model simulations, which are discussed in the companion paper (Carter, 1995), are also shown.

is just starting to occur when the run is terminated after 6 hours of irradiation, so the final ozone yield is highly sensitive to the ozone formation rate. This is an appropriate type of experiment to assess maximum reactivities of VOCs, since maximum reactivities are determined primarily by effect of the VOCs on ozone formation rates (Carter, 1994). A total of 15 base case experiments were conducted in Set 1, interdispersed with runs with added ethane, n-butane, propene or toluene.

The Set 1 experiments were characterized by relatively high initial NO oxidation rates compared to the subsequent sets. Model simulations of characterization runs (Carter et al., 1993) could fit the data only if it is assumed that non-negligible amounts of nitrous acid are present initially in these experiments. This is undesirable because initial HONO is a source of uncontrolled variability which cannot be measured directly, and which must be treated as an adjustable parameter when modeling the runs. HONO could be introduced either as a contaminant in the NO tank or by heterogeneous hydrolysis of the NO₂ being prepared for injection. To reduce these possibilities, for subsequent sets a modified NO_x injection procedure was employed where molecular sieves were used to remove HONO from the NO and to remove H₂O from the diluent gases. A vacuum rack was employed to store NO after purification and to prepare NO and NO₂ for injection.

The Set 2 runs had the same initial reactant concentrations as Set 1, but changing the NO_x injection procedure significantly changed the results, as shown in Figure 1. Set 2 base case runs had slower initial rates of NO oxidation, and as a result ozone formation only just began before the runs ended. Model simulations of Set 2 runs and tracer-NO_x-air control experiments (Carter et al., 1982) suggest that HONO is no longer initially present. Although only very low amounts of O₃ are formed in the Set 2 base case runs, these experiment still provide useful information concerning ozone reactivities of VOCs because the chemical processes which cause NO to be consumed when it is in excess are the same as those which cause ozone formation once the NO has reacted. A total of 27 base case runs were conducted in Set 2, interdispersed with runs with the test VOCs studied in Set 1, and several others.

For Set 3 the initial concentration of the mini-surrogate components was increased from ~3.5 to ~4.5 ppm to increase the amount of ozone formed in the base case experiment. This experiment still represented maximum reactivity conditions because O₃ was still increasing at the end of the run, indicating that the final O₃ yield is still determined by the rate of its formation. The final ozone formed in the experiment depended on the average temperature in the run (see below), but was typically ~0.30 ppm. Results of a typical Set 3 base case run are shown on Figure 1. Set 3 includes the majority of the experiments discussed here, including 92 base case runs, interdispersed with runs with all the test VOCs reported here except for propene and ethanol.

A large number of repeated base case experiments were carried out for each set so a good baseline for determining the effects of adding the test VOCs could be established. The reproducibility of these experiments are shown on Figure 2, which show plots, against experiment number, of the observed 2-, 4-, and 6-hour $d(\text{O}_3\text{-NO})^{\text{base}} / \text{IntOH}^{\text{base}}$ and of the 6-hour $d(\text{O}_3\text{-NO})^{\text{base}} / \text{IntOH}^{\text{base}}$ data. There is significant

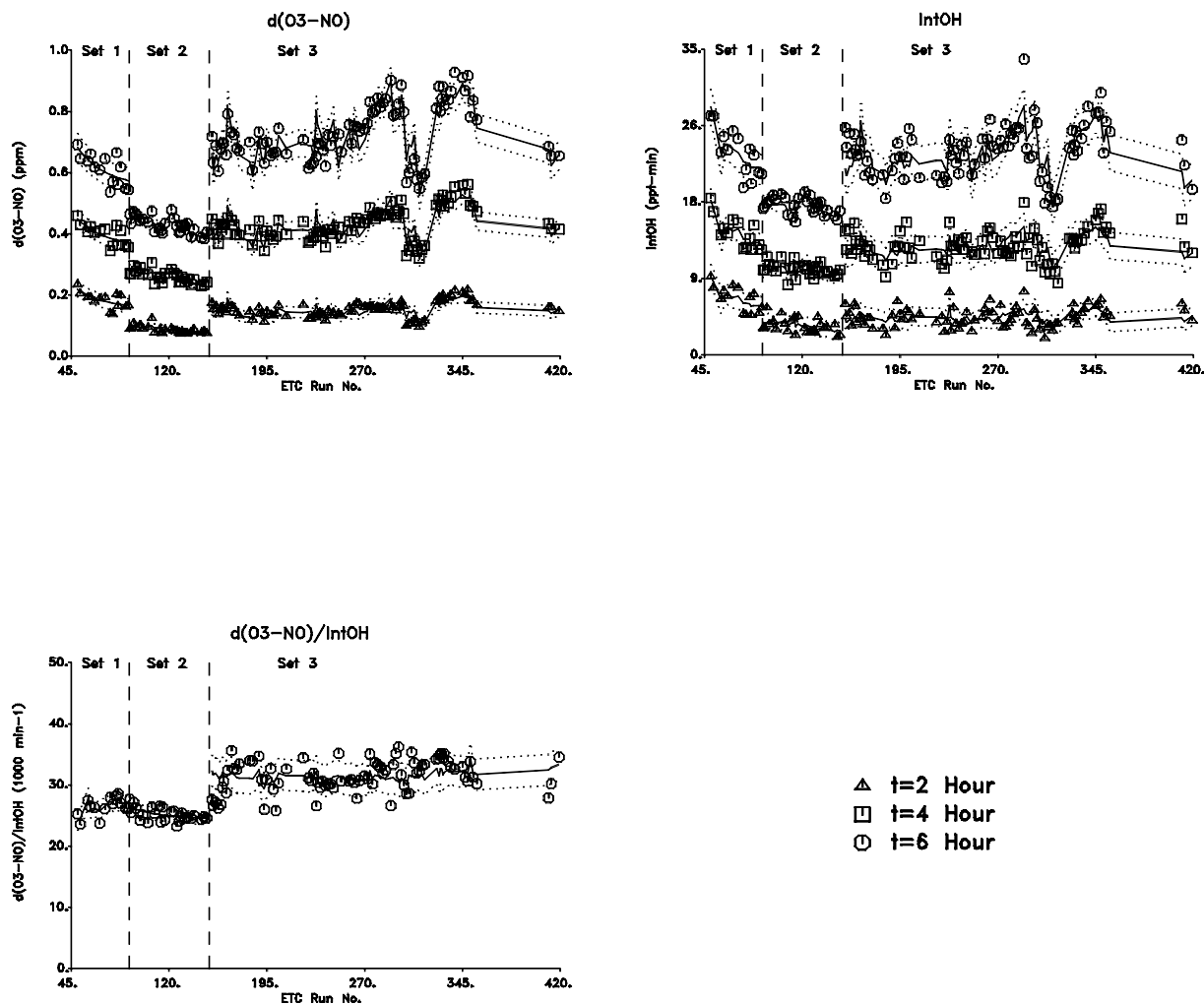


Figure 2. Plots of the $d(O_3-NO)$, IntOH and $d(O_3-NO)/IntOH$ results for selected run times against run number for the base case experiments. Solid lines show the values estimated using the regression fits, and dotted lines show the (one σ) uncertainty ranges of the estimates. (The dip in $d(O_3-NO)$ and IntOH observed around runs 300-325 are attributed to lower than usual temperatures in the laboratory — see text.)

variability in the $d(\text{O}_3\text{-NO})$ and IntOH , with the data for the Set 1 and (to a lesser extent) Set 2 runs tended to decrease with time, and the results of the Set 3 runs had large variability around the time of runs 300-320. On the other hand, the $d(\text{O}_3\text{-NO})/\text{IntOH}$ ratios were almost constant, changing only when the initial mini-surrogate was changed for Set 3.

Most of this variability in the base case results can be attributed to known variabilities in run conditions. The results of the periodic NO_2 actinometry experiments indicated that the light intensity decreased by $\sim 17\%$ during Set 1 and by $\sim 7\%$ during Set 2, presumably due to the ageing of the blacklights. This can explain the tendency of the $d(\text{O}_3\text{-NO})^{\text{base}}$ and $\text{IntOH}^{\text{base}}$ to decrease with run number for these sets. The temperature in the experiments was controlled primarily by the building air conditioner, and occasional problems resulted in average temperatures as high as 305°K or as low as 297°K in a few experiments. These deviations in temperature explain the large deviations in the results of the runs around 300-320. The initial reactant concentrations had a 5-10% variability, which can also account for some of the variability in the results.

A linear multiple regression analysis was conducted to provide a means to correct for these variations when determining the effects of the added VOCs. The temperature, light intensity (as determined by fits of the results of the separate NO_2 actinometry experiments to run number) and measured initial reactant concentrations were used as the prediction parameters, though most of the variability could be explained by the variation in temperature and light intensity alone. The solid lines on Figure 2 show the predictions of these regressions, and the dotted lines show the (one σ) uncertainties of the estimates for each run. It can be seen that the regression explained most of the observed variabilities in the $d(\text{O}_3\text{-NO})^{\text{base}}$ and $\text{IntOH}^{\text{base}}$ results. The results of these regressions were then used to predict base case values corresponding to the temperatures, light intensities, and initial reactant concentrations of each of the added test VOC runs.

The uncertainty levels of these regressions estimates are important because they provide an estimate of the run-to-run variability in our experiments, which ultimately limits the precision of the reactivity measurements. For example, the uncertainties of the estimates of the 6-hour $d(\text{O}_3\text{-NO})^{\text{base}}$ for the Set 3 runs were typically 6%, and typically the addition of a test VOC causes a 40% increase in $d(\text{O}_3\text{-NO})$. If the $d(\text{O}_3\text{-NO})^{\text{test}}$ is assumed to have the same uncertainty due to run-to-run variability as $d(\text{O}_3\text{-NO})^{\text{base}}$, then this yields a 21% estimated uncertainty in the change in $d(\text{O}_3\text{-NO})$ caused by adding the VOC. This is larger than the uncertainty in the amount of test VOC added and is usually larger than the uncertainty in the amount reacted. Thus this is the major factor affecting the stated uncertainties of most of the incremental and mechanistic reactivity measurements.

Reactivity Results

A summary of the major results of each reactivity experiment is given in Table 1. This includes the run set and run number, the amount of test VOC added and reacted, the 6-hour d(O₃-NO) incremental and mechanistic reactivities, and the direct and indirect mechanistic reactivities. Footnotes indicate whether the amounts reacted were determined by direct measurement or derived from the measured IntOH's and the VOC's OH rate constant. The uncertainties in the amounts added and reacted refer to measurement precision (not accuracy) and, when applicable, uncertainties in measured IntOH due to variabilities in the m-xylene or radical tracer data. The uncertainties in the reactivities reflect these uncertainties in amounts added or reacted, run-to-run variability (discussed above), and, for direct and indirect reactivities, uncertainties in IntOH determinations. These can be thought of as reflecting one σ confidence levels. More detailed tabulations of the results of these experiments are given elsewhere (Carter et al., 1993). Direct mechanistic reactivities are not shown for those VOCs for which the derivation is not considered to be meaningful (discussed below). Plots of selected reactivity results as a function of reaction time for selected experiments or VOCs are shown in the companion paper, which discusses model simulations of these data (Carter, 1995).

The amounts of test VOC reacted could not be determined in the formaldehyde experiments. The IntOH method (Equation X) is inappropriate because formaldehyde is significantly by photolysis, and the direct method could not be used because formaldehyde is a product from the mini-surrogate components (especially ethylene). However, to allow for comparisons with mechanistic reactivities for other VOCs, Table 1 gives estimates of their mechanistic reactivities derived from the experimental incremental reactivities and estimates of amounts reacted derived from computer model calculations (Carter, 1995). The model calculation affects only the comparison of the magnitudes of the mechanistic reactivities with those for the other VOCs, and not the results in terms of the relative importance of the direct vs indirect reactivity components. The model calculation for the amount of formaldehyde reacted is unlikely to be significantly in error because most of the added formaldehyde is calculated to react. (The stated uncertainty levels for formaldehyde Table 1 do not take modeling uncertainty into account.)

At least two, and usually more, reactivity determinations were carried out for each VOC, though not all experiments provided useful data. This is because some experiments had insufficient test VOC added for its effect to be significantly above run-to-run variability. Because of this, data from only one useful experiment each are available for n-hexane and ethylbenzene.

The results of most of the experiments were reasonably consistent with each other given the experimental uncertainties and variabilities, with the exception of one CO run and several ethane, n-butane and propene runs. In the case of CO, the CO was not purified in the first run (number 414) carried out for that compound, and a theoretically unreasonable (see below) direct mechanistic reactivity, due to an anomalously high IntOH, was observed. The CO was purified for subsequent runs, which gave more theoretically reasonable results. Three of the nine ethane runs gave higher reactivities than the other runs,

Table 1. Summary of Reactivity Results for the Test VOC Experiments.

Set Run	Added (ppm)	Reacted		Incremental (mol O ₃ -NO/mol added)	Reactivity Mechanistic (mol O ₃ -NO/mol reacted)		
		(ppm)	(meth) [a]		Total	Indirect [b]	Direct [c]
Carbon Monoxide							
4 418	102.	0.731 (4%)	I	0.0048 (10%)	0.7 + 0.1	-0.3 + 0.3	0.9 + 0.3
4 416	147.	0.879 (5%)	I	0.0034 (11%)	0.6 + 0.1	-0.3 + 0.3	0.8 + 0.3
				Wt. Avgs =	0.6 + 0.1	-0.3 + 0.2	0.9 + 0.2
Ethane							
1 68	9.99	0.092 (4%)	I	[e]			
1 62	17.6	0.153 (4%)	I	0.0142 (23%)	1.6 + 0.4	-0.5 + 0.4	2.1 + 0.4
1 79	17.9	0.140 (5%)	I	0.0075 (43%)	1.0 + 0.4	-0.5 + 0.5	1.5 + 0.4
1 73	18.1	0.129 (5%)	I	0.0053 (60%)	0.7 + 0.4	-1.0 + 0.5	1.7 + 0.4
1 88	24.3	0.189 (5%)	I	0.0123 (20%)	1.6 + 0.3	-0.3 + 0.4	1.9 + 0.3
2 92	17.5	0.114 (5%)	I	0.0067 (18%)	1.0 + 0.2	-0.3 + 0.3	1.3 + 0.2
2 99	17.6	0.107 (6%)	I	0.0069 (17%)	1.1 + 0.2	-0.5 + 0.3	1.6 + 0.3
3 332 [d]	20.0	0.191 (4%)	I	0.0129 (22%)	1.4 + 0.3	-0.4 + 0.5	1.8 + 0.5
3 333 [d]	21.1	0.247 (3%)	I	0.0217 (12%)	1.9 + 0.2	0.5 + 0.4	1.4 + 0.4
3 235	43.4	0.324 (5%)	I	0.0057 (23%)	0.8 + 0.2	-0.5 + 0.3	1.2 + 0.2
				Wt. Avgs =	1.0 + 0.3	-0.5 + 0.2	1.5 + 0.3
Propane							
3 226	11.28	0.250 (6%)	I	[e]			
3 305	20.3	0.473 (6%)	I	0.0154 (18%)	0.7 + 0.1	-0.5 + 0.2	1.2 + 0.2
3 230	28.0	0.526 (8%)	I	0.0171 (12%)	0.9 + 0.1	-0.6 + 0.2	1.5 + 0.2
				Wt. Avgs =	0.8 + 0.2	-0.6 + 0.1	1.3 + 0.2
n-Butane							
1 59	1.82	0.127 (5%)	I	0.0654 (49%)	0.9 + 0.5	-1.0 + 0.8	1.8 + 0.7
1 51	2.35	0.164 (5%)	I	0.0625 (43%)	0.9 + 0.4	-1.2 + 0.5	2.2 + 0.5
1 53 [d]	5.22	0.385 (4%)	I	0.0395 (30%)	0.5 + 0.2	-0.4 + 0.2	0.9 + 0.2
1 82	6.75	0.276 (7%)	I	0.0282 (31%)	0.7 + 0.2	-1.0 + 0.3	1.7 + 0.2
1 86	6.98	0.280 (8%)	I	0.0333 (25%)	0.8 + 0.2	-1.0 + 0.3	1.8 + 0.2
2 135	6.03	0.215 (9%)	I	0.0217 (16%)	0.6 + 0.1	-0.8 + 0.1	1.4 + 0.2
2 97	6.17	0.214 (9%)	I	0.0281 (12%)	0.8 + 0.1	-1.0 + 0.2	1.7 + 0.2
2 94	7.11	0.272 (8%)	I	0.0189 (19%)	0.5 + 0.1	-0.7 + 0.1	1.1 + 0.1
3 224	10.00	0.358 (9%)	I	0.0212 (27%)	0.6 + 0.2	-1.1 + 0.3	1.7 + 0.2
				Wt. Avgs =	0.6 + 0.1	-0.9 + 0.2	1.5 + 0.3
Isobutane							
3 228	2.69	0.135 (6%)	I	[e]			
3 303	6.65	0.306 (6%)	I	0.0322 (27%)	0.7 + 0.2	-0.9 + 0.3	1.6 + 0.2
3 241	10.32	0.457 (6%)	I	0.0488 (11%)	1.1 + 0.1	-0.6 + 0.2	1.7 + 0.2
3 232	20.8	0.545 (11%)	I	0.0327 (9%)	1.3 + 0.2	-0.7 + 0.2	2.0 + 0.2
				Wt. Avgs =	1.1 + 0.2	-0.7 + 0.2	1.7 + 0.2
n-Hexane							
3 201	1.44	0.049 (25%)	I	-0.0831 (47%)	-2.5 + 1.3	-11.1 + 3.3	8.6 + 2.4
3 209	1.61	0.101 (13%)	I	-0.105 (33%)	-1.7 + 0.6	-3.8 + 1.0	2.2 + 0.7
				Wt. Avgs =	-1.8 + 0.6	-4.5 + 2.3	2.7 + 1.8
Isooctane							
3 291	10.07	0.402 (11%)	I	0.0147 (40%)	0.4 + 0.2	-1.5 + 0.3	2.0 + 0.3
3 293	10.73	0.430 (11%)	I	0.0136 (41%)	0.3 + 0.1	-1.4 + 0.3	1.8 + 0.2
				Wt. Avgs =	0.4 + 0.1	-1.4 + 0.2	1.8 + 0.2
n-Octane							
3 239	1.57	0.083 (19%)	I	-0.234 (16%)	-4.4 + 1.1	-6.8 + 1.8	2.4 + 0.9
3 237	1.68	0.120 (14%)	I	-0.222 (15%)	-3.1 + 0.6	-4.6 + 1.0	1.4 + 0.5
				Wt. Avgs =	-3.4 + 0.8	-5.1 + 1.3	1.7 + 0.6
Ethene							
3 203	0.176	0.077 (26%)	D	1.09 (31%)	2.5 + 1.0	2.3 + 1.3	
3 199	0.354	0.173 (14%)	D	1.31 (14%)	2.7 + 0.5	1.7 + 0.6	1.0 + 0.6
				Wt. Avgs =	2.6 + 0.4	1.8 + 0.6	1.0 + 0.6
Propene							
1 65	0.087	0.074 (2%)	D	1.75 (37%)	2.1 + 0.8	1.2 + 1.0	1.0 + 0.9
1 72	0.124	0.098 (3%)	D	0.750 (61%)	1.0 + 0.6	0.8 + 0.7	0.1 + 0.6
2 110	0.083	0.058 (3%)	D	2.39 (11%)	3.4 + 0.4	0.6 + 0.5	3.0 + 0.5
2 106	0.089	0.066 (3%)	D	2.37 (10%)	3.2 + 0.3	1.5 + 0.4	1.7 + 0.4
2 108	0.091	0.064 (3%)	D	1.79 (13%)	2.6 + 0.3	1.4 + 0.4	1.4 + 0.4
2 118	0.168	0.128 (3%)	D	1.48 (10%)	1.9 + 0.2	0.8 + 0.2	1.0 + 0.2
				Wt. Avgs =	2.4 + 0.7	1.0 + 0.3	1.3 + 0.8

Table 1 (continued)

Set Run	Added (ppm)	Reacted		Incremental (mol O ₃ -NO/mol added)	Reactivity Mechanistic (mol O ₃ -NO/mol reacted)		
		(ppm)	(meth) [a]		Total	Indirect [b]	Direct [c]
Isobutene							
3 257	0.108	0.108	(2%) D	2.66 (20%)	2.7 + 0.5	2.3 + 0.8	
3 255	0.195	0.195	(2%) D	2.13 (14%)	2.1 + 0.3	2.3 + 0.5	
3 253	0.211	0.211	(2%) D	2.27 (12%)	2.3 + 0.3	2.0 + 0.4	
				Wt. Avgs =	2.3 + 0.2	2.2 + 0.3	
trans-2-Butene							
3 309	0.071	0.071	(2%) D	5.29 (15%)	5.3 + 0.8	4.1 + 1.3	
3 307	0.095	0.095	(2%) D	4.29 (14%)	4.3 + 0.6	4.3 + 1.0	
				Wt. Avgs =	4.6 + 0.7	4.3 + 0.8	
Benzene							
3 265 [3]	5.78	0.123	(7%) I	0.0257 (22%)	1.2 + 0.3	0.9 + 0.4	-0.3 + 0.5
3 263 [3]	6.77	0.159	(7%) I	0.0246 (20%)	1.0 + 0.2	0.7 + 0.4	-0.3 + 0.4
				Wt. Avgs =	1.1 + 0.2	0.7 + 0.3	-0.3 + 0.3
Toluene							
1 64	0.061	0.014	(12%) D	1.27 (74%)	5.7 + 4.3	4.1 + 5.2	
1 69	0.095	0.022	(11%) D	1.83 (33%)	7.9 + 2.7	8.4 + 3.2	
1 61	0.174	0.047	(9%) D	2.31 (14%)	8.5 + 1.4	6.7 + 1.5	
2 101	0.171	0.035	(12%) D	1.23 (10%)	5.9 + 0.9	4.5 + 1.0	
2 103	0.176	0.040	(11%) D	1.33 (9%)	5.8 + 0.8	4.3 + 0.9	
				Wt. Avgs =	6.3 + 1.1	4.8 + 1.2	
Ethylbenzene							
3 313	0.103	0.015	(19%) I	[e]			
3 311	0.106	0.020	(14%) I	[e]			
3 315	0.247	0.043	(15%) I	0.836 (28%)	4.9 + 1.6	1.1 + 2.1	3.8 + 1.9
o-Xylene							
3 259	0.063	0.026	(6%) D	4.21 (21%)	10.3 + 2.2	8.8 + 3.4	
3 261	0.065	0.030	(5%) D	3.98 (22%)	8.5 + 1.9	7.9 + 2.9	
				Wt. Avgs =	9.3 + 1.7	8.2 + 2.2	
m-Xylene							
3 301	0.055	0.036	(9%) D	5.14 (21%)	7.9 + 1.8	6.1 + 2.5	
3 207	0.056	0.036	(9%) D	5.96 (18%)	9.4 + 1.8	8.3 + 2.7	
3 196	0.058	0.036	(9%) D	4.54 (23%)	7.3 + 1.7	5.2 + 2.4	
3 344 [4]	0.079	0.045	(9%) D	5.90 (9%)	10.5 + 1.3	8.2 + 2.0	
				Wt. Avgs =	9.1 + 1.5	7.0 + 1.8	
p-Xylene							
3 348	0.075	0.037	(2%) I	2.12 (38%)	4.3 + 1.6	3.9 + 2.5	
3 346	0.080	0.041	(2%) I	3.37 (23%)	6.6 + 1.5	3.9 + 2.1	
				Wt. Avgs =	5.6 + 1.6	3.9 + 1.6	
135-trimethyl-Benzene							
3 249	0.045	0.044	(2%) D	12.6 (10%)	13.0 + 1.3	13.2 + 2.2	
124-trimethyl-Benzene							
3 267	0.037	0.027	(3%) D	6.90 (22%)	9.6 + 2.1	5.1 + 3.2	
3 269	0.041	0.030	(3%) D	6.00 (23%)	8.3 + 1.9	6.6 + 2.9	
				Wt. Avgs =	8.8 + 1.6	5.9 + 2.3	
123-trimethyl-Benzene							
3 299	0.036	0.030	(2%) D	9.23 (18%)	10.9 + 2.0	11.2 + 3.1	
3 297	0.043	0.037	(2%) D	8.39 (17%)	9.8 + 1.6	10.7 + 2.5	
				Wt. Avgs =	10.3 + 1.4	10.9 + 2.0	
Methanol							
3 287	0.826	0.029	(4%) I	[e]			
3 289	2.37	0.094	(3%) I	0.0455 (55%)	1.1 + 0.6	-0.1 + 0.9	1.4 + 1.0
3 285	7.70	0.337	(3%) I	0.0503 (15%)	1.1 + 0.2	0.5 + 0.3	0.7 + 0.3
				Wt. Avgs =	1.1 + 0.2	0.5 + 0.3	0.7 + 0.4
Ethanol							
2 133	2.94	0.207	(6%) I	0.0600 (14%)	0.9 + 0.1	-0.2 + 0.1	1.1 + 0.1
2 131	3.12	0.220	(6%) I	0.0569 (12%)	0.8 + 0.1	-0.2 + 0.1	1.0 + 0.1
2 138	3.14	0.215	(6%) I	0.0526 (13%)	0.8 + 0.1	-0.1 + 0.1	0.9 + 0.1
				Wt. Avgs =	0.8 + 0.1	-0.2 + 0.1	1.0 + 0.1
Isopropanol							
2 148	4.55	0.608	(5%) I	0.0902 (5%)	0.7 + 0.0	0.1 + 0.0	0.6 + 0.1
3 157	0.977	0.202	(13%) D	0.132 (46%)	0.6 + 0.3	0.1 + 0.4	0.3 + 0.4
3 159	1.20	0.383	(8%) I	0.111 (44%)	0.3 + 0.2	0.2 + 0.2	0.1 + 0.2
3 155	1.35	0.244	(3%) I	0.190 (23%)	1.1 + 0.2	0.5 + 0.4	0.4 + 0.4
				Wt. Avgs =	0.7 + 0.1	0.1 + 0.1	0.6 + 0.1

Table 1 (continued)

Set Run	Added (ppm)	Reacted		Incremental (mol O ₃ -NO/ mol added)	Reactivity Mechanistic (mol O ₃ -NO/mol reacted)		
		(ppm)	(meth) [a]		Total	Indirect [b]	Direct [c]
Dimethyl Ether							
3 295	2.11	0.205 (4%)	I	0.0964 (29%)	1.0 + 0.3	-0.4 + 0.4	1.5 + 0.4
3 283	2.12	0.214 (4%)	I	0.141 (19%)	1.4 + 0.3	-0.4 + 0.4	1.9 + 0.4
3 281	3.41	0.352 (4%)	I	0.107 (16%)	1.0 + 0.2	-0.1 + 0.2	1.2 + 0.2
3 279	4.05	0.439 (4%)	I	0.118 (12%)	1.1 + 0.1	0.0 + 0.2	1.1 + 0.2
				Wt. Avgs =	1.1 + 0.1	-0.1 + 0.2	1.3 + 0.3
Formaldehyde							
3 352	0.100	(0.079 [f])		2.61 (22%)	3.3 + 0.7	4.1 + 1.2	
3 357	0.257	(0.210 [f])		1.47 (15%)	1.8 + 0.3	2.7 + 0.5	
				Wt. Avgs =	2.0 + 0.6	2.9 + 0.7	
Acetaldehyde							
3 335	0.645	0.260 (6%)	D	0.264 (33%)	0.7 + 0.2	-0.8 + 0.4	1.5 + 0.3
3 338	1.21	0.433 (7%)	D	0.145 (32%)	0.4 + 0.1	-0.9 + 0.2	1.3 + 0.2
				Wt. Avgs =	0.5 + 0.2	-0.9 + 0.2	1.4 + 0.2

[a] Method used to derive amount reacted: D = direct method (Equation IX); I = IntOH Method (Equation X).

[b] Estimated using Equation (VIII).

[c] Estimated using Equation (VII).

[d] Data from this run appear to be anomalous and were not used for computing average reactivities. See text.

[e] Uncertainty is greater than magnitude of reactivity.

[f] The amounts of formaldehyde reacted could not be determined. The amounts reacted used to derive the mechanistic reactivities were estimated using model calculations of fractions reacted. The model calculations used the updated mechanism as discussed by Carter et al. (1995). Uncertainty estimates in mechanistic reactivities do not include uncertainty in amounts reacted.

with run 333 being clearly anomalous. This is attributed to contamination by some reactive impurity in the ethane sample — relatively large amounts of ethane (over 20 ppm in the case of the most anomalous run) are needed to yield a useful reactivity measurement. One n-butane run had an anomalously high IntOH reactivity, and another had an anomalously high direct reactivity compared to the other seven runs carried out with this compound. In the case of propene, two of the Set 2 runs had 6-hour d(O₃-NO) reactivities which were about twice as high as two Set 1 runs or the Set 2 run with the most precise reactivity measurement. The ethane and CO runs with probable contaminants (332, 333 and 412) and the most anomalous n-butane run (53) were not used in computing the average reactivities for the purpose of evaluating model predictions, but the data from the other runs mentioned above were not rejected.

The experiments with added benzene were somewhat unique in that these were the only runs where a "true" ozone maximum was observed. This can be seen on Figure 3, which compares the concentration-time plots for d(O₃-NO) in a representative benzene run with comparable data for several other VOCs. This is predicted by the model calculations (Carter, 1995). These results indicate that O₃ is NO_x-limited in these experiments, since the decline in the ozone concentration can be attributed to the NO_x being consumed, ending ozone formation, since NO_x is required for ozone to form. (The uncorrected NO₂ data do not give a good indication of NO_x consumption, since the instrument also responds to organic nitrates and HNO₃ [Winer et al., 1974]. The calculated NO₂ does not include this interference.) This means that the assumptions underlying the derivations of the direct and indirect reactivities are not valid throughout these runs, though they are valid in the 3-4 hours in the run before the NO_x is consumed. For

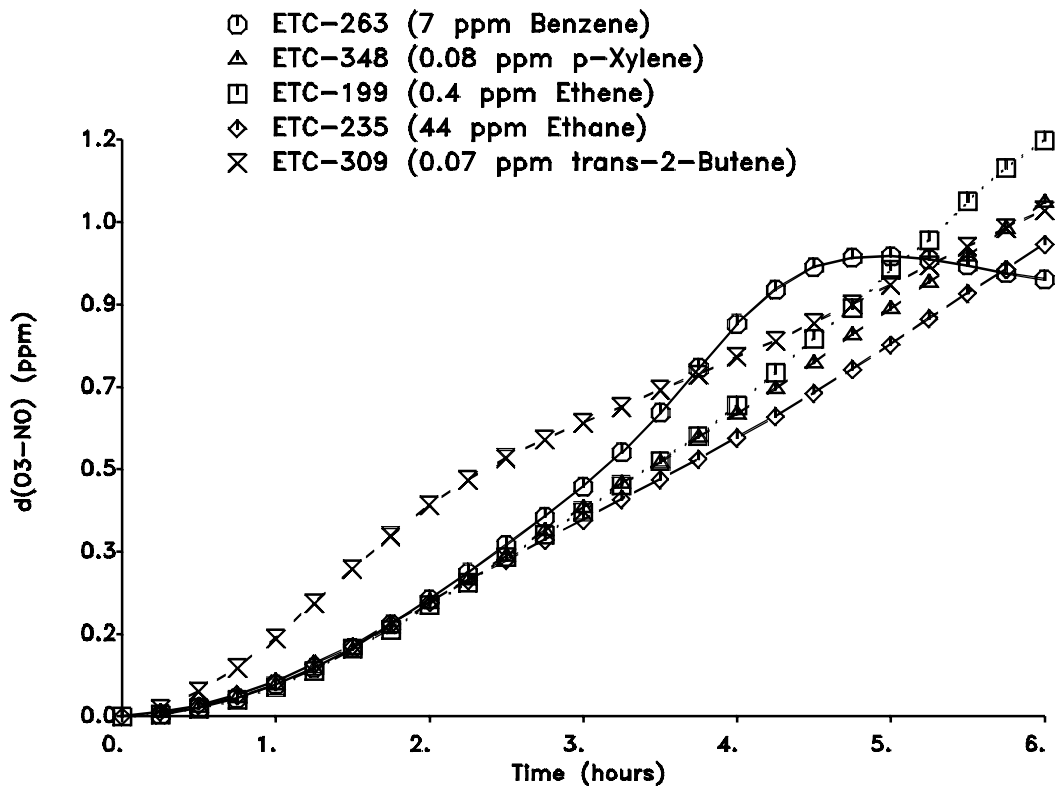


Figure 3. Concentration-time plots for $d(O_3-NO)$ in representative reactivity experiments for benzene and selected other VOCs where comparable initial NO_x oxidation rates were observed.

better comparability with the data shown for the other VOCs, which are all for conditions where NO_x is still remaining, the data shown on Table 1 for benzene are for $t=3$ hours, rather than $t=6$. Benzene is the only VOC for which NO_x -limited ozone formation was apparently observed; for all other added VOC runs the production of ozone was still occurring at a significant rate at the end of the runs.

Table 1 also shows the weighed averages of the mechanistic reactivities for the various compounds. Data for experiments which are considered to be anomalous, as indicated in the discussion above and the footnotes to the table, are not included in the averages.

DISCUSSION

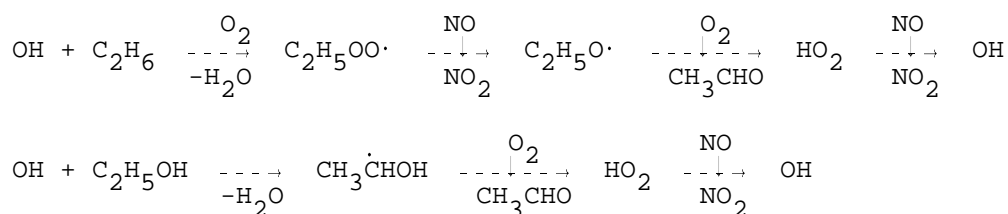
The results of these experiments are consistent with previous experimental (Carter and Atkinson, 1987) and computer modeling (e.g., Dodge, 1984; Carter and Atkinson, 1989a; Chang and Rudy, 1990; Carter, 1991) studies in showing that different VOCs have significantly different effects on ozone formation, even after differences in reaction rates are taken into account (Carter and Atkinson, 1989a; Carter, 1991). The measure which has the most direct relationship to the effect of a VOC's reactions on ozone formation is its mechanistic reactivity with respect to $d(O_3\text{-NO})$. This quantity, expressed as moles O_3 formed + NO oxidized per mole VOC reacted, ranges from highs of approximately 10-15 for the trialkylbenzenes to lows of ~5 for n-octane. On a per-carbon basis, the compound with the highest measured $d(O_3\text{-NO})$ mechanistic reactivity is formaldehyde (with an average of ~2 moles $O_3\text{-NO}$ formed per mole C reacted), followed by methanol (1.4), the alkylbenzenes (but not benzene) (0.7-1.5), the alkenes (0.6-1.3), and ethane (~0.6). These are the compounds which cause the most ozone formation once they react. Propane, n-butane, isobutane, isooctane, benzene, acetaldehyde, and the C3+ alcohols and ethers also promote ozone formation, but with much less efficiency, with the efficiency being lowest for isooctane and benzene. The C6+ n-alkanes inhibit NO oxidation and ozone formation in our experiments.

The processes by which VOCs promote or inhibit ozone formation involve the interaction of a number of factors. VOCs promote ozone formation by reacting to form peroxy radicals which react to oxidize NO and shift the NO, NO_2 , ozone photostationary state towards higher ozone levels. The maximum amount of ozone formation which can be directly caused by a VOC's reactions is the amount of NO it oxidizes when it reacts. However, VOCs also affect ozone formation indirectly, by affecting how much ozone is formed from the reactions of all other VOCs. If the reactions of a VOC enhance or inhibit overall radical levels, it would affect how rapidly all VOCs present react and form ozone. This is important for determining maximum reactivities of VOCs, since these reflect primarily how VOCs affect ozone formation rates (Carter, 1991). The presence of NO_x is required for ozone formation to occur, and if the reactions of a VOC enhance the rate of NO_x removal, it will reduce the maximum ozone formation potential from reactions of all VOCs. This affects reactivities only when ozone is NO_x limited, which is not the case for the experiments discussed here, except for those with benzene.

The measurements of direct mechanistic reactivities provide an indication of the amount of ozone formation directly caused by the reaction of the VOCs, independent (to a first approximation) of how the VOC's reactions affect the reactions of other VOCs. Unfortunately, experimental uncertainties tend to dominate the derivation of this quantity for compounds with large positive IntOH reactivities, and the direct reactivities derived for the alkylbenzenes and most of the alkenes have such high uncertainties that they are probably not meaningful. The assumption that the VOC is not affecting ratios of amounts of ozone directly formed to amounts of ROG reacted for the base ROG components may break down when the test VOC has a large effect on the radicals in the system, because the test VOC would also have a large effect on the extent of reaction of the base ROG components. For that reason, direct mechanistic

reactivities for VOCs with indirect (i.e., radical) reactivities greater than ~2 are not shown on Table 1. As discussed above, the assumptions involved in the derivation of direct reactivities are not valid for the final periods of the added benzene runs, where ozone is apparently NO_x limited. However, information could be obtained concerning the direct reactivity of benzene from the data from the early periods of the runs.

Useful information concerning direct reactivities were obtained for the alkanes, alcohols, and ethers. In most cases the results were consistent with our understanding of the atmospheric reactions of these VOCs. For example, the major processes consuming both ethane and ethanol involve formation of acetaldehyde, but two NO to NO₂ conversions are involved in the ethane mechanism, while only one is involved for ethanol (excluding the estimated 10% reaction at the methyl group):



Thus, the expected direct mechanistic reactivities are 2 for ethane and 1 ethanol. These are consistent with the observed values of 1.7 ± 0.3 and 1.0 ± 0.1 , respectively. The other alcohols are expected to have similar mechanisms as ethanol, and indeed they also have relatively low direct mechanistic reactivities compared to the alkanes. CO is also expected to have a direct mechanistic reactivity of ~1, and this is indeed what is observed (except for the experiment where the CO was not purified). The MR^{direct} values for the alkanes are in the 1.5 - 2.5 range, tending to increase with the size of the molecule. The higher alkanes have the highest direct mechanistic reactivities of all the VOCs studied. This is expected because higher alkanes have an increased tendency to have alkoxy radical decompositions and isomerization which cause multi-step mechanisms involving additional NO oxidations.

Note that the direct reactivity by itself gives a poor prediction of a VOC's effect on ozone. For example, despite having the highest direct mechanistic reactivities, the higher alkanes form little ozone or are ozone inhibitors in these experiments. The effect of the VOCs on radical levels, which are directly measured by the IntOH reactivities (which are used to derive the indirect reactivities), appears to be a more important factor. This is shown on Table 1, where it can be seen that for many VOCs the indirect reactivities are higher in magnitude than the direct reactivities. Without exception, the VOCs which are the highest in indirect (i.e., IntOH) reactivities also have the highest in d(O₃-NO) reactivities, and those with the most negative IntOH reactivities are also the strongest ozone inhibitors. Thus the major factor accounting for extremes in reactivity is not the amount of ozone the VOC forms directly, but the extent to which it affects how much ozone is formed from other VOCs.

Approximately half the compounds studied tended to enhance radical levels under the conditions of these experiments, with the rest tending to inhibit radicals to various degrees. All the VOCs which enhanced radicals had high mechanistic reactivities towards forming ozone. These included formaldehyde, methanol, the alkenes and the alkylbenzenes. The enhancement caused by formaldehyde is attributed to its direct photolysis to form radicals, while in the case of methanol and the aromatics the enhancement is attributed to the formation of radical initiating products. In the case of methanol the radical initiating product is formaldehyde, while in the case of the aromatics the known radical initiating products are α -dicarbonyls such as methyl glyoxal. Aromatics also apparently form other photoreactive products which have not been identified as such, since only models which assume this (or which use unrealistically high α -dicarbonyl yields) can account for the high reactivities of aromatics. In the case of the alkenes, radical formation can come directly from the reaction of the alkene with ozone, or indirectly from the formation of photoreactive products such as formaldehyde.

Most other VOCs tend to suppress radical levels. In the case of alkanes this is attributed to removal of peroxy radicals by reactions with NO to form alkyl nitrates, while in the case of acetaldehyde and ethanol (which forms acetaldehyde), this is attributed to the removal of acetyl peroxy radicals by reaction with NO₂ to form PAN. In the case of isobutane, removal of alkoxy radicals by reaction with NO₂ to form a nitrate also appears to be significant under the conditions of these experiments (Carter et al., 1993), though this is expected to be less important in the atmosphere because the NO₂ levels are generally lower. However, the inhibition by the peroxy + NO reactions in the other alkane systems or the PAN formation from acetaldehyde are expected to be of comparable importance in the atmosphere as they are in these experiments, since the relative importance of these reactions are not dependent on total NO₂ levels (though it does depend on the NO₂/NO ratio).

It is interesting to note that CO also has a slight tendency to suppress radicals, despite the fact that no radical terminations are involved in its photooxidation. Its only reaction is to convert OH to HO₂, and it forms no reactive products. Thus, simply converting NO to NO₂ (as results when HO₂ reacts with NO to regenerate OH) must cause at least some suppression of integrated OH radical levels in these experiments. This is probably due to the enhanced reactions of OH with NO₂ resulting from the more rapid increase of NO₂ caused by this conversion. Since essentially all VOCs have some reactions which convert NO to NO₂, they would all inherently have this slight tendency to reduce radicals, even if they or their products did not have direct radical termination reactions.

Most of the compounds which suppress radical levels still have positive d(O₃-NO) reactivities, i.e., still cause enhanced ozone formation under the conditions of our experiments. In these cases the additional ozone formation caused by the VOC's direct reactions is sufficient to counter their effects on reducing ozone formation from other VOCs (see Table 1, above). In the case of acetaldehyde, direct radical formation from its photolysis would also counter inhibition due to PAN formation, which becomes increasingly important with reaction time since PAN formation becomes more favorable as NO is converted to NO₂. This is consistent with the fact that the IntOH mechanistic reactivity of acetaldehyde

decreases with reaction time [see Figure 6 in the companion paper (Carter, 1995)]. In general, as one would expect, the efficiency in ozone formation (i.e., the $d(O_3\text{-NO})$ mechanistic reactivities) decrease as the tendency to suppress radicals increased, and when the suppression becomes sufficiently large, it overwhelms the positive effect on ozone formation of the VOC's direct reactions, making the compound a net ozone inhibitor. This is the case for the C_{6+} n-alkanes under the conditions of our experiments.

Thus for VOCs which are radical inhibitors, there is a balance between opposing effects of the VOC causing additional ozone formation from its direct reactions, and its causing lower radicals and thus less ozone formation from other VOCs. Which effect is more important can vary depending on conditions. Model simulations suggest that this balance is somewhat different under atmospheric conditions than in these experiments, since n-hexane and n-octane, which are correctly predicted by the model to have negative reactivities in these experiments, are predicted by the same model to have positive (though small) maximum incremental reactivities in the atmosphere (Carter, 1991, 1994). Apparently effects on radicals are somewhat less important in affecting ozone reactivities in the atmosphere, or in the presence of the more complex atmospheric mixtures, than in these experiments. However, the small magnitudes of the atmospheric reactivities of these radical inhibiting VOCs indicate that the radical inhibition is still significantly suppressing their reactivities in the atmosphere.

CONCLUSIONS

We believe that this study has provided data which will be useful for reducing the chemical mechanistic uncertainties in maximum incremental reactivity scales for ozone formation in the atmosphere. Data were obtained which can test model predictions of maximum reactivities of a variety of different VOCs, including representative alkanes, alkenes, aromatic hydrocarbons, alcohols, and ethers. Other types of compounds were also studied (Carter et al., 1993), which will be discussed in subsequent papers. A number of these compounds have never been studied previously in environmental chamber experiments suitable for model evaluation, except perhaps as parts of complex mixtures of many other VOCs, or in experiments whose results are dominated by poorly characterized chamber effects. This study has provided the most useful presently available data concerning ozone reactivities of alkanes, because results of experiments where alkanes are irradiated in the absence of other VOCs are so dominated by chamber effects that they are essentially useless for mechanism testing (Carter and Lurmann, 1991). It has also provided a needed addition to the existing data set for the other VOCs, most of which have not been previously studied in this way.

It is important, however, to recognize that reactivities measured in these experiments should not be extrapolated to the atmosphere without taking into account the differences in conditions between these experiments and the atmosphere. These differences include spectral characteristics of the light sources, higher absolute pollutant concentrations, the lack of dilution and continuous emissions, the lack of background or entrained pollutants, and the highly simplified base ROG surrogate in the experiments. The

extrapolation to atmospheric conditions can be carried out by using these data to evaluate the chemical mechanisms used in the airshed models to calculate atmospheric reactivity, or by using models to derive relationships which can be used to estimate atmospheric reactivities from those measured in the chamber.

The ultimate practical benefit of these data will come when the mechanisms used to calculate VOC reactivities in the atmosphere are updated to take these results into account. An initial evaluation of chemical mechanisms using the data from this work, and additional data needs required for mechanism evaluation, is discussed in the companion paper (Carter, 1995).

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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. (1990): "Gas-Phase Tropospheric Chemistry of Organic Compounds: A Review," Atmos. Environ., 24A, 1-24.

- 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," J. Geophys. Res., in press.
- CARB (1990): "Low-Emission Vehicles/Clean Fuels -- Technical Support Document," Mobile Source Division, Research Division, Stationary Source Division, and Technical Support Division, California Air Resources Board, Sacramento, CA.
- CARB (1991): "Proposed Reactivity Adjustment Factors for Transitional Low-Emissions Vehicles: Technical Support Document," California Air Resources Board, Sacramento, CA., September 27.
- Carter, W. P. L. (1990): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," Atm. Environ., 24A, 481-518.
- Carter, W. P. L. (1991): "Development of Ozone Reactivity Scales for Volatile Organic Compounds", EPA-600/3-91/050, August.
- 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 Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Submitted to Atmos. Environ.
- Carter, W. P. L. and R. Atkinson (1987): "An Experimental Study of Incremental Hydrocarbon Reactivity," Environ. Sci. Technol., 21, 670-679
- Carter, W. P. L. and R. Atkinson (1989a): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environ. Sci. and Technol., 23, 864-880.
- 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., 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," Atmos. Environ., 25A, 2771-2806.
- Carter, W. P. L., J. A. Pierce, I. L. Malkina, D. Luo, and W. D. Long (1993): "Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Report on Coordinating Research Council Project ME-9 and California Air Resources Board Contract No. A032-0692, April 1.

- Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1994): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO_x," Draft 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. September 10.
- Chang, T. Y. and S. J. Rudy (1990): "Ozone-Forming Potential of Organic Emissions from Alternative-Fueled Vehicles," *Atmos. Environ.*, 24A, 2421-2430.
- Dodge, M. C. (1984): "Combined Effects of Organic Reactivity and NMHC/NO_x Ratio on Photochemical Oxidant Formation -- A Modeling Study," *Atmos. Environ.*, 18, 1657-1665.
- 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.
- 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.
- Johnson, G. M. (1983): "Factors Affecting Oxidant Formation in Sydney Air," in "The Urban Atmosphere -- Sydney, a Case Study." Eds. J. N. Carras and G. M. Johnson (CSIRO, Melbourne), pp. 393-408.
- NRC (1991): "Rethinking the Ozone Problem in Urban and Regional Air Pollution", National Research Council Committee on Tropospheric Ozone Formation and Measurement, National Academy Press, Washington, DC.
- Russell, A. G. (1990): "Air Quality Modeling of Alternative Fuel Use in Los Angeles, CA: Sensitivity of Pollutant Formation to Individual Pollutant Compounds," the AWMA 83rd Annual Meeting, June 24-29.
- 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.
- Tuazon, E. C., R. Atkinson, S. M. Aschmann, M. A. Goodman and A. M. Winer (1988): "Atmospheric Reactions of Chloroethenes with the OH Radical," *Int J. Chem. Kinet.*, 20, 241-265.
- Tuazon, E. C., R. Atkinson, A. M. Winer and J. N. Pitts, Jr. (1984): "A Study of the Atmospheric Reactions of 1,3-Dichloropropene and Other Selected Organochlorine Compounds," *Arch. Environ. Contam. Toxicol.*, 13, 691-700.
- Winer, A. M., J. W. Peters, J. P. Smith, and J. N. Pitts, Jr. (1984): "Response of Commercial Chemiluminescent NO-NO₂ Analyzers to Other Nitrogen-Containing Compounds," *Environ. Sci. Technol.*, 8, 1118-1121.
- Zafonte, L., P. L. Rieger, and J. R. Holmes (1977): "Nitrogen Dioxide Photolysis in the Los Angeles Atmosphere," *Environ. Sci. Technol.*, 11, 483-487.