

ATMOSPHERIC CHEMISTRY AND CHEMICAL MECHANISMS

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W.P.L. Carter¹, D.R. Crosley², D.M. Golden², L.T. Iraci²,
J.C. Johnston², and P.A. Makar³

¹ University of California, Riverside

² SRI International

³ Environment Canada

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INTRODUCTION

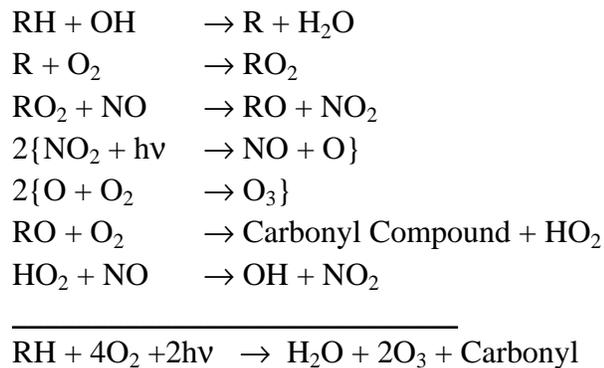
In this chapter we summarize the status of understanding of the gas phase chemistry and photochemistry that is the basis of the mechanisms used in models of the chemical transformations involved in ozone formation. Given that gas phase processes lead to the formation of secondary aerosol particles and that verification of gas-phase mechanisms is often

based on smog chamber data that is influenced by wall effects, we discuss some heterogeneous chemistry in this section as well.

OVERVIEW OF ATMOSPHERIC VOC OXIDATION

The gas phase chemistry important in photochemical smog has been the subject of much study over the last fifty years. Our current understanding of the elementary reactions are given in various reviews and evaluations (Atkinson, 1989; 1990; 1991; 1994; 1997; Atkinson and Carter, 1984; Atkinson et al., 1997; NASA, 1997), the most recent being the NARSTO assessment of the atmospheric chemistry of VOCs and NO_x prepared by Atkinson (1999). The discussion in those documents will be only briefly summarized here.

The oxidation of hydrocarbons begins with the abstraction of a proton by the hydroxyl radical. In the presence of NO_x , the subsequent reactions result in the conversion of molecular oxygen to ozone, as illustrated below for a general alkane.



Ozone production continues as long as sufficient NO_x is present so that reactions of peroxy radicals (RO_2) with NO compete effectively with their reactions with other peroxy radicals.

Note that the OH radical levels are particularly important in affecting the O_3 formation rate in the presence of NO_x because reaction with OH is a major (and in many cases the only) reaction pathway for VOCs. Thus, if a VOC reacts in such a way that it initiates radical levels (or forms a product that does), it would enhance the rate of ozone formation from all VOCs present. This would result in a larger effect on O_3 than other VOCs that react at the same rate. If the VOC's reactions in the presence of NO_x have a radical termination process, it will cause all other VOCs to react more slowly and form less O_3 . In some cases, this reduced O_3 formation from other VOCs may be more than enough to counter the ozone formation from the VOC's direct reactions. In such cases the VOC would have a negative effect on the formation of O_3 in the presence of NO_x (Carter and Atkinson, 1989; Carter, 1994).

Although an OH reaction is the major atmospheric loss process for most VOCs, some VOCs are also consumed to a nonnegligible extent by reaction with O_3 or NO_3 or by direct

photolysis. In most cases, these processes will also form RO₂ radicals, which convert NO to NO₂. In addition, and perhaps more significantly, many of these processes initiate the formation of “new” radicals, which ultimately cause higher OH radical levels and thus higher rates of reactions of the other VOCs present. This is particularly significant in the case of compounds that can photolyze, because photolysis reactions are the main sources of radicals in photochemical smog. For example, it is because of photolysis that formaldehyde has a much larger effect on ozone than one would estimate based on its OH rate constant alone.

Ozone formation stops once NO_x is consumed to sufficiently low levels. NO_x is removed from the atmosphere more rapidly than total VOCs, since the NO_x + OH rate constant exceeds that of most hydrocarbon + OH rate constants, and since the NO_x removal processes generally involve a single step (such as the reaction of OH with NO₂) while most VOC reactions form products which are also reactive VOCs,. Therefore, NO_x availability ultimately limits O₃ formation. If the NO_x levels are high enough that it is not consumed before the end of the day, it is mainly the rate of the VOC's reactions, and their effects on OH radicals, which affect ozone levels. Indeed, high levels of NO_x inhibit O₃ because reaction of OH with NO₂ reduces OH levels. High nighttime NO_x levels may also reduce ozone, via conversion to NO₃ and HNO₃. If, however, NO_x is consumed before the end of the day, O₃ is NO_x-limited, and increasing NO_x would cause increased O₃ formation. Under such conditions, if a VOC's reactions caused NO_x to be removed more rapidly than if the VOC were absent (such as, for example, by forming nitrogen-containing products such as PANs from aldehydes and nitrophenols from aromatics), this would have a negative effect on O₃ yields, and tend to reduce the amount of O₃ formation caused by the VOCs reactions. *Under highly NO_x-limited scenarios, this becomes sufficiently important to cause VOCs with significant NO_x sinks in their mechanisms to have negative effects on final O₃ yields—even for those that may have highly positive effects on O₃ under conditions where NO_x is plentiful.*

Another factor affecting the behavior of VOCs and NO_x in ozone formation is competition for the hydroxyl radical. When the instantaneous VOC-to-NO₂ ratio is sufficiently low, OH reacts predominantly with NO₂, removing radicals and retarding ozone formation. Under these conditions, a decrease in NO_x concentration favors ozone formation. At a sufficiently low concentration of NO_x, or a sufficiently high VOC-to-NO₂ ratio, a further decrease in NO_x favors peroxy-peroxy reactions, which retard ozone formation by removing free radicals from the system. Although, in general, higher VOC concentrations mean more ozone, increasing NO_x may lead to either more or less ozone depending on the prevailing VOC-to-NO_x ratio. As a result, the rate of ozone production is not simply proportional to the amount of NO_x present; at a given level of VOC, there exists a NO_x concentration at which a maximum amount of ozone is produced, or an optimum VOC-to-NO_x ratio. Using an average VOC-OH reaction rate constant, representing reactions occurring in an average urban mix of VOCs, the ratio of the OH-NO_x to OH-VOC rate constants is about 5.5. Thus, this optimum VOC-to-NO_x ratio is approximately 5.5:1 for an average urban area, with the VOC concentration expressed on a carbon atom basis. For ratios less than this optimum ratio, NO_x increases lead to ozone decreases, while at ratios higher than this optimum ratio, NO_x increases lead to ozone increases.

Thus it can be seen that there are many mechanistic factors which must be appropriately represented in models used to predict the effects of a VOC on ozone formation. The specific mechanisms used to represent these processes in airshed models are discussed in a later section. First, we will give a brief summary of the current state of knowledge of the various types of reactions involved.

CURRENT STATE OF KNOWLEDGE

Inorganic Reactions

In contrast to the many remaining uncertainties in our knowledge of VOC chemistry, reactions involving non-carbon-containing species are more thoroughly understood. The inorganic reactions are continuously reviewed by the NASA Stratospheric Data Panel (NASA, 1997) and the IUPAC Panel (Atkinson et al., 1997). Very recent data from the NOAA Aeronomy Laboratory (Ravishankara, 1998, personal communication) has elucidated the quantum yield for $O(^1D)$ formation from ozone in the 320 nm region. Also, new data (Brown et al., 1998; Dransfield et al., 1998) and re-evaluations of older data (Williams and Golden, 1998, personal communication) for the reaction of $OH+NO_2$ have removed much of the uncertainty associated with this reaction. However, current evaluations still give different recommendations concerning this extremely important reaction.

One serious uncertainty in the knowledge of inorganic species concerns the formation of HONO. This important species, which photolyzes to produce OH, is probably formed heterogeneously in the atmosphere and in smog chambers. The characterization of this heterogeneous process is crucial, both for modeling the atmosphere and for understanding smog chamber data. Several studies have examined the heterogeneous formation of HONO for a variety of aerosol types. The most likely reaction pathway for HONO formation is via $2NO_2 + H_2O \rightarrow HONO + HNO_3$, rather than $NO_2 + NO(N_2O_3) + H_2O \rightarrow 2 HONO$ (Andres-Hernandez et al., 1996; Kleffmann et al., 1997). The formation rate is highly dependent on the aerosol substrate and its age. Laboratory determined aerosol uptake coefficients for NO_2 range from 10^{-1} on freshly formed flame soot (Gerecke et al., 1997), to 10^{-4} on aged soot (Kamm et al., 1997) to 10^{-6} on aqueous aerosols (Kleffmann et al., 1997). The observed rapid change in soot aerosol HONO formation rates with time (Ammann et al., 1998) may indicate that chamber HONO formation may be strongly affected by the availability of reducing surface molecules on the chamber walls. Studies of HONO production on sulfuric acid and aqueous droplets (Iraci and Tolbert, 1997; Bambauer et al., 1994) suggest that heterogeneous processes occurring outside urban areas may also affect the HONO budget. The heterogeneous processes involving HONO formation are probably different in the atmosphere than in environmental chambers, but the extent to which they are different is unclear and represents an uncertainty in the use of chamber-evaluated mechanisms in atmospheric simulations.

Another important process, which is presumed to be primarily heterogeneous, is the hydrolysis of N_2O_5 to HNO_3 . This reaction can affect ozone yields because it can be a non-

negligible ozone sink, because it amounts to the formation of relatively unreactive HNO_3 from the reaction of ozone with NO_2 . The gas-phase reaction is believed to be relatively slow, but the heterogeneous processes are non-negligible in chamber experiments, and their importance in the atmosphere varies with environmental conditions. Recent ambient atmosphere measurements and simulations (Makar et al., 1998c) indicate substantial losses of nitrate to the particle phase following the reaction of NO_x with O_3 at night. The formation rate of gas-phase HNO_3 was significantly enhanced through the effects of heterogeneous chemistry.

Organic Reactions

The most complex and uncertain area of atmospheric chemistry is the photooxidation reactions of the many types of VOCs that can be emitted. Our current state of knowledge of the atmospheric reactions of VOCs is discussed in various reviews by Atkinson (1989; 1990; 1991; 1994), the most recent being the NARSTO assessment (Atkinson, 1999). Current European laboratory work can be found in the proceedings of the Eurotrac-2 Chemical Mechanism Development Subproject meetings (Ammann and Lorenzen, 1997).

The aspects of the organic reactions that must be considered are the rate constants, the photooxidation steps, and the mechanisms of the products formed. These are summarized briefly below.

The least uncertain aspect of the atmospheric reactions of the organic compounds concerns their initial rates of reaction with OH or NO_3 radicals or with ozone. Many references appear in the Atkinson reviews (Atkinson, 1989; 1991; 1994; Atkinson and Carter, 1984) and in the NASA and IUPAC compilations (Atkinson et al., 1997; NASA, 1997). Modern rate constant measurements are often precise, and where individual rate constants have been measured they are often known fairly well. Nevertheless, the stated uncertainties in rate constants in the compilations are almost always 25% or greater and higher uncertainties should be assumed if there is only a single measurement, and if the compound is of low volatility or has high surface affinity. For most compounds it is usually not particularly difficult or costly to obtain these rate constants if no data are available.

Methods exist for estimating rate constants for the reactions of VOCs with OH and NO_3 radicals which can be used when data are not available (e.g., Kwok and Atkinson, 1995; Atkinson, 1997). These estimates may be good to +/- 50% in the most favorable cases, but a factor of 2 is probably a more realistic uncertainty estimate for most VOCs. Obviously the estimates are probably not reliable if the VOC has functional groups which have not been studied. Also, it should be noted that ozone rate constants appear to be difficult to estimate reliably (see Atkinson and Carter, 1984).

Data concerning rate constants for the reactions of the radical intermediates are much more limited and are usually restricted to the simplest cases. It has been assumed that the higher molecular weight radicals react with the same rate constant.

An interesting question is the extent to which reactions that are pressure dependent, such as radical-radical processes, have been treated correctly in the chemical mechanisms. In addition, the special nature of H₂O as a “third body” may need to be taken into account.

A very important process involving the reaction of peroxy radicals with NO remains to be understood on a fundamental level. This interaction seems to follow two competing pathways. One pathway forms alkoxy radicals and NO₂, perpetuating the free radical chemistry, whereas the other forms organic nitrates and removes radicals from the system. The branching ratio for this process has a significant effect on a VOC's ozone reactivity because organic nitrate formation is a radical and NO_x sink process, while the alkoxy + NO₂ branch is neither. This branching ratio has been measured accurately for only a few types of peroxy radicals; for most VOCs this has to be treated as an adjustable parameter, or the existing product yield data must be extrapolated to similar compounds.

Much of the complexity in organic photooxidation mechanisms comes from the various alternative reactions alkoxy radicals can undergo. These include, but may not be limited to: (1) reactions with O₂ forming HO₂ and the corresponding carbonyl compound (for radicals with alpha hydrogens), (2) beta-scission decomposition forming a carbonyl compound and another radical; and (3) hydrogen shift isomerizations forming a hydroxy substituted radical. More recently, Tuazon et al. (1998) found that alkoxy radicals formed in the photooxidations of esters can undergo a previously-unsuspected “ester rearrangement” reaction involving hydrogen transfer to the carbonyl group.

Absolute rate constants have been measured for only a few of the most simple alkoxy radical reactions, and most of the other available data concerns ratios of rate constants which can be inferred from results of product studies. This type of information is becoming available for an increasing number of systems because of ongoing product studies, though these branching ratios still need to be estimated for the large majority of VOCs emitted into the atmosphere.

Based on the limited information available, Atkinson (1997) developed methods for estimating rate constants (or rate constant ratios) for the alkoxy and peroxy radical reactions occurring in the alkane and alkene + OH reaction systems. This was recently extended by Carter (unpublished work, 1998) to the reactions of other classes of compounds, primarily various oxygenates (this is discussed further below). Although these estimates provide means to derive mechanisms which represent the “best estimate” given available data, the estimation methods only approximately fit the available data. For example, it would not be unexpected for the nitrate yield estimates for RO₂+NO reactions to be off by 50% to a factor of 2, or for the alkoxy radical branching ratios to be off by a factor of 5.

As discussed by Atkinson (1999), much greater uncertainties are involved in our understanding of the atmospheric reaction mechanisms of aromatic hydrocarbons and the mechanisms for the reactions of ozone with double bonds. Progress has been made in these areas, but the available information is far from sufficient to derive predictive chemical mechanisms for modeling ozone and other impacts of VOCs. In both cases, uncertain parts of the mechanisms have to be parameterized or adjusted so that model predictions are consistent with environmental chamber data.

Very limited information is available concerning the atmospheric reactions of compounds containing atoms other than C, H, or O. Although many halogenated compounds have been studied in the context of their impacts on remote atmospheres or the stratosphere, data on their ozone impacts are extremely limited, and recent studies of trichloroethylene and alkyl bromides show that current estimated mechanisms cannot successfully predict their reactivities in environmental chamber experiments. Ozone impacts of volatile siloxanes have also been studied, but the reactivity data obtained are difficult to reconcile with results of product studies (Hobson et al., 1997).

The various areas where research is most needed concerning the atmospheric reactions of organics are summarized below. Most of these are from the conclusions of the NARSTO evaluation (Atkinson, 1999).

- Rate constants and mechanisms for reactions of peroxy radicals with NO, HO₂, other RO₂, and NO₂ radicals. This would include additional data for nitrate yields from peroxy + NO reactions, particularly for non-hydrocarbon reactions.
- Branching ratios for the competing reactions of alkoxy radicals, particularly those not formed from alkanes and alkenes.
- Details of the reactions of ozone with alkenes and other VOCs containing double bonds *under atmospheric conditions*. Total radical yields are particularly important in model simulations of VOC reactivity.
- Thermal decompositions and other atmospherically important reactions of the higher PAN analogues, such as that formed from methacrolein and isoprene.
- Mechanisms and products of the reactions of OH - aromatic adducts with O₂ and NO₃. *Quantitative* yield information and studies of the reactions (including photolysis) of these aromatic products are especially needed.
- Tropospheric chemistry of the oxygenated products formed from the radical - NO_x and radical - radical reactions in the photooxidation of the VOCs requires study.
- Quantitative understanding of reaction sequences leading to secondary organic aerosol formation.
- Information concerning reactions of halogen-containing radicals under tropospheric conditions is also needed before reactivities of halogen-containing compounds can be assessed with any accuracy.
- Information concerning the reactions of radicals formed from the reactions of amines and other nitrogen-containing compounds is needed before reactivities of such compounds can be assessed with any accuracy.

Theoretical Estimates

In recent years the development of *ab initio* theoretical methods for the calculation of potential energy surfaces allows the direct computation of some rate constants. (See for example Irikura and Frurip, 1998). Transition state theory can also be utilized in this regard. These

computational techniques have not yet been exploited to any significant extent in the uncertain areas of atmospheric chemistry, and the time seems right for a serious theoretical look at many of these processes. Some exploratory studies have used these methods to suggest mechanistic pathways for the photooxidation of naphthalene (Lane et al. 1996). These theoretical techniques should be tested through comparison to known processes (e.g., oxidation of the lower C number alkanes and alkenes), then applied towards predicting mechanisms and reaction rates which are currently unknown. *Ab initio* methods may provide a useful means for reducing the time required for laboratory confirmation of these processes, by suggesting specific product compounds for analysis in chamber experiments.

Estimates of heats of reaction are also used in many of the estimation methods referenced above, and often can be used to rule out chemically unreasonable reaction schemes. Group additivity methods based on the work of Benson (1976) are obviously very useful in this regard, but there are all too often groups for which no data are available. Theoretical calculations could potentially be very useful in providing the data needed to support application of thermochemically-based estimation methods and evaluating proposed reaction sequences.

CHEMICAL MECHANISMS

The chemical mechanism is the portion of the airshed models that represents the gas-phase reactions discussed in the previous section. Because of the large number of compounds emitted or formed in polluted troposphere and the large numbers of reactions they, and their reactive products, can undergo, these mechanisms must necessarily contain significant simplifications and approximations. Furthermore, because of limitations in our knowledge, these mechanisms must necessarily contain assumptions and extrapolations to represent processes that are important but whose details are unknown. Different mechanism developers can apply different approaches to simplify the mechanism to make it tractable and can use different assumptions and extrapolation methods when representing the main areas of uncertainty.

In the past the main limiting factor has been computer-related limitations, but this is becoming much less of a factor now as computers become more powerful and as software used to implement mechanisms become more capable and flexible. The main limitation now is our level of knowledge of the many processes which must be represented, and our ability to generate and manage highly complex reaction schemes in a manner that is appropriate given our level of knowledge. Obviously, it is not appropriate or a good use of computer power to use highly complex and explicit reaction schemes if the added complexity is speculation and the resulting predictions no more accurate than predictions from the highly condensed mechanisms used in the current generation of models. Given the development of the “Morphecul” approach of Jeffries and co-workers (see Dodge, 1999) and the mechanism generation approach being developed by Carter (summarized below), in the very near future our level of knowledge is going to be the main factor limiting the level of detail and size of the current mechanisms.

Most, though not all, of the mechanisms used in the current generation of models have been summarized by Bergin et al. (1997) and Dodge (1999). The major mechanisms relevant to

current reactivity assessments are summarized below. When considering mechanisms to be used in reactivity assessment, the following issues need to be addressed:

- How is uncertainty dealt with?
- What are the approximations and lumping approaches used?
- How up-to-date are the rate constants used?
- To what extent have the mechanisms been evaluated?

Summary of Chemical Mechanisms Currently in Use

The Carbon Bond IV (CB4) mechanism (Gery et al, 1988, 1989) is important because it is widely used in regulatory models. Its rate constants and reaction schemes represent the state of knowledge as of approximately 1997, although some important rate constants have been updated since then (see Dodge, 1999). This uses a highly condensed method to represent reactions of individual VOCs, with the goal being to predict ozone from ambient mixtures as accurately as possible but with high computational efficiency. (Lumping techniques are discussed in more detail below.) It was evaluated against a large number of environmental chamber experiments (Gery et al, 1988), and was reasonably successful in predicting ozone formation from complex mixtures. However, it is not suitable for assessing reactivities of individual VOCs because of its high level of condensation, and some of the simplifications and approximations it employs are now believed to be inappropriate.

The RADM-2 mechanism developed by Stockwell et al. (1990) is used in the EPA's Regional Acid Deposition (RADM) model and is the only mechanism currently incorporated in the EPA's Models-3 system. Its rate constants represent the state of knowledge as of 1989. It is a condensed mechanism which represents reactions of groups of similarly reacting VOCs with a single model compound with fixed parameters, so it, like CB4, is not strictly suitable for reactivity assessment of individual VOCs. It accounts for reactivity differences among individual VOCs in a given class by using "reactivity weighting", where the amount of model compound used to represent the VOC is greater if the rate of reaction of the compound is greater, and vice-versa (see discussion of compression methods, below). A relatively limited number of model compounds are used to represent reactions of higher molecular weight organic oxidation products. However, it represents more classes of compounds using reactivity compression, which probably introduces fewer errors than the condensation approach used in CB4. This mechanism has the most detailed (and probably most accurate) representation of the low-NO_x peroxy radical reactions than most of the other mechanisms, including the SAPRC mechanisms discussed below. This mechanism was extensively evaluated against available chamber data by Carter and Lurmann (1990), and performed reasonably well in simulating ozone in experiments with complex mixtures and individual compounds which this mechanism is designed to represent. Its treatment of many of the more important uncertain reactions is similar to that of the SAPRC-90 mechanism, discussed below.

The RADM-2 mechanism was recently updated and expanded by Stockwell et al. (1997) who renamed it the RACM ("Regional Atmospheric Chemistry Mechanism"). It is the most updated of the published mechanisms in terms of its rate constants and the mechanisms for its

explicit reactions. It has a similar condensation approach as RADM-2, though the number of classes of compounds which are represented separately have been increased. It was evaluated against a limited number of chamber experiments, and against the predictions of the more thoroughly evaluated RADM-2 mechanism.

The SAPRC mechanisms are important because they are designed specifically for VOC reactivity assessment, and have been employed to generate reactivity scales which have been or are being considered for use in regulatory applications (Carter, 1994; CARB, 1993). Condensed versions of this mechanism have been adapted for use in Eulerian airshed models (e.g., Lurmann et al, 1991; see also references in the “Reactivity Assessments” section), but its primary use in reactivity assessments has been to calculate incremental reactivities in EKMA-type model scenarios (Carter, 1994). This mechanism can separately represent the reactions of over 100 different types of VOCs by using generalized reactions with variable parameters which are assigned based on the known or estimated rate constants and products of the compounds. This feature makes it particularly useful for assessing reactivities of a large number of VOCs. Nevertheless it uses a very condensed representation of the reactive organic oxidation products (though not as condensed as CB4, RADM-2 or RACM), and uses a much more condensed representation of peroxy + peroxy reactions than does RADM-2 or RACM (though not as condensed as CB4).

The best documented version is SAPRC-90 (Carter, 1990), whose rate constants represent the state of the art as of 1989, and is thus approximately contemporary with CB4 and RADM-2. The SAPRC-90 mechanism has been evaluated against results of approximately 500 chamber experiments and in most cases fits the ozone data to within $\pm 30\%$, which, in the case of complex mixtures representative of atmospheric conditions, is comparable to the performance of RADM-2 (Carter and Lurmann, 1991) or CB4 (Carter, unpublished results). However, the performance is obviously better in simulations of the individual compounds that SAPRC-90 represents explicitly, but which are not well represented by the model species used in the condensed mechanisms.

The SAPRC mechanism has been updated several times since SAPRC-90, based on results of chamber experiments on individual compounds (e.g., Carter et al., 1993; Carter, 1995; Carter et al., 1997), though the updates have not been comprehensively documented in peer-reviewed journals. The latest version incorporates a complete update of the rate constants and updated estimates for a variety of compounds, and slight improvements in the level of detail in representing reactive products and low-NO_x peroxy radical reactions. The automated procedure for generated alkane reaction mechanisms was updated based on the results of the evaluation of Atkinson (1997) and an independent evaluation of alkoxy radical reactions (Carter, unpublished results, 1998), and it was extended to include alkenes (with no more than one double bond), and many classes of oxygenates including alcohols, ethers, glycols, esters, aldehydes, ketones, glycol ethers. Although many of the estimated rate constants and rate constant ratios are highly uncertain (see discussion of atmospheric chemistry, above), this procedure provides a consistent basis for deriving “best estimate” mechanisms for chemical systems which are too complex to be examined in detail in a reasonable amount of time. The mechanism generation program allows for assigning or adjusting rate constants or branching ratios in cases where data are available, or where adjustments are necessary for model simulations to fit chamber data. Various “lumping rules” are used to convert the detailed generated mechanisms and product distributions into the

lumped reactions and model species distributions actually used in the model. The use of this program has permitted estimation of detailed mechanisms for a much larger number of compounds than otherwise would be possible.

The latest updated SAPRC mechanism was evaluated using the indoor environmental data base, including relevant runs carried out very recently for VOC reactivity assessment (see reports at <http://cert.ucr.edu/~carter/bycarter.htm>). Uncertainty classifications were derived for the various classes of VOCs represented in the mechanisms. Additional information concerning this mechanism, the listing and uncertainty classifications of the VOCs which it can represent, and updated MIR and other reactivity calculations are available at <http://cert.ucr.edu/~carter/r98tab.htm>.

An alternative to the SAPRC mechanisms for reactivity assessment are being developed and applied by researchers in Europe (e.g., Derwent and Jenkin, 1991; Andersson-Skold et al., 1992; Derwent et al., 1996; Jenkin et al., 1997). These mechanisms are based on the concept of representing the reactions, the significant or representative VOCs, and also their major or representative oxidation products, explicitly. Probably the most detailed of these is the "Master Chemical Mechanism" (MCM) of Derwent and co-workers, which can be seen at <http://www.chem.leeds.ac.uk/Atmospheric/MCM/main.html>. Although these mechanisms are nominally explicit, condensation is employed by excluding minor processes and products, in effect representing them by major or representative species. Also, as with all other mechanisms, no attempt is made to represent the unknown aromatic ring fragmentation products in detail. These mechanisms are not used in the United States because the model software is not adapted to mechanisms of this size. Also, they have not yet (to our knowledge) been evaluated against results of environmental chamber experiments.

In Canada, the ADOM-II mechanism (Stockwell and Lurmann, 1989; Lurmann et al., 1986) is currently used for reactivity simulations. The mechanism went through several stages of development, from its initial creation as an urban-scale ozone prediction mechanism (Lurmann et al., 1986), updating and comparison to 490 chamber experiments (Carter et al., 1986; Lurmann et al., 1987), and "updating the most condensed mechanism of Lurmann et al.(1987) to be consistent with Atkinson (1988) and Carter (1988) and adding species and reactions important for long-range transport and acid-deposition modeling" (Stockwell and Lurmann, 1989). Further smog chamber testing of the ADOM-II mechanism is currently underway for comparison with the AURAMS mechanism, described below.

A new Canadian mechanism is under development for gas-phase and particulate modeling in the AURAMS model (Moran et al., 1998) which will have updated rate constants and a greater level of chemical detail than the ADOM-II mechanism (Makar et al., 1998a). Some of the features of this mechanism currently include:

- A revised and detailed biogenic hydrocarbon mechanism, based on the detailed isoprene mechanism of Carter and Atkinson (1996), the photolysis data of Raber and Moortgat (1996) and Gierczak et al. (1997), and the alpha-pinene mechanistic data of Hakola et al. (1994) and Hatakeyama et al. (1989, 1991). Methacrolein and methylvinylketone are included, as are their oxidation pathways by OH, O₃ and NO₃, as is the formation of MPAN. Explicit RO₂-RO₂ reactions between the generic isoprene organic radical, the

alpha-pinene organic radical, and the eighteen other organic radicals of the mechanism are included. In the context of biogenic chemistry, the mechanism was recently used to simulate the emission, transport and chemical loss of biogenic compounds with good agreement to ambient measurements (see Makar et al., 1998b for further mechanism description and references).

- An updated aromatic mechanism, with a simplified broken-ring oxidation pathway based on the work of Becker (1994), with muconaldehyde, oxybutanal and methylglyoxal as dicarbonyls formed from the broken-ring pathway. The non-ring-breaking pathway products include benzaldehyde and a generic aromatic nitric anhydride cycle. Toluene, di- and tri-methyl benzene are the three aromatic species resolved.
- Internal and terminal bond alkenes resolved as separate species, with separate radicals and pathways for NO_3 oxidation as well as OH oxidation. The biradical stabilization pathway for the alkenes (including the biogenic species isoprene and alpha-pinene) is based on the work of Horie et al. (1994).
- Five alkane species; methane, ethane, propane, C_4 - C_5 alkanes and C_6 - C_7 alkanes; the last being generic species.
- Alcohols up to C_3 are resolved, organic acids are represented by formic and acetic acid, as is peroxypropyl nitrate. A single generic organic peroxide is resolved, although current plans are to include an additional generic hydroxy-organic peroxide to better simulate biradical stabilization following ozone oxidation of alkenes.
- Detailed, speciated organic radical reactions ($\text{RO}_2 + \text{RO}_2$, $\text{RO}_2 + \text{R(O)O}_2$, $\text{RO}_2 + \text{HO}_2$, $\text{RO}_2 + \text{NO}_3$, $\text{RO}_2 + \text{NO}$). The self-reactions and HO_2 reactions are of particular concern for low NO_x environments with high VOC emissions, such as the boreal forests of Canada. The mechanisms and rates of these reactions are highly uncertain, and are based on extrapolation from the limited available laboratory data as well as the rate estimation procedures of Atkinson (1997b).

Both the AURAMS mechanism and the ADOM-II mechanism have been compared to a limited number of smog chamber data (UNC chamber single species tests); further testing against complex mixtures and SAPRC data was to take place by March of 1998. The tests to date have shown that the new mechanism shows a significant improvement in the ability to predict chamber data compared to the ADOM-II mechanism. Further testing will take place using the SMVGEAR code (Jacobson and Turco, 1994) to facilitate rapid comparison to a large number of chamber runs.

Lumping Techniques for Atmospheric Chemical Mechanisms

The gas-phase reaction mechanisms used in predicting atmospheric reactivity frequently have simplified or compressed VOC kinetics. Detailed, highly speciated mechanisms are available, but their use can be impractical for large numbers of simulations, for either multiple box model calculations or the chemical integrations for a regional reaction/transport model. For some types of integration routines, the processing time required to perform a single chemical integration may be dependent on a power law function of the number of variables. The storage

of the mixing ratios of the hundreds to thousands of species found in the real atmosphere may also place a burden on the available computational resources. These combined limitations of processing time and memory space have resulted in the creation of simplified mechanisms for atmospheric chemistry.

The main use for these simplified mechanisms has been the prediction of acid precipitation and ozone production. As a result, the mechanisms have attempted to preserve the reactivity of the simulated atmosphere, while using less model species than occur in the real atmosphere.

One common aspect to all of the reduced mechanisms is the use of a smaller number of oxygenated species than is present in the real atmosphere. For example, the OH radical oxidation of a long chain alkane may create several organic radicals, in turn leading to the formation of several different carbonyls after reaction with NO. A compressed reaction mechanism may represent these species with a single organic radical and a single carbonyl. The rationale for this form of simplification is two-fold. First, the rate of the $RO_2 + NO$ reaction is relatively invariant across different RO_2 species, hence a single RO_2 may be sufficient to accurately convert NO to NO_2 within the model. Second, the carbonyl species are assumed to have a secondary importance to the initial hydrocarbon with regards to ozone formation, and that simplifications to broad classes of oxygenated species are therefore justifiable. The second assumption is weaker than the first; recent laboratory work on the mechanistic pathways of species like the aromatic compounds have shown that the oxygenated product species can be very reactive, with the reactivity varying widely for the different carbonyls formed. This has resulted in increased speciation of oxygenated compounds in mechanisms which have been recently published (e.g., RACM; Stockwell et al., 1997) or are under development (Canadian AURAMS mechanism), compared to their predecessors.

The unoxxygenated species have been “reduced” (or “lumped” or “compressed”) using several methods, usually in two to three stages. The detailed, speciated emissions are combined into a smaller number of species representing broad chemical classes, which are then combined to the model speciation using reactivity weighting (cf., Middleton et al., 1990, and the Emissions section of this report). Finally, in the chemical mechanism itself, some form of lumping is used to attempt to create the same product distribution as in the unlumped mechanism. This stage deals with the question of how to combine reactions such as



to give a net reaction:



The focus of the problem being how to determine a net reaction rate constant k_3 and new product coefficients A and B which have the same effect on the OH, net hydrocarbon, and product mixing ratios as the original system of two (or more) reactions.

Different methods for mechanism compression include those based on reactivity, concentration weighting, and reactivity across carbon bonds within the molecules of each individual species. Bond (CB4) and concentration-based compression methods are described in (Dodge, 1999). Several papers have been published on the mathematical aspects of reactivity-based compression. These compare the lumping methods used in the ADOM-II mechanism (Stockwell and Lurmann, 1989; Lurmann et al., 1986), and the RADM2 mechanism (Stockwell et al., 1990), and devising more accurate reactivity-based methods (cf., Makar et al., 1996; Makar and Polavarapu, 1997; Makar, 1998). The earlier reactivity-based methods made use of an average OH concentration integrated over time, and knowledge of the hydrocarbon solution at either small or infinite times to form approximate product yields (Makar et al., 1996). An improved approximate solution using both small and long time scale limits was proposed (Makar et al., 1996), but subsequent work (Makar and Polavarapu, 1997; Makar, 1998) has shown that an arbitrarily large number of unoxygenated hydrocarbons with more than one oxidant can be compressed with no loss in accuracy. In addition, the earlier techniques such as that used in the RADM mechanism could sometimes lead to large underpredictions in the ozone mixing ratio. The technique has recently been expanded to oxygenated species (Makar, 1998).

One potential use of the compression numerics is to compress the mechanism in a transient fashion; retain the detailed speciation until chemical integration is required, then compress the mechanism for the purposes of integration. Post-integration, the original information may be recovered. This concept of temporary mechanism compression has appeared twice in the literature, in the context of lumping by reactivity (Makar, 1998) and by concentration (Morpheculc mechanism; Dodge, 1999). A comparison between these methods might be worthwhile, given their similar aims yet different mathematical approaches (Concentration weighting may lead to errors, depending on the relative reactivities of the compressed species, and the case of multiple oxidants needs to be considered. The details of the morpheculc mathematics were not given in, 1998, precluding a comparison here). The advent of these methods will allow increased hydrocarbon speciation in future modeling of reactivity. At the same time, as noted in Dodge (1999), increased model speciation, created in the absence of laboratory based mechanistic or kinetic data, will add little confidence to model results. In addition, the ozone forecasts from mechanisms with a variety of complexities (from highly parameterized to very detailed) has been shown to have a relatively minor effect on the magnitude of ozone produced (Kuhn et al., 1998; see also the section on model intercomparisons of chemical mechanisms). The extent to which the use of detailed, temporarily compressed mechanisms improves ozone simulations has yet to be determined, and would be another area worthwhile of further study.

As indicated above, most current mechanisms use a limited number of model species to represent the large number of higher molecular weight oxidized product species. An indication of the importance of this was obtained during the latest update of the SAPRC mechanism, when a new model species was added to represent the reactions of the more reactive ketones and other non-aldehyde oxygenated products (previously MEK was used for all these products.) It was found that this modification caused an increase of approximately 30% in the calculated MIR for compounds such as glycol ethers, even though it caused almost no change in the model simulations of the incremental reactivity chamber experiments with those compounds (Carter, unpublished results). This indicates the importance of accurate representation of oxidation products.

Environmental Chamber Evaluations

Before any chemical mechanism—whether detailed or condensed—is incorporated in an airshed model, it must be demonstrated to predict at least the major features of the VOC-NO_x-air photooxidation process. The only practical means for doing this is to conduct experiments using an environmental chamber, also called a smog chamber, where the chemical processes of interest are occurring under controlled and well-characterized conditions. It can then be determined whether the experimental results are consistent with the predictions of the chemical mechanism. Chemical mechanism development experiments have been performed in indoor chambers of approximately 3000–5000 liters using artificial light sources (Carter et al., 1995), much larger outdoor chambers (Jeffries et al., 1982; Wang et al., 1992; Odum et al., 1996), and with smaller indoor reaction bags (Kelly et al., 1994; Kelly and Wang, 1996).

Various types of chamber experiments are used to test different aspects of the chemical mechanisms. Irradiations of single VOCs in the presence of NO_x and air test the mechanisms for the individual compounds; NO_x-air irradiations of more complex VOC mixtures test the performance of the model as a whole and experiments where the effect of adding single VOCs to irradiations of NO_x and complex mixtures test model predictions of the VOC's incremental reactivity. Evaluation of chemical mechanisms with chamber data is complicated by uncertainties in chamber effects (Carter and Lurmann, 1990; 1991; Jeffries et al., 1992), and separate characterization experiments are needed to evaluate models for these effects. Although this introduces uncertainties in such evaluations, the uncertainties in evaluating chemical mechanisms using chamber data are far less than the uncertainties in attempting to evaluate mechanisms by comparing full airshed modeling results with ambient air data. With chamber experiments, the amounts of input pollutants are accurately known, and no uncertainties regarding dilution or transport need to be considered.

Current chamber data are available to test the mechanisms for only a subset of the many types of VOCs emitted into the atmosphere. However, ongoing studies, motivated largely by the need for data to support potential VOC exemption petitions or the need to reduce uncertainties so reactivity considerations in VOC regulations, is resulting in an ever-increasing number of compounds for which environmental chamber data are available for mechanism evaluation.

Although there are really no practical alternatives at the present time, use of environmental chambers for mechanism evaluation is not without significant problems. Given that smog chamber experiments are carried out under conditions where trace species are much more concentrated than under ambient conditions, great care must be taken in extrapolating the smog chamber data to atmospheric conditions. Perhaps the time derivative of the ozone concentration would be a more appropriate indicator than absolute ozone concentration. An important point to consider is whether or not the chemical mechanism is reproducing the correct ozone behavior for the right reasons. The comparison of additional species would allow for more thorough evaluation of the mechanism and the possibility of counterbalancing errors. Another issue worth addressing is whether total oxidants (O₃ + H₂O₂ + ROOH) would be a more complete way of diagnosing the reactivity of a particular VOC than just looking at ozone formation or ozone formation + NO oxidation, as is usually employed. If downstream effects are

important, the first round of organic products needs to be predicted and tracked accurately so their impact during and after multi-day transport can be assessed.

Important analytical issues and some possible shortcomings of chamber experiments are listed below:

- Intensity and spectral characteristics of the chamber light sources are difficult to characterize.
- It is difficult to perform experiments at low concentrations, so experiments are usually not directly representative of environmental conditions. Additionally, the VOC/NO_x ratios are usually higher than in the atmosphere.
- Wall reactions that can be the principle source of radicals are not understood.
- How well are temperature and relative humidity monitored in the smog chambers? Are these parameters included in the models?
- Are fast analytical techniques available for monitoring appropriate intermediate species? Carbonyls, if measured, are often collected using cartridge techniques. What is the integration time for the PAN GC/ECD technique?
- There are problems with complex mixtures where components cannot be completely identified.
- Low volatility may lead to decreased concentration of a VOC in the gas phase, but will heterogeneous reactions on aerosols or in the soil release product species that may lead to smog formation?
- Few multi-day chamber experiments are available for testing downstream predictions.
- Chamber experiments tend to be much less sensitive to the representation of the reactions of reactive organic products than do model simulations of the atmosphere. This is because the integrated OH radical levels tend to be lower in current chamber experiments than in atmospheric scenarios.

Mechanism Intercomparisons

The comparison of the predictions of different tropospheric reaction mechanisms for a common set of initial and boundary conditions is a useful means of identifying factors affecting the accuracy of reactivity simulations. The intercomparisons also highlight sources of reactivity simulation uncertainty and needs for further laboratory work. Two recent papers (Kuhn et al., 1998; Olson et al., 1997) have examined several mechanisms in this fashion; their results are summarized here.

Variation in Model Predictions due to Photolysis Parameterizations and NMHC Reaction Mechanisms (Olson et al., 1997)

The reaction rates for non-methane hydrocarbon (NMHC) chemistry from twenty-one modeling groups were compared for a common set of atmospheric and radiative parameters and

initial conditions (clear sky, solar zenith angle = 23°, latitude = 45° N, July 1, US Standard Atmosphere, 4 NMHC initial concentration regimes). Sixteen of the groups also examined NMHC effects in two addition test cases.

The diurnal averages of the photolysis rates for the reactions $O_3 + hv \rightarrow O(^1D) + O_2$, $H_2O_2 + hv \rightarrow 2 OH$, $NO_2 + hv \rightarrow NO + O(^3P)$ and $HCHO + hv \rightarrow H + CHO$ were calculated by the different models and compared at four altitudes. Ozone and hydrogen peroxide photodissociation mean values were essentially identical (with overlapping rms errors). NO_2 and formaldehyde photolysis rates for models employing multistream methods were significantly larger than two-stream models. Multistream NO_2 photodissociation mean values were about $10 s^{-1}$ larger than two stream rates at all levels (an increase of approximately 20%), while formaldehyde rates increased by approximately 25%.

Five day diurnal box model simulations were used to compare the mixing ratios of O_3 , NO , H_2O_2 and diurnal values of HO_2 and OH . For simulations lacking NMHCs, variations in O_3 and NO_x predicted by the different models was small; less than 5%. With in the inclusion of NMHC's O_3 and NO_x means and medians diverged by up to 25%

Analysis of the surface level “no-NMHC” cases showed that the models fell into three subsets based on HO_x and O_3 mixing ratios. Models lacking the pressure and water-vapor pathways of the HO_2 self-reactions tended to have lower H_2O_2 mixing ratios in favor of increased HO_2 . Differences in HO_x between the remaining two subsets were attributed to differences in the H_2O_2 and $HCHO$ reservoir concentrations, in turn dependent in part on photodissociation rates.

The case of a NO_x (no VOC) plume had O_3 differences of 11% after 5 days of simulation, attributed to differences in the ozone photolysis rate predicted by the different models.

The hydrocarbon test runs showed a wider variation in model results, due to the different hydrocarbon oxidation schemes used. The hydrocarbon schemes could be grouped into three categories, depending on their original source and form of chemical lumping. These categories included: those mechanisms based on the lumped molecule approach (e.g. RADM-II; Stockwell et al., 1990), the lumped molecule with surrogate species approach (e.g. Lurmann et al, 1986), and lumped structure mechanisms (e.g., Carbon-Bond IV; Gery et al., 1989). The choice of a lumping method had no consistent effect on the predicted O_3 or NO_x concentrations; differences in predictions did not correlate with the mean values of compression used in the given mechanism. The NMHC tests showed a much larger rms error for NO_x between mechanisms (40% vs. 15%) than the “no-NMHC” tests, and the rms error for O_3 doubled.

Although much of the model variation was attributed to differences in the photolysis calculations, the authors noted that the 5-15% rms variation about the mean for the photodissociation rates was within the range of accuracy of the measurements of quantum yields and cross-sections (cf., DeMore et al., 1992).

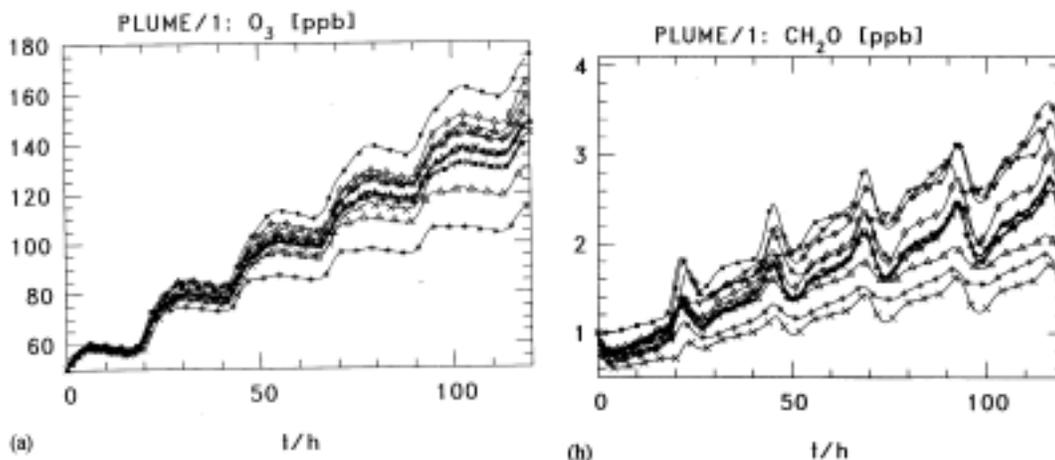
Variations due to NMHC Chemistry (Kuhn et al., 1998)

Twelve different mechanisms were compared in several tests, including one (PLUME1) in which photolysis rates were prescribed and typical emission levels for continental European air were included as first order production terms. The mechanisms included four variations on the RADM2 mechanism, three derived from the Carbon Bond-IV mechanism, the EMEP mechanism, the ADOM-II mechanism, and four explicit schemes.

As in the other intercomparison noted above, the pressure and water vapor pathways of the HO₂ self reaction were not incorporated in all mechanisms, sometimes leading to significant differences in H₂O₂ predictions. Other causes included variations in the rate constants for organic peroxides with OH, and the level of detail with which RO₂ and HO₂ reactions were treated in each mechanism.

The rms variation between different mechanisms for O₃ production in the PLUME1 case was 16% of the mean, with individual mechanisms being up to 27% higher than the mean (EMEP) and 35% less than the mean (CB4-TNO) (See Figure 1, below). The authors noted that the NO_x emission level had a greater effect on O₃ than VOCs for the simulations, with the need for improved treatment of HO₂ – RO₂ interactions and peroxide formation having a significant effect on model results. This was identified as a weak point in many reaction mechanisms. Other sources of model differences included the extent of speciation (e.g., the 1640 reaction, 715 species IVL scheme had larger “higher aldehyde” concentrations than the other schemes due to increased speciation). Mixing ratios of H₂O₂, organic peroxides, and higher aldehydes all had higher rms errors, with deviations about the mean of 30%, 56%, and 50%. Formaldehyde values

Figure 1 (From Kuhn et al, 1998) Left: Ozone concentrations over 5 days of diurnal chemistry with emissions, results from 12 mechanisms. Right: Formaldehyde concentrations, results from 12 mechanisms.



(Figure 1) varied by up to +63% to -67% of the mean value by the end of the five day diurnal simulation.

One of the main conclusions from (Kuhn et al., 1998) was that similar O₃ mixing ratios were predicted by the different mechanisms, despite differences in the hydrocarbon parameterization. The use of more detailed oxygenated hydrocarbon mechanisms tended to result in higher ozone predictions, due the increase in the RO₂ production associated with these species. OH radical differences were also small (rms difference of 19% for the Plume 1 case). Concentrations of the longer lived species varied considerably.

As noted by Kuhn et al., (1998), model intercomparisons are not sufficient for determining the reliability of a mechanism in predicting actual ozone mixing ratios; this must be done through comparisons to measurements. However, the above studies have some common results that are of relevance to the accurate prediction of reactivity.

First, the prediction of ozone concentrations will have less of a mechanism-related bias than other species such as HCHO, and organic peroxides, which are more heavily dependent on the details of the chemical mechanism. This does not imply that the mechanisms are “correct”, but does imply that the ozone predictions resulting from the use of different mechanisms may be similar.

Second, some of the observed differences may be due to differences in the HO₂ and RO₂ reactions used. The use of pressure and H₂O dependant rates for the HO₂ self-reaction has a significant effect on the HO_x budget in the simulations.

Third, variations in the treatment of photolysis for clear sky conditions may affect O₃ mixing ratios, but the effects of the different treatments have a similar magnitude to the measurement errors in the input data used in the models. Increased precision in these measurements is required to improve the estimates of photodissociation rates. Finally, mechanisms with increased speciation *or* production of oxygenated hydrocarbons such as organic peroxides and aldehydes tended to have higher ozone production than other mechanisms (Kuhn et al., 1998). However, this does not necessarily imply that these species will necessarily be in abundance in the real atmosphere. Deposition and particle formation may result in lower mixing ratios of these species than would be predicted by “gas-phase chemistry alone” box models as employed in the above studies. In addition, the kinetics and mechanisms of many oxygenated species have yet to be determined in the laboratory; current detailed mechanisms extrapolate from known chemistry. The kinetics and atmospheric fate of the oxygenated compounds are poorly known relative to the unoxxygenated species and are worthy of further study. Accurate predictions of these species are a much more stringent test of the accuracy of a model’s VOC oxidation pathways than the model’s predictions of ozone mixing ratios.

CURRENT STATUS FOR REACTIVITY MODELING

Given below is a brief summary of the status and updates to the latest version of the SAPRC mechanism for the various major classes of compounds, and the results of the evaluation

of those mechanisms, where applicable. Although this discussion is strictly speaking applicable only to that mechanism, it is probably reasonably representative of the current state of the science of reactivity assessment for various classes of compounds.

Alkanes. Atkinson (unpublished results) has obtained new product yields for alkyl nitrates from C₅ – C₁₀ n-alkanes indicating that the previously published yields in these systems may be high by about 30%. When the nitrate yields for the higher alkanes are reduced accordingly, it is now possible to fit the chamber data for the C₈+ n-alkanes without making the unreasonable assumption that nitrate formation does not occur from the peroxy radicals formed after 1,4-H shift isomerizations. The estimated mechanism gave generally satisfactory fits to reactivity data for most alkanes except for iso-octane (2,2,4-trimethylpentane), where some adjustments were necessary. There may be a tendency for the mechanism to overpredict the inhibition by the higher alkanes in the mini-surrogate runs, but it is unclear whether this is a consistent bias.

Mineral Spirits. The individual branched and cyclic alkane isomers which were used to represent the various classes of the alkane mineral spirits which were studied (Carter et al., 1997b) were modified somewhat based on the analyses supplied by Safety-Kleen corporation. Their analysis indicated that the mixtures are characterized by somewhat less highly branched isomers than we had been assuming previously. With this change, and the change in estimated nitrate yields in the general alkane mechanism as discussed above, the model could successfully simulate the results of the mineral spirits reactivity experiments without adjustment. Additional data from our ongoing programs will be needed to confirm this. However, the uncertainty classifications for the higher branched and cyclic alkane classes have been reduced based on these current results.

Alkenes. The automated mechanism generation procedure used with the SAPRC-98 mechanism allows for more realistic and complex mechanisms to be generated for the higher alkanes, though it is still assumed that all the reaction with OH radicals is by addition to the double bond. However, the evaluations of the mechanisms for the simpler alkenes (whose mechanisms are not significantly affected by the use of this automated procedure) indicate problems and inconsistencies that have not been satisfactorily resolved. In particular, in order to fit chamber data for 1-butene and 1-hexene, it is necessary to assume lower OH radical yields in the reactions of O₃ with these compounds than is consistent with recommendations of Atkinson (1997) based on results of various other laboratory studies. In fact, the previous version of the mechanism also performed poorly in simulating experiments with these compounds, though this had not been recognized until this re-evaluation. It is also necessary to assume that essentially no radicals are formed in the reactions of O(³P) with C₃+ monoalkenes, contrary to the assumptions of previous models. On the other hand, the isoprene data are still best fit if the relative high radical yields in the O₃ and O(³P) reactions of this compound are assumed, and the terpene data are also reasonably well fit using the recommended (generally relatively high) OH yields in their O₃ reactions. Although the mechanisms for the various alkenes were adjusted if needed to fit the available chamber data, their mechanisms must be considered to be somewhat uncertain until these inconsistencies are resolved.

Aromatics. Despite considerable research in recent years and some progress, the details of the aromatic ring opening process is remains sufficiently poorly understood that use of parameterized and adjusted mechanisms is still necessary. Some changes were made to the details of the parameterization to permit use in the model of the actual observed dicarbonyl products, but the general parameterization approach was the same. The parameters were optimized to fit the chamber data for the various compounds for which data are available, and the fits to the chamber data were comparable (though usually slightly better) to those for the SAPRC-97 mechanism (Carter et al., 1997). The approach for representing the higher aromatics in the model was also modified somewhat. Ethylbenzene, which was found to have a lower mechanistic reactivity than toluene, was used rather than toluene to represent the higher monoalkylbenzenes. The generic di- and tri- or polyalkylbenzenes were represented by mixtures of xylene or trialkylbenzene isomers, rather than just m-xylene or 1,3,5-trimethylbenzene, as was the case previously. This was done to eliminate a potential source of bias in the mechanism by representing each of these classes by what is essentially the most reactive member of the class

Ketones. The previous mechanism used methylethyl ketone (MEK) to represent essentially all ketones other than acetone, and chamber data with methyl isobutyl ketone (MIBK) has shown this to be unsatisfactory. The current mechanism represents individual ketones based on their estimated individual reactions, generated as discussed above for alkanes and other oxygenates. This has resulted in significant changes in predicted reactivities for the higher ketones.

Other Oxygenated Species. The estimated mechanisms of alcohols, ethers, glycols, esters, etc. were generated using the automated procedure discussed above, with nitrate yields and other uncertain branching ratios in the mechanism being adjusted to fit chamber data if necessary. Footnotes in the reactivity data tabulations indicate the types of adjustments that were made, if necessary. All the chamber data obtained in the just-completed CARB consumer products reactivity program have been utilized and incorporated in developing and adjusting these mechanisms (Carter et al., unpublished results). The chamber data for most of these compounds could be fit with the model simulations after adjustments that were considered to be within the uncertainty range of the estimation method. A very preliminary analysis of the differences in reactivities between the initially estimated mechanisms and those adjusted to fit chamber data suggests that the MIR differences are usually less than a factor of 1.5, though a more complete analysis is needed. Based on this preliminary analysis, we conclude that at least for C₈- oxygenated compounds, the generated using the estimated mechanism are probably not off by more than a factor of two.

Halogenated Compounds. With the exception of chloropicrin, which appears to have relatively simple and unique chemistry (Carter et al., 1997c), the few halogenated compounds we have studied (trichloroethylene and alkyl bromides) indicate that current mechanisms cannot reliably predict MIR's for these compounds (Carter et al., 1996, 1997d). The current version of the mechanism does not yet include halogen chemistry, though chlorine and bromine reactions may be added before the mechanism is finalized.

Nitrogen Containing Compounds. The only nitrogen-containing compound with an evaluated mechanism in the current list is n-methyl pyrrolidinone (NMP). For the simple amines for which OH radical rate constants are available, highly simplified "placeholder" mechanisms

with the appropriate OH rate constant, are used to provide “best estimate” reactivities. These must be considered to be highly uncertain.

Other Organic Classes. Although data are available for toluene diisocyanate and some volatile silicone compounds, these compounds, which appear to inhibit ozone under most if not all conditions, are not yet represented in the current mechanism. Other classes of compounds, which were represented by highly approximate placeholder mechanisms, are also omitted from this version of the mechanism.

CONCLUSIONS

There has been significant progress in recent years in improving our understanding and ability to model the gas-phase reactions of pollutants in the troposphere. Chemical mechanisms have been or are being developed which are able to predict ozone impacts in simulated atmospheric conditions for many of the types of organic compounds that are emitted into the atmosphere, particularly those emitted in large amounts. Nevertheless, there remain major gaps in our understanding in the details of these gas-phase reactions, and our understanding of potentially significant heterogeneous processes is even more incomplete. Many of the mechanisms used to predict ozone are highly parameterized and simplified, with empirical adjustments to fit chamber data, and with no reliable ability to predict impacts other than on ozone and perhaps overall OH radical levels. Although methods exist for estimating mechanisms for VOCs for which there are no data, at best these estimates have large uncertainties, and for many classes of compounds no reliable estimation methods exist.

Ongoing improvements in airshed model hardware and software is permitting use of ever more detailed atmospheric mechanisms, which have the potential to give more accurate and comprehensive atmospheric impact predictions for any VOC of interest. However, without the knowledge of the mechanistic details, the predictions using these detailed mechanisms may be no more reliable than those of the simplified and parameterized mechanisms currently in use. Therefore, the main factor limiting the chemical accuracy of current state-of-the-art and future airshed models is limitations in our knowledge of atmospheric chemistry, and limitations in the environmental chamber data base needed to verify the accuracy of the chemical model predictions.

Specific areas where research is needed to improve the chemical mechanisms needed for VOC reactivity assessment are as follows:

Basic kinetic and mechanistic studies are needed to improve our understanding and to reduce uncertainties concerning the atmospheric reactions of many types of VOCs, in particular with regard to the reactions of the intermediate radicals and reactive products they form. Atkinson (1999) has suggested a number of areas where work is needed, and additional areas are discussed in this document. These include, but are not limited to, areas which have traditionally been recognized as uncertainties in atmospheric chemistry, such as mechanism for reactions of aromatics, the ozone – olefin reactions, organic nitrate yields from peroxy + NO reactions, relative rates of the many competing alkoxy radical reactions, photolysis of oxygenated product

species (particularly from aromatics), reducing the uncertainty in the cross-sections and quantum yields of other species, including inorganics, etc.

Our understanding and ability to predictively model the heterogeneous reactions in the atmosphere and in environmental chambers needs to be improved. This includes, but is not limited to, reactions involving HONO formation, N_2O_5 hydrolysis, and reactions involved in secondary formation, including secondary organic aerosols. Laboratory and ambient air measurements are required to determine the atmospheric fate of potentially reactive oxygenated species, particularly for those with a high OH reactivity (or expected high OH reactivity) and a known or expected low volatility. Better understanding of reactions in smog chambers is needed to reduce uncertainties and sources of errors when using environmental chamber data to evaluate and develop chemical mechanisms. Issues brought up in the NARSTO review of heterogeneous processes in aqueous media by Daniel Jacob (1999) need to be considered.

There needs to be improvement in the environmental chamber methodologies used to develop and evaluate mechanisms for atmospheric models. Improved facilities are needed to evaluate mechanisms under lower pollutant conditions than is currently possible, and improved instrumentation is needed to monitor trace species and intermediates and VOC reaction products. This is needed for more comprehensive and reliable mechanism evaluation, particularly for impacts other than ozone, and improved confidence that the mechanism will give correct predictions under ambient conditions. On the other hand, methodologies need to be developed to screen or assess reactivity more readily and at lower cost than is currently possible. In addition to the obvious practical benefits in aiding implementation of reactivity-based control strategies, such methodologies will provide valuable data needed to improve and evaluate estimation methods.

Of critical importance to developing improved chemically detailed mechanisms is developing improved and more reliable estimation techniques. This provides the only practical means for developing and implementing fully detailed mechanisms for the full variety of VOCs of interest in the foreseeable future. Structure-reactivity methods such as those developed by Atkinson and others have proven to be powerful tools, but the theoretical and experimental data base limits their utility to restricted classes, and many estimates are uncertain. Theoretical calculations of the most uncertain reactions and targeted experimental studies to provide needed data to establish or evaluate relationships are needed.

A serious sensitivity analysis should be applied to the mechanisms to help decide which processes will be most important to study in the future. This requires quantifying the uncertainties involved, not only in the elementary rate constants, but also in parameterization methods in mechanisms adjusted to fit chamber or other data. Progress is being made in this area by Milford and others, but the results are still of limited utility.

Although computer hardware and software is improving the level of chemical detail that can be represented in models, fully explicit *and complete* mechanisms are not now and probably will never be practical. Initial numerical intercomparisons between chemical mechanisms of very different levels of complexity have shown relatively small variations in ozone predictions compared to other species. Work is needed to assess the optimum level of detail for atmospheric chemical mechanisms, given the modeling application and the level of knowledge of the

processes being represented. The creation of a minimum list of inorganic reactions required for photochemical reactivity calculations should be formed, which includes the pressure and water vapor dependent pathways of HO₂. A model comparison of highly speciated versus lumped versus temporarily compressed mechanisms should be performed for a realistic atmospheric conditions, to determine the relative merits of model speciation in reactivity estimates. The implementation of the Morphecule approach needs to be completed, and its advantages over alternative methods for representing chemical detail in models need to be assessed.

REFERENCES

- Andersson-Skold, Y., Grenfelt, P., and Pleije, K. (1992): *J. Air Waste Mgmt. Assoc.*, 42:1152–1158.
- Ammann, M. and R. Lorenzen (Editors) *Proceedings of the 1st workshop of the EUROTRAC-2 Subproject Chemical Mechanism Development*, PSI-Proceedings 97-02, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, 1997.
- Ammann, M., M. Kalberer, D. T. Jost, L. Tobler, E. Rossler, D. Piguet, H. W. Gaggeler, and U. Baltensperger (1998): "Heterogeneous production of nitrous acid on soot in polluted air masses," *Nature*, 395, 157-160.
- Andres-Hernandez, M.D., J. Notholt, J. Hjorth and O. Schrems, "A DOAS study on the origin of nitrous acid at urban and non-urban sites", *Atm. Env.*, 30, 175-180, 1996.
- Atkinson, R. (1999): "Atmospheric Chemistry of VOCs and NO_x. 1998 NARSTO Assessment – Critical Review", *Atmos. Environ.*, in press. (This can be downloaded from http://www.cgenv.com/Narsto/assess_activities.html)
- 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. (1988): "Gas-phase atmospheric chemistry of organic compounds," Final Report to the California Air Resources Board, Contract No. A5-122-32, Sacramento, Ca.
- 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.
- Atkinson, R. (1991): "Kinetics and Mechanisms of the Gas-Phase Reactions of the NO₃ Radical with Organic Compounds," *J. Phys. Chem. Ref. Data*, 20, 459-507.
- Atkinson, R. (1994): "Gas-Phase Tropospheric Chemistry of Organic Compounds," *J. Phys. Chem. Ref. Data*, Monograph No. 2.

- Atkinson, R. (1997): "Gas Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes," *J. Phys. Chem. Ref. Data*, 26, 215-290.
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe (1997): "Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V., IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry," *J. Phys. Chem. Ref. Data*, 26, 521-1011.
- Bambauer, A., B. Brantner, M. Paige, and T. Novakov (1994): *Atmos. Environ.*, 28, 3225.
- Becker, K.H., "The atmospheric oxidation of aromatic hydrocarbons and its impact on photo-oxidant chemistry," in *Proceedings of Eurotrac Symposium '94*, Editors P.M. Borrel, P. Borrel, T. Cvitas, and W. Seilev, SPB Academic Publishing bv, The Hague, Netherlands, 66-74, 1994.
- Benson, S. W. (1976): *Thermochemical Kinetics*, 2nd Ed., John Wiley and Sons, New York.
- Bergin, M. S., A. G. Russell, W.P.L. Carter, B. E. Croes and J. H. Seinfeld (1997): "Ozone Control and VOC Reactivity," in *Encyclopedia of Environmental Analysis and Remediation*, Wiley.
- Brown et al.1998, S. S., Talukdar, R.K. and Ravishankara, A. R. (1998): *Chem. Phys. Lett.* (submitted)
- CARB (1993): "Proposed Regulations for Low-Emission Vehicles and Clean Fuels — Staff Report and Technical Support Document," California Air Resources Board, Sacramento, CA, August 13, 1990. See also Appendix VIII of "California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles," as last amended September 22, 1993. Incorporated by reference in Section 1960.1 (k) of Title 13, California Code of Regulations.
- Carter, W.P.L. (1988): "Documentation of a gas phase photochemical mechanism for use in airshed modeling," Final Report to the California Air Resources Board, Contract No. A5-122-32, California Air Resources Board, Sacramento, Ca.
- 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., F.W. Lurmann, R. Atkinson and A.C. Lloyd (1986): "Development and testing of a surrogate species chemical reaction mechanism, Volume 1," PB 86-212 404/AS, National Technical Information Service, Springfield, Va.
- Carter, W. P. L. and R. Atkinson (1989): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", *Environ. Sci. Technol.*, 23, 864.
- 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.* 25A, 2771-2806.
- Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1993): "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. (This can be downloaded from <http://cert.ucr.edu/~carter/bycarter.htm>)
- Carter, W. P. L., D. Luo, I. L. Malkina, and D. Fitz (1995b): "The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanism. Indoor Chamber Experiments through 1993," Report submitted to the U. S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, NC., March 20. (This can be downloaded from <http://cert.ucr.edu/~carter/bycarter.htm>)
- Carter, W. P. L., D. Luo, and I. L. Malkina (1996): "Investigation of the Atmospheric Ozone Formation Potential of Trichloroethylene," Report to the Halogenated Solvents Industry Alliance, August. (This can be downloaded from <http://cert.ucr.edu/~carter/bycarter.htm>.)
- Carter, W. P. L., D. Luo, and I. L. Malkina (1997): "Environmental Chamber Studies for Development of an Updated Photochemical Mechanism for VOC Reactivity Assessment," final report to California Air Resources Board Contract 92-345, Coordinating Research Council Project M-9, and National Renewable Energy Laboratory Contract ZF-2-12252-07. November 26. (This report can be downloaded from <http://helium.ucr.edu/~carter/bycarter.htm>.)
- Carter, W. P. L., D. Luo, and I. L. Malkina (1997b): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Mineral Spirits Mixtures," Report to Safety-Kleen Corporation, July 25. . (This report can be downloaded from <http://helium.ucr.edu/~carter/bycarter.htm>.)
- Carter, W. P. L., D. Luo and I. L. Malkina (1997c): "Investigation of that Atmospheric Reactions of Chloropicrin," *Atmos. Environ.* 31, 1425-1439.

- Carter, W. P. L., D. Luo, and I. L. Malkina (1997c): "Investigation of the Atmospheric Ozone Formation Potential of Selected Alkyl Bromides," Report to Albemarle Corporation, November 10. . (This can be downloaded from <http://cert.ucr.edu/~carter/bycarter.htm>.)
- Derwent, R.G., M.E. Jenkin and S.M. Saunders (1996): "Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions," *Atmos. Environ.* 30,189.
- Derwent, R. G. and M.E. Jenkin (1991): "Hydrocarbons and the long range transport of ozone and PAN across Europe," *Atmos. Environ.* 25A 1661.
- Dodge M.C., (1999): Chemical oxidant mechanisms for air quality modeling: critical review paper for 1998 ozone assessment (to be submitted to Atmospheric Environment Available at http://narsto.owt.com/Narsto/assess_activities.html.)
- Dransfield et al. 1998, T. J., Sprengnether, M. M., Perkins, K. K., Donahue, N. M. and Anderson, J. G. (1998) *Geophys. Res. Lett.* (submitted)
- Gerecke, A., A. Thielmann, L. Gutzwiller and M.J. Rossi, "The chemical kinetics of HONO formation resulting from heterogeneous interaction of NO₂ with flame soot", *Proceedings of the 1st workshop of the EUROTRAC-2 Subproject Chemical Mechanism Development, Editors M. Amman and R. Lorenzen, 23-26, PSI-Proceedings 97-02, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, 1997.*
- 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.
- Gery M.W., G. Z. Whitten, J.P. Killus, and M.C. Dodge, A photochemical kinetics mechanism for urban and regional scale computer modeling, *J. Geophys. Res.*, 94, 12925-12956, 1989.
- Gierczak, T., J.B. Burkholder, R.K. Talukdar, A. Mellouki, S.B. Barone, A.R. Ravishankara, "Atmospheric fate of methyl vinyl ketone and methacrolein," *J. Photochem. and Photobio. A: Chem.*, 1-10, 1997.
- Hobson, J. F., R. Atkinson and W. P. L. Carter (1997): "Volatile Methylsiloxanes," in Handbook of Environmental Chemistry, Vol. 3, Part H: Organosilicon Materials, Springer-Verlag.
- Horie, O., P. Neeb, S. Limbach and G.K. Moortgat, Formation of formic acid and organic peroxides in the ozonolysis of ethene with added water vapour, *Geophys. Res. Lett.*, *21*, 1523-1526, 1994
- Iraci, L. T., and M. A. Tolbert (1997): "Heterogeneous interaction of formaldehyde with cold sulfuric acid: Implications for the upper troposphere and lower stratosphere," *J. Geophys. Res.*, 102, 16,099-16,107.

- Irikura, K. K., and D. J. Frurip, Editors (1998): Computational Thermochemistry; ACS Symposium Series #677
- Jacob, D (1999): "Heterogeneous Chemistry and Tropospheric Ozone," Critical review paper for NARSTO, Atmospheric Environment, in press. Available at http://www.cgenv.com/Narsto/assess_activities.html.
- Jacobson, M.Z., and R.P. Turco, SMVGEAR: A sparse-matrix, vectorized Gear Code for Atmospheric Models, *Atm. Env.*, 28, 273-284, 1994
- Jeffries, H. E., M. W. Gery and W. P. L. Carter (1992): "Protocol for Evaluating Oxidant Mechanisms for Urban and Regional Models," Report for U. S. Environmental Protection Agency Cooperative Agreement No. 815779, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC.
- Jeffries, H. E., R. M. Kamens, K. G. Sexton, and A. A. Gerhardt (1982): "Outdoor Smog Chamber Experiments to Test Photochemical Models", EPA-600/3-82-016a, April.
- Jenkin, M.E., S.M. Saunders and M.J. Pilling (1997): "The tropospheric degradation of volatile organic compounds: a protocol for mechanism development," *Atmos. Environ.* 31, 31.
- Kamm, S., O. Mohler, K.-H. Naumann, H. Saathoff, U. Schurath, "Temperature dependence of slow heterogeneous reactions on soot aerosol", *Proceedings of the 1st workshop of the EUROTRAC-2 Subproject Chemical Mechanism Development, Editors M. Amman and R. Lorenzen*, 29-31, PSI-Proceedings 97-02, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, 1997.
- Kelly, N.A.; Wang, P.; Japar, S.M.; Hurley, M.D.; and Wallington, T.J. (1994). Measurement of the Atmosphere Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies, First-Year Final Report, CRC Contract No. AQ-6-1-92, Environmental Research Consortium.
- Kelly, N.A. and Wang, P. (1996) Part I: Indoor Smog Chamber Study of Reactivity in Kelly, N.A.; Wang, P.; Japar, S.M.; Hurley, M.D.; and Wallington, T.J. (1996). Measurement of the Atmosphere Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies, Second-Year Final Report, CRC Contract No. AQ-6-1-92 and NREL Contract No. AF-2-112961. Environmental Research Consortium, - (September).
- Kleffmann, J., K.H. Becker and P. Wiesen, "Mechanisms of heterogeneous HONO formation in urban areas", *Proceedings of the 1st workshop of the EUROTRAC-2 Subproject Chemical Mechanism Development, Editors M. Amman and R. Lorenzen*, 32-34, PSI-Proceedings 97-02, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, 1997.

- Kuhn, M., P.J.H. Builtjes, D. Poppe, D. Simpson, W.R. Stockwell, Y. Andersson-Skold, A. Baart, M. Das, F. Fiedler, O. Hov, F. Kirchner, P.A. Makar, J.B. Milford, M.G.M. Roemer, R. Ruhnke, A. Strand, B. Vogel, and H. Vogel, Intercomparison of the gas-phase chemistry in several chemistry and transport models, *Atm. Env.*, 32, 693-709, 1998.
- Kwok, E. S. C., and R. Atkinson (1995): "Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update," *Atmos. Environ* 29, 1685-1695.
- Lane, D.A., S.S. Fielder, S.J. Townsend, N.J. Bunce, J. Zhu, L. Liu, B. Wiens, and P.Pond, "Atmospheric photochemistry of naphthalene: A practical and theoretical approach", *Polycyclic Aromatic Compounds*, 9, 53-59, 1996.
- Lurmann, F.W., A.C. Lloyd, R. Atkinson (1986): A chemical mechanism for use in long-range transport/acid deposition computer modeling, *J. Geophys. Res.*, 91, 10905-10936.
- Lurmann, F.W., W.P.L. Carter and L.A. Coyner (1987): "A surrogate species chemical reaction mechanism for urban-scale air quality simulation models: Volume 1. Adaptation of the mechanism," PB 87-180 592/AS, National Technical Information Service, Springfield, Virginia.
- Lurmann, F. W., M. Gery, and W. P. L. Carter (1991): "Implementation of the 1990 SAPRC Chemical Mechanism in the Urban Airshed Model," Final Report to the California South Coast Air Quality Management District, Sonoma Technology, Inc. Report STI-99290-1164-FR, Santa Rosa, CA.
- Makar, P.A., S.-M. Li, P.B. Shepson, and J. Bottenheim (1998): The AES gas-phase mechanism for tropospheric chemistry: theoretical formulation, *AES Internal Report*, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, Canada.
- Makar, P.A., J.D. Fuentes, D. Wang, R.M. Staebler, H.A. Wiebe (1998b): "Chemical processing of biogenic hydrocarbons within and above a temperate deciduous forest," *J. Geophys. Res.* (accepted; in press).
- Makar, P.A., H.A. Wiebe, R.M. Staebler, S.M. Li and K. Anlauf (1998c): "Measurement and modeling of particle nitrate formation," *J. Geophys. Res.*, 103, 13095-13110.
- Makar, P.A. (1998): The use of transient mechanism compression to reduce chemical integration processing time, *Proceedings, International Conference on Air Pollution Modelling and Simulation (APMS'98)*, 435-444 (also currently under review for journal special issue on conference).
- Makar, P.A., W.R. Stockwell, and S.M. Li (1996): Gas-phase chemical mechanism compression strategies: treatment of reactants, *Atm. Env.*, 30, 831-842.

- Makar, P.A. and S.M. Polavarapu (1997): Analytic solutions for gas-phase chemical mechanism compression, *Atm. Env.*, 31, 1025-1039.
- Middleton, P, W.R. Stockwell, and W.P.L. Carter, Aggregation and analysis of volatile organic compound emissions for regional modelling, *Atm. Env.*, 24, 1107-1123, 1990.
- Moran, M.D., A. Dastoor, S.-L. Gong, W. Gong, P.A. Makar, "Conceptual design for the AES regional particulate-matter model/unified air quality model," AES Internal Report, Air Quality Modelling and Integration Division, 4905 Dufferin St., Downsview, Ontario, Canada, 100 pp., 1998.
- NASA (1997): "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 12," JPL Publication 97-4, Jet Propulsion Laboratory, Pasadena, California, January.
- Odum, J.R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R.C.; and Seinfeld, J.H. (1996). *Environ. Sci. Technol.*, 30:2580–2585.
- Olson, J., M. Prather, T. Berntsen, G. Carmichael, R. Chatfield, P. Connell, R. Derwent, L. Horowitz, S. Jin, M. Kanakidou, P. Kasibhatla, R. Kotamarthi, M. Kuhn, K. Law, J. Penner, L. Perliski, S. Sillman, F. Stordal, A. Thompson, O. Wild, Results from the Intergovernmental Panel on Climate Change photochemical model intercomparison (PhotoComp), *J. Geophys. Res.*, 102, 5979-5991, 1997.
- Stockwell, W.R., F. Kirchner, M. Kuhn, and S. Seefeld, A new mechanism for regional atmospheric chemistry modeling. *J. Geophys. Res.*, 102, 25847-25880, 1997.
- 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.
- Stockwell, W.R. and F.W. Lurmann, Intercomparison of the ADOM and RADM gas-phase chemical mechanisms, *Electric Power Research Institute Topical Report*, EPRI, Palo Alto, Ca, 1989.
- Tuazon, E. C., S. M. Aschmann, R. Atkinson and W. P. L. Carter (1998): "The Reactions of Selected Acetates with the OH Radical in the Presence of NO: Novel Rearrangement of Alkoxy Radicals of Structure RC(O)OCH(O)R", *J. Phys. Chem.* 102, 2316-2321.
- Wang, S.C.; Flagan, R.C.; and Seinfeld, J.H. (1992). *Atmos. Environ.*, 26A, 421–434.
- Williams, L. R. and Golden, D. M. (1998) Evaluation prepared for the next JPL Panel Report.