

3. Evaluation of the VOCs Represented Using the Assigned Mechanistic Parameter Method

Atmospheric chemical mechanisms can be generated through the use of computer based methods. These automatic procedures should allow mechanisms to be generated more objectively and with fewer typographical errors than manual molecule-by-molecule assignments. In the new version of the SAPRC mechanism, Dr. Carter has expanded the use of objective measures to include almost all organic compounds except for the chemistry of aromatics and terpenes.

The SAPRC automatic mechanism generation procedure treats the reaction of HO with all organic compounds of atmospheric interest. The group additivity methods for the reactions of HO with organic compounds as developed by Kwok and Atkinson (1995) and Kwok et al. (1996) are well established. The SAPRC automatic mechanism generation procedure treats the reaction of alkenes and selected dialkenes with O₂, O³P and NO₃; and it treats the photolysis of carbonyls and organic nitrates. The range of organic species treated by this software is adequate for most VOCs that are now emitted into the atmosphere. But the range of reactions might require expansion to treat new low reactive organic compounds that may be emitted due to the effects of reactivity based emission regulations. The treatment of reduced sulfur containing compounds might be useful for certain applications.

The mechanism generation program on the web was examined. The system was relatively easy to use and the online documentation although brief was clear. The method of specifying the structures of organic compounds is logical and it should be possible to specify the organic compounds treatable by the program. It would be helpful if more detailed instructions were provided for first-time users.

HO REACTIONS

The approach to estimating the HO rate constants for the rate parameters, excluding propene from the calculation of group rate constants for monosubstituted alkenes, is valid since the estimates will be made for the higher molecular weight compounds. The exclusion of abstraction reactions from alkenes also seems to be a valid simplification due to the lack of estimation methods for unsaturated radicals.

The methods for estimating the products for the reactions of HO with alkenes depend upon data with some significant uncertainties. In contrast to the rate constants the fraction of HO radicals that react with the least substituted end of a double bond is very poorly known. The only available experimental data are available for terminal alkenes, CH₂=CH-. The only available data (Cvetanovic, 1976) was only published as a conference proceeding. For all other alkenes the fraction of HO radicals that react with

the least substituted end of a double bond are estimated on the basis of little data. New measurements are required to determine the site of HO addition to alkenes.

One concern is that the HO rate parameters for compounds containing oxygen tend to be the most inaccurate. The difference between the estimated and measured values for some oxygenated compounds is greater than 400% (Table II-8 in the mechanism documentation). Since many of the proposed substitute low reactivity organic compounds are highly oxygenated compounds this may represent a significant source of uncertainty in the calculations.

NO₃ REACTIONS

The discussion on the treatment of NO₃ radical reactions by the SAPRC automatic mechanism generation procedure needs to be clarified in places. The following needs to be said more clearly. The program considers only the abstraction of hydrogen atoms by NO₃ from aldehydes and the addition of NO₃ to alkenes. If rate constants for the abstraction of hydrogen atoms by NO₃ from aldehydes are estimated then the same rate parameter for the reaction of NO₃ from acetaldehyde is used. If the compound is an acid R-(CO)OH or a formate X⁺H(CO)O⁻ then the rate parameter is assumed to be zero.

These assumptions are reasonable but as noted for Reaction PAN3 this procedure may underestimate the rate parameter for this reaction. Figure 2 in Atkinson (1991) suggests that there is a roughly log-linear relationship between k_{HO} and k_{NO_3} for HCHO and CH₃CHO that may extend to higher aldehydes. For example, if the most recent values for k_{HO} and k_{NO_3} for HCHO and CH₃CHO are fit, extrapolation yields a k_{NO_3} of 5.0E-15 for propionaldehyde if a k_{HO} of 2.0E-11 for propionaldehyde is assumed.

The addition of NO₃ primarily to the least substituted end of a molecule is a reasonable assumption but there are much less data available to support this assumption than available for the addition reactions of HO with alkenes.

Assigned NO₃ Radical Rate Constants

It should be stressed that there is very limited data available for the abstraction of hydrogen atoms from -CHO groups. Data is available for only HCHO and CH₃CHO.

Estimated NO₃ Radical Rate Constants

Dr. Carter's discussion is a significant improvement over previous treatments. In comparison with hydroxyl radical reactions there is little data available for NO₃ that can be used to estimate trends. More data is required to reduce the uncertainties in NO₃ radical rate parameters.

Assigned Mechanisms for Initial NO₃ Reactions

There is very little data available on these mechanisms. The uncertainty in the mechanisms for the reactions of NO₃ is extremely high.

O₃ REACTIONS

There are much more data available for the reactions of ozone with alkenes and measured rate parameters are used for most of the O₃ - VOC reactions in the mechanism. The use of average rate parameters for alkenes according to the number of substituents on the double bond is the best that can be done now but this procedure is highly uncertain. From the trends in the rate parameters it appears that steric effects compete with electron donating effects in the determination of the rate parameters. The treatment of the branching ratios for biradical formation are consistent with the available data.

Assigned O₃ Rate constants

There is much data available for the alkenes in the emission inventories and Dr. Carter's choices are reasonable.

Estimated Total Rate Constants

Dr. Carter shows that there is considerable variation in the rate parameters for the O₃ + alkene reactions for alkenes with the same configurations of constituents attached to the double bond. This high variability in the rate parameters makes estimation very difficult. Dr. Carter's approach is reasonable but new methods for estimating the impact of steric effects on the O₃ + alkene rate parameters need to be developed.

Branching Ratios for Biradical Formation

Dr. Carter's approach is reasonable given the available data.

Assigned Mechanisms for Initial O₃ Reactions

Dr. Carter's approach is reasonable given the available data.

In Table 21 the "excited" label seems redundant and misplaced. The "excited" label is always on the -OO- although the entire reactive intermediate is excited.

O³P REACTIONS

It is valid to include these reactions in the mechanism due to the possibility of it being used to describe the chemistry of plumes with relatively high pollutant concentrations or for the mechanism's evaluation by environmental chamber data. The rate parameters for these reactions are relatively well known but the mechanisms of these reactions are poorly known. Environmental chamber data are not fit well by mechanisms that incorporate recently measured branching ratios. Given the importance of chamber data in the evaluation of mechanisms this introduces some uncertainty in their evaluation and could involve compensating errors. Further research is required to evaluate the mechanisms of O³P reactions.

The treatment of these reactions is reasonable but the most of the data are old from Atkinson and Lloyd (1984). The reactions of O³P are not very important for most atmospheric conditions. These reactions may be important when chamber experiments are used to evaluate the mechanism due to the high VOC concentrations used in chamber experiments.

Assigned O³P Rate Constants

Dr. Carter's approach is reasonable given the available data.

Estimated O³P Rate Constants

Dr. Carter's approach is reasonable given the available data.

Estimated Mechanisms for O³P Reactions

These mechanisms appear to be uncertain because the best available data does not give simulations that test well against chamber data. This may represent an important uncertainty if these reactions affected the evaluation of the mechanism when it was tested against chamber data.

Assigned Mechanisms for Dialkenes

Dr. Carter's approach is reasonable given the available data.

Photolysis Reactions

In this section the term "photolysis rate" is misleading. It would be much better to replace "photolysis rate" with the term "photolysis rate parameter" or "photolysis frequency". A

photolysis rate is the product of a photolysis rate parameter and the concentration of the chemical species that is undergoing photolysis.

It is not completely clear how “groups” are counted in Table 26. For example, is $\text{CH}_3\text{-CH}_2\text{-CO-CH}_2\text{-CH}_2\text{-CH}_3$ a molecule with 6 groups?

The cross sections and quantum yields of higher carbonyl compounds are assumed to be the same as those for lower molecular weight carbonyl compounds. The most chemically similar compound is chosen from those available. The same procedure is applied for organic nitrates. This is a reasonable procedure and an advance over the previous mechanism.

The assumption that the carbonyl compounds break along the -CHO bond is consistent with acetaldehyde photolysis and the assumption that ketones break along the bond with the lowest estimated heat of reaction is consistent with the photolysis of methyl ethyl ketone. These are reasonable assumptions to apply to estimate the photolysis mechanisms of other aldehydes and ketones. The use of specific mechanisms for the photolysis of unsaturated aldehydes is reasonable.

The assumptions regarding the cross sections and that the quantum yield for the formation of NO_2 from organic nitrate photolysis appear to be valid.

Default Carbonyl Unsaturated Carbonyl and Organic Nitrate Photolysis Photolysis Mechanisms

The treatment of these reactions is reasonable.

Reactions of Carbon Centered Radicals

Dr. Carter’s approach is reasonable given the available data. There are significant uncertainties in the treatment of allylic radicals. As Dr. Carter points out the treatment of allylic radicals is not always consistent. The inconsistencies in the treatment of allylic radicals are due to need to be consistent with product data.

Reactions of Peroxy Radicals

The fraction of peroxy radicals that react to produce organic nitrate is an important sink of NO_x . From the discussion given on page 89 it appears that earlier measurements of the organic nitrate yield were too high. Lower yields of organic nitrates lead to better fits of chamber experiments. However, Dr. Carter states at the end of the first paragraph: “Therefore, the earlier nitrate yields of Atkinson et al (1982b, 1983b, 1984), which are all based on similar analytical methods, appear to be low.” Does he not mean high?

The data set is not extensive enough to allow trends to be estimated accurately. For example, the data in Figures 5 and 6, pages 99 and 100 respectively, show no trends if each class of organic compound is examined individually.

Reactions of Alkoxy Radicals

H-Shift Isomerizations

Dr. Carter's approach is reasonable given the available data. The acronym BDE (bond dissociation energy) should be defined at the top of page when it is first used.

Beta Scission Decomposition

For Table 34 the criteria for judging the quality of the agreement between estimation and experimental are not clear. What level of agreement is "ok"? It is more important to have good agreement with the minimum, "Exp'd" or maximum values? Is "Exp'd" the best experimental value?

Isomerization Corrections, Ester Rearrangement, Acyloxy Radicals, Explicit Alkoxy Reaction Assignments

Dr. Carter's approach is reasonable given the available data.

Thermochemical Assignments Used in Estimates

Dr. Carter's approach is reasonable but it appears that the more recent data needs to be incorporated in to the database in the future.

Reactions of Crigiee Biradicals

Dr. Carter's approach is reasonable given the available data.

HCHO₂ Biradicals, RCHO₂ Biradicals and R₂COO Biradicals

Dr. Carter's approach is reasonable given the available data.

Page 152 is the "size" of a substituent is much more clearly defined here than the number of "groups" in Table 26.

Assigned Reactions of α -Carbonyl or Unsaturated Crigiee Biradicals

Dr. Carter's approach is reasonable given the available data.

Lumping Assignments

Dr. Carter's approach is reasonable and the description is clear.

Representation of Aromatics

Aromatics, Benzene, Terpenes and Other Compounds

Dr. Carter's approach is reasonable given the available data. It is important to stress that these mechanisms are based on fits to chamber data and that there is uncertainty in extrapolating these results to the real atmosphere.

Detailed Model Species

The choice of the acronym DMS is unfortunate because it often means dimethyl sulfide. I suggest avoiding this acronym in this report.

4. Evaluation of the Use of the "Lumped Molecule" Approach

It is not possible to represent all possible chemical reactions explicitly in the mechanism because of unknowns in the chemistry and also because of the potentially excessive demands on computational resources. It is currently not possible to run a complex 3-d air quality model with a mechanism with thousands of chemical species and reactions. Current detailed chemical mechanisms do contain over 10,000 reactions and species to describe the chemistry of about 100 emitted organic species.

The "lumped molecule" approach refers to model species that react with average rate parameters and average product yields. But it must be recognized that it is unavoidable that information must be lost when different real species are grouped or "lumped" together into model species.

The lumped molecule approach is applied to the chemistry of some of the higher ketones, alcohols and other highly reactive saturated oxygenated compounds that are not aromatics or aldehydes. These compounds represent product species that are more reactive than methyl ethyl ketone. The model PROD2 is used to represent these species. The approach is also applied to the chemistry of various organic nitrates and these are represented as RNO3.

The procedure used to derive the rate parameters and product yields for the model species is valid. Tables 4 and 5 in the mechanism documentation that describe the contributions of various types of model species in the base ROG mixture to the formation of the PROD2 and RNO3 lumped product species, respectively, were examined and appear to be reasonable. The range of compounds represented by PROD2 and NO3 as given in Tables 6 and 7, respectively, of the mechanism documentation are also reasonable. Given the large number of compounds that could be in the mechanism if they were all explicitly included in the mechanism and the uncertainties in their individual chemistries this lumped approach is both necessary and reasonable.

The lumped molecule approach is applied very heavily to uncharacterized aromatic ring products. There is not yet sufficient understanding to treat the aromatic reaction mechanism from a fundamental and explicit point of view. The model species DCB1, DCB2 and DCB3 are used to characterize the reactivity of uncharacterized ring-fragmentation products. The names are appropriate because these compounds are probably dicarbonyls. DCB1 reacts with HO and ozone but it does not undergo significant photolysis. DCB2 and DCB3 photolyze rapidly enough that the ozone reaction is assumed to be negligible. The reactions of HO with DCB2 and DCB3 are included.

The reactions of the lumped aromatic species are based on fits of environmental chamber data as all other atmospheric chemistry mechanisms for air quality modeling. This does introduce significant uncertainty into the mechanism when it is applied to aromatic species. However mechanisms are improving due to the studies cited by Carter in the documentation.

There are several “unreactive species” that are within the category of lumped molecule species. These are treated sufficiently well within the mechanism

5. Evaluation of the Handling of Uncertainty in both the MIR and the Regulation

Sources of Mechanistic Uncertainty

There are many sources of uncertainty in current atmospheric chemistry mechanisms for air quality modeling. These are documented relatively well in the mechanism documentation. Dr. Carter is to be commended for developing a high quality mechanism that is state of the science for air quality modeling. The mechanism makes full use of the available kinetic data and reflects the considerable progress that has been made in improving our understanding of atmospheric chemistry. However there remain several important outstanding issues to be resolved by further experimental studies.

Better mechanistic data for most higher molecular weight organic compounds and their photooxidation products are needed. Most of the mechanism for compounds with carbon numbers greater than 3 or 4 are based on analogy with the reactions and rate parameters of lower molecular weight compounds. While the rate parameters for the reactions of HO with a wide range of parameters are relatively well known, in contrast, much more data are needed for the rate parameters for the reactions of NO₃ and O₃. It is surprising that rate constants for the reactions of NO₃ with propionaldehyde and higher aldehydes are not available. The quantum yields, absorption cross sections and product yields for photolysis reactions for most higher aldehydes, ketones, alcohols, dicarbonyls and similar compounds are not well known.

More data are required for the product yield for the reactions of HO, NO₃ and O₃ with alkenes. HO and NO₃ add to the double bonds of alkenes but the site is relatively unknown. There is a little data available for the site of the HO addition but almost no available information available for NO₃. For some alkenes this uncertainty may affect the estimated organic product yields. Given the relatively high reactivity of alkenes this may be significant.

The product yields for the reactions of ozone with alkenes are in relatively better condition than they are for either the HO or NO₃ reactions. But product yields for the reactions of ozone with alkenes could be better characterized especially for any Criegee biradicals beyond those produced from ethene and propene. The required data include the nature and yield of radicals and organic acids.

Better data are required for the reactions of peroxy radicals with NO₃ and for their reactions with other RO₂. The reactions of NO₃ with RO₂ are important during the night when NO₃ concentrations may be high (Stockwell et al., 1995). The reactions of RO₂ with RO₂ may be important under some nighttime conditions and when there are low concentrations of nitric oxide (Stockwell et al., 1995).

The mechanism for aromatic species is not known in explicit detail and therefore the uncertainties are very high. There has been much progress during recent years but the nature of many products remains unknown. Especially the nature of the ring

fragmentation products has not been determined. All aromatic chemistry mechanisms for air quality models are based upon parameterizations from environmental chamber experiments. It is possible that the parameterizations are not always applicable to the real atmosphere.

The mechanism is clearly within the realm of the best available science. Air quality models that make use of previous versions of Dr. Carter's mechanism should update to this new version. But are the uncertainties low enough that the mechanism can be used to reliably estimate the incremental reactivity of VOCs for regulatory purposes? Russell et al. (1995) examined this question for a previous version of Dr. Carter's mechanism. They found that although there were significant uncertainty in the calculated MIR and MOIR values that the relationships between the incremental reactivities were relatively robust. This would be expected to be true of MIR and MOIR values calculated from the present mechanism with significantly reduced uncertainty.

Treatment of Mechanistic Uncertainties in the Regulation

Evaluation of Dr. Carter's Scheme for Classifying Mechanistic Uncertainties

In this section Dr. Carter's uncertainty scheme and its application to MIR value uncertainties is evaluated. Dr. Carter defines 11 categories or "bins" to describe the "certainty" of the chemical mechanism used to determine MIR values. The uncertainty scale, Table 5-1, is subjective but it is Dr. Carter's best judgment of a chemical mechanism's certainty for an organic compound and its effect on a compound's estimated MIR value.

The uncertainty scheme must be understandable to the stakeholders and the general public so it must be relatively simple. It is proposed for the regulation that these 11 bins should be used as a basis for estimating an uncertainty in an organic compound's MIR. In the proposed regulation compounds in uncertainty bins 1 through 5 have no error bars (adjustments) on their MIR value while compounds in bins 6, 7, 8, 10, 11 have an uncertainty adjustment factor of 2 unless the MIR is the calculated upper limit MIR.

Some measure of the uncertainty in a MIR is required to account for the possibility that a MIR value could change due to new mechanistic data. If a MIR increases in the future due to new data, an air quality disbenefit could result unless the reactivity based regulation makes some allowance for present uncertainty. Consideration of uncertainty in the regulation is required because both regulators and other stakeholder need to account for the "stability" of the MIR value.

Table 5-1. Dr. W.P.L. Carter's "certainty" scale for MIR values.

Certainty	Description
0	Not applicable: No estimated mechanism, or believed to be unreactive.
1	Considered to be least uncertain
2	Some uncertainties but not likely to change significantly
3	Uncertain but not likely to change significantly
4	Uncertain adjusted mechanism may change somewhat if refined, but change not expected to be large. If the compound is predicted to inhibit O ₃ , changes are not expected to affect predicted inhibition, but may affect magnitude of inhibition.
5	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. However, change in MIR is expected to be less than a factor of two.
6	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.
7	Uncertain and is expected to change if compound is studied or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.
8	Non-negligible chance of estimate being significantly incorrect. It is recommended that uncertainty adjustments be employed in regulatory applications.
9	Current mechanism is expected to (or has been found to) over predict reactivity. Uncertainty adjustments may be appropriate if the reactivity of this compound is used to determine a baseline in regulatory applications.
10	Current mechanism is expected to (or has been found to) under predict reactivity. It is recommended that uncertainty adjustments be employed in regulatory applications.
11	Current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain. It is recommended that uncertainty adjustments be employed in regulatory applications.

The scheme in Table 5-1 is reasonable way to assign uncertainties to an overall mechanism and Dr. Carter has made reasonable assignments of uncertainty to the compounds in his new mechanism. This scheme is an advance over the scheme presented in Carter (1994) as discussed below.

Evaluation of the Stability of MIR Values and Uncertainty Multipliers from Monte Carlo Analysis

It is difficult to estimate what effect new data will have on any compound's MIR. The uncertainty scale developed by Carter (1994) was somewhat different from his 1998 scale but bin 1 represents the most certain mechanism and bin 9 represents the least certain mechanism, Table 5-2. Both scales are an acceptable measure of uncertainty in Dr. Carter's mechanism and for constancy in this analysis we used Carter's original scheme, Table 5-2.

Table 5-2. Dr. W.P.L. Carter's "certainty" scale for MIR values from Carter (1994).

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

A concern is that, since MIRs are calculated for mixtures of organic compounds, the MIR for even a compound with a relatively certain mechanism might still have an uncertain MIR because of the interactions between all of the oxidation mechanisms. Thus it is difficult to assign MIR multiplication factors to account for the uncertainty in the mechanisms of individual compounds. To examine this question we examined coefficients of variation for the MIRs calculated by Yang (1995), these are given in Table 5-3 along with the assigned uncertainties of Carter (1994).

Yang (1995) performed Monte Carlo calculations based on mechanistic uncertainties in rate parameters and product yields. The analysis of mechanistic uncertainties in rate parameters and product yields was based on a detailed analysis of the uncertainties in each reaction (Yang et al., 1995). The coefficient of variation for a compound is the average value of its MIRs determined from the Monte Carlo calculations divided by its standard deviation (Yang, 1995). The average coefficient of variation in Table 5-3 is 0.41

and Figure 5-1 shows that coefficient of variation does not correlate well with assigned mechanistic uncertainty.

The work of Yang (1995) has been updated recently (L. Wang and J.B. Milford, private communication). Table 5-4 gives new coefficients of variation and Carter's mechanistic uncertainty assignments (Carter, 8/6/98). The coefficients of variation are lower, the average coefficient of variation is 0.28. Figure 5-2 shows a plot of the new coefficients of variation as a function of Carter's mechanistic uncertainty assignments (Carter, 8/6/98). For these compounds the coefficient of variation does not correlate well with assigned mechanistic uncertainty.

On the basis of these two studies the average coefficient of variation ranges between 0.28 and 0.41. These studies also show that the coefficient of variation is not very dependent on the assigned mechanistic uncertainty. On the basis of these two studies it would be better to assume that the one-sigma uncertainties are at least $\pm 30\%$ and that a multiplier of 1.3 would be more realistic for the certain and less certain compounds. However, the historical record supports a somewhat higher multiplier for the certain compounds.

Table 5-3. Coefficients of Variation from (Yang, 1995) and Mechanistic Uncertainties from Carter (1994).

Compound	Coefficients of Variation	1994 Mechanistic Uncertainty
Formaldehyde	0.25	1
Ethene	0.42	1
Ethanol	0.66	1
Methanol	0.47	1
Butane	0.54	1
MTBE	0.49	1
Propane	0.54	2
Ethane	0.61	2
Methane	0.45	2
Propene	0.37	4
Acetaldehyde	0.41	4
m,p Xylene	0.43	4
Toluene	0.52	4
Benzene	0.65	4
Propionaldehyde	0.4	5
Methylethylketone	0.49	5
Acetone	0.33	5
Benzaldehyde	-0.48	5
124-trimethylbenzene	0.37	7
3-m-Cyclopentene	0.35	7
2-m-2-Butene	0.34	7
2-m-1-Butene	0.36	7
m-cyclopentane	0.44	7
Ethylbenzene	0.52	7
ETBE	0.4	7
2-m-Pentane	0.48	7
224-tri-m-Pentane	0.51	7
1,3-Butadiene	0.35	8

Table 5-4. Coefficients of Variation from (L. Wang and J.B. Milford, private communication) and Mechanistic Uncertainties from Carter (8/6/98).

Compound	Coefficients of Variation	1998 Mechanistic Uncertainty	Compound	Coefficients of Variation	1998 Mechanistic Uncertainty
Methane	0.29	1	Toluene	0.27	4
Ethane	0.34	1	Ethyl Benzene	0.28	4
Propane	0.31	1	2-Butoxy Ethanol	0.24	4
n-Butane	0.35	1	n-Butyl Acetate	0.37	4
Ethanol	0.34	1	a-Pinene	0.21	4
Methyl t-Butyl Ether	0.30	1	Benzaldehyde	0.80	4
Formaldehyde	0.27	1	1,3,5-Trimethyl Benzene	0.31	5
Acetaldehyde	0.21	1	1,2,3-Trimethyl Benzene	0.31	5
n-Hexane	0.31	2	1,2,4-Trimethyl Benzene	0.33	5
Ethene	0.24	2	Benzene	0.31	5
Propene	0.21	2	2-Methyl Pentane	0.31	5
trans-2 Butene	0.22	2	1,3-Butadiene	0.21	5
Isoprene	0.20	2	2-Methyl-1-Butene	0.20	5
Methanol	0.34	2			
C4 Ketones	0.26	2			
m-Xylene	0.29	3			
o-Xylene	0.27	3			
p-Xylene	0.28	3			
Methylcyclopentane	0.29	3			
2-Methyl-2-Butene	0.29	3			
Ethyl t-Butyl Ether	0.24	3			
Acetone	0.23	3			
C3 Aldehydes	0.23	3			

Figure 5-1. Coefficients of Variation from (Yang, 1995) as a Function of the Mechanistic Uncertainties from Carter (1994).

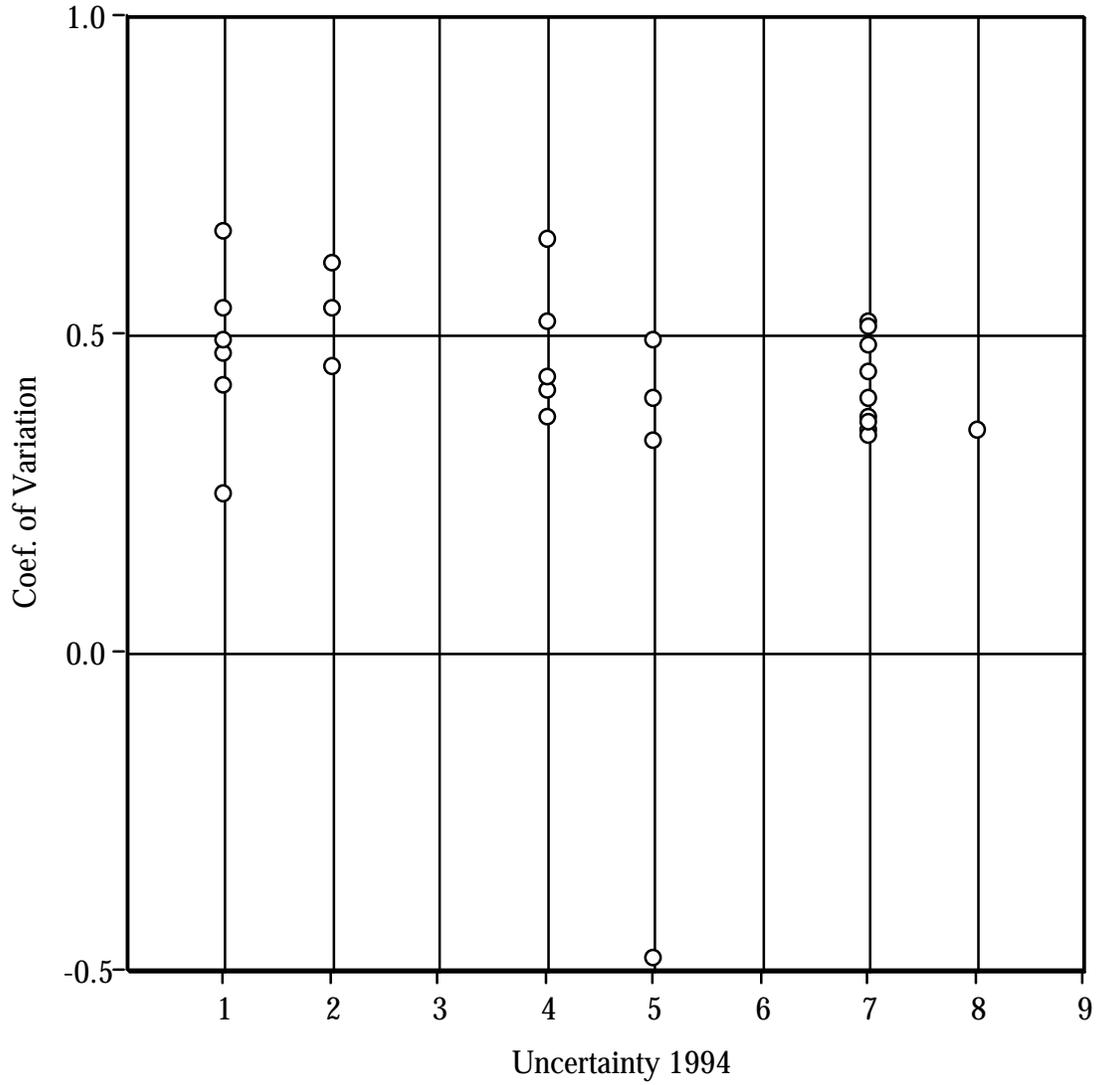
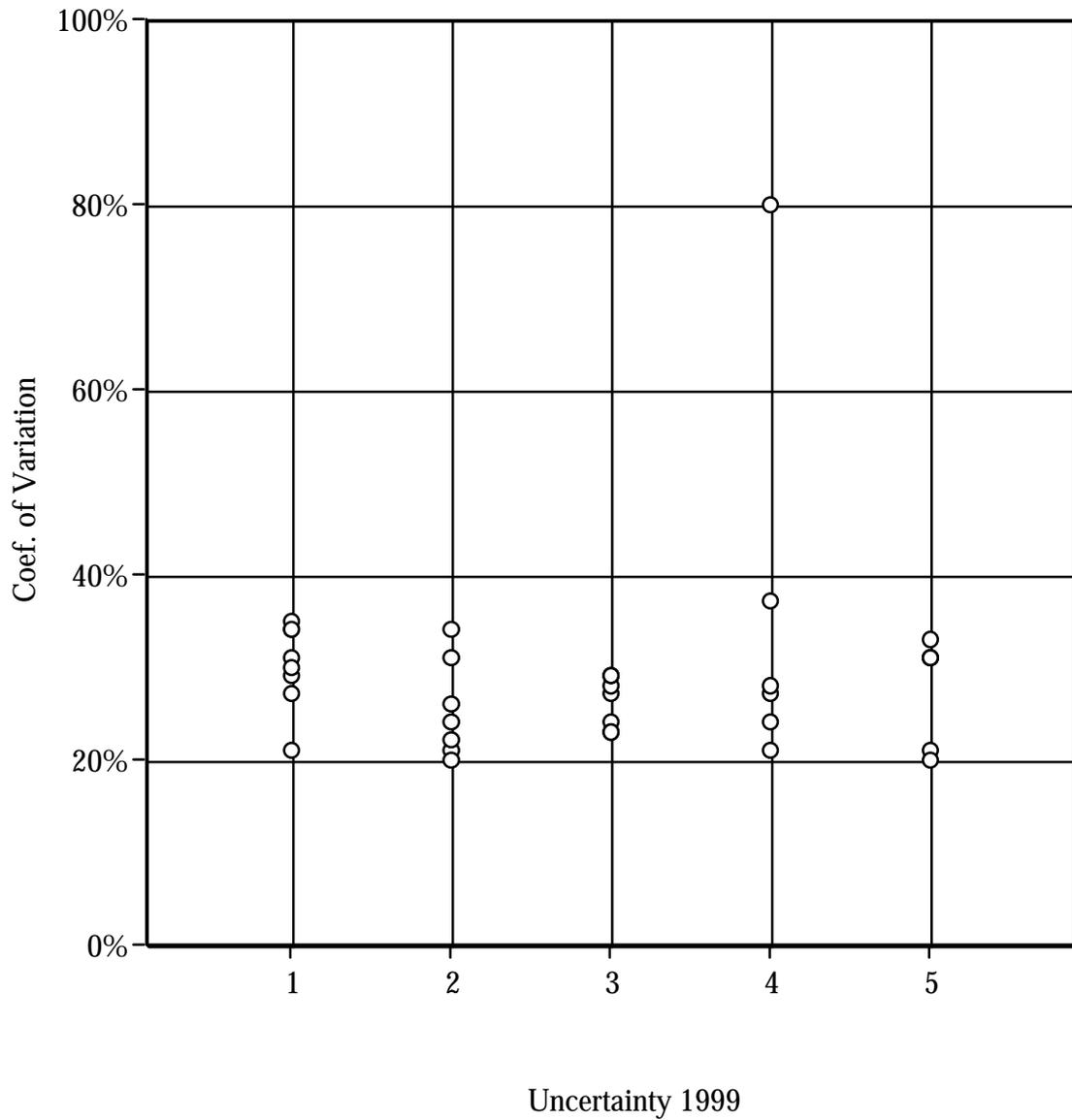


Figure 5-2. Coefficients of Variation from (L. Wang and J.B. Milford, Private Communication) as a Function of the Mechanistic Uncertainties from Carter (8/6/98).



Evaluation of the Stability of MIR Values and Uncertainty Multipliers from Experience
Since Dr. Carter did provide MIR values and estimates of their uncertainty in Carter (1994), it is possible to evaluate how these have changed between 1994 and the currently available values from August 6, 1998. Comparison of the percent change in MIR values between 1994 and 1998 is an estimate of the stability of MIR values. When the changes in MIR values between 1994 and 1998 are compared with the assigned uncertainties from 1994 the effect of uncertainty can be estimated. However, in 1999 there is much more data available and Dr. Carter has incorporated this new data into his mechanism so it would be expected that this approach might yield an overestimate of the instability of MIR values and of the uncertainty multipliers that should be assigned to the MIRs.

In Table 5-5 the mechanistic uncertainty, the MIRs, the percent change in the MIR, the rank of the compounds MIR values estimated by Carter (1994) and by Carter (August 6, 1998), and the change in the rank of the MIR value between 1994 and 1998 are shown for the compounds that were common to both assessments.

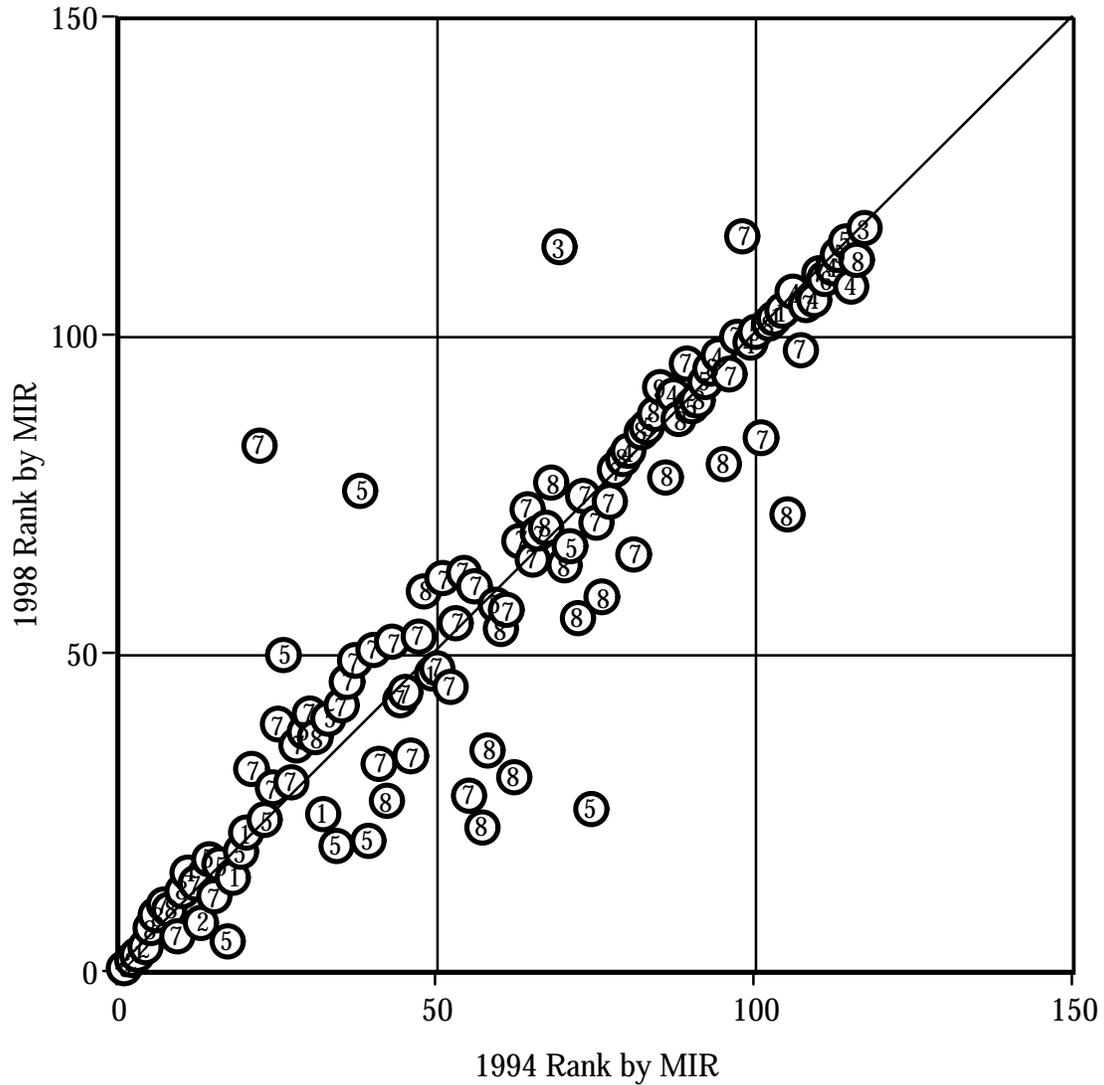
Figures 5-3 and 5-4 show a comparison of the ranks of the MIR values determined in 1994 with those determined in 1998. In these figures the rank of the 1998 MIR is plotted as a function of the rank of the 1994 MIR. The diagonal line represents the line of perfect agreement in the two ranks. The assigned uncertainty (Carter, 1994) is given in the center of each data point. Figure 5-3 is the same as Figure 5-4 except only the ranks of the 50 most reactive compounds are plotted.

Figures 5-3 and 5-4 show that the relative ranking of the MIR values was remarkably stable between 1994 and 1998. The greatest changes in the ranking of the MIRs have occurred for compounds with assigned uncertainties greater than 5 except for one point with an uncertainty of 3. A large change occurred for glyoxal which was assigned to bin 3 but its MIR changed by over 550%. Overall, this stability is surprising because of the relatively high uncertainty in the mechanisms assigned in 1994. This result supports the hypothesis that MIRs can be used in a relative fashion and this result is in accord with Russell et al. (1995).

The percent change in the MIR values between 1994 and 1998 as a function of the assigned uncertainty (Carter, 1994) is plotted in Figure 5-5. The 1998 MIR values are an average of 47 % greater than the values estimated by Carter (1994). This suggests that a multiplier of 1.5 would be more realistic.

Figure 5-5 shows that in general the greater the assigned mechanistic uncertainty the greater the percent change between 1994 and 1998. Since compounds with greater uncertainties may have greater changes in their MIR values the values should be multiplied by a greater uncertainty factor.

Figures 5-3. A comparison of the ranks of the MIR values determined in 1994 with those determined in 1998. The rank of the 1998 MIR is plotted as a function of the rank of the 1994 MIR. The diagonal line represents the line of perfect agreement in the two ranks. The assigned uncertainty (Carter, 1994) is given in the center of each data point.



Figures 5-4. A comparison of the ranks of the MIR values determined in 1994 with those determined in 1998 for the 50 most reactive compounds in 1994. The rank of the 1998 MIR is plotted as a function of the rank of the 1994 MIR. The diagonal line represents the line of perfect agreement in the two ranks. The assigned uncertainty (Carter, 1994) is given in the center of each data point.

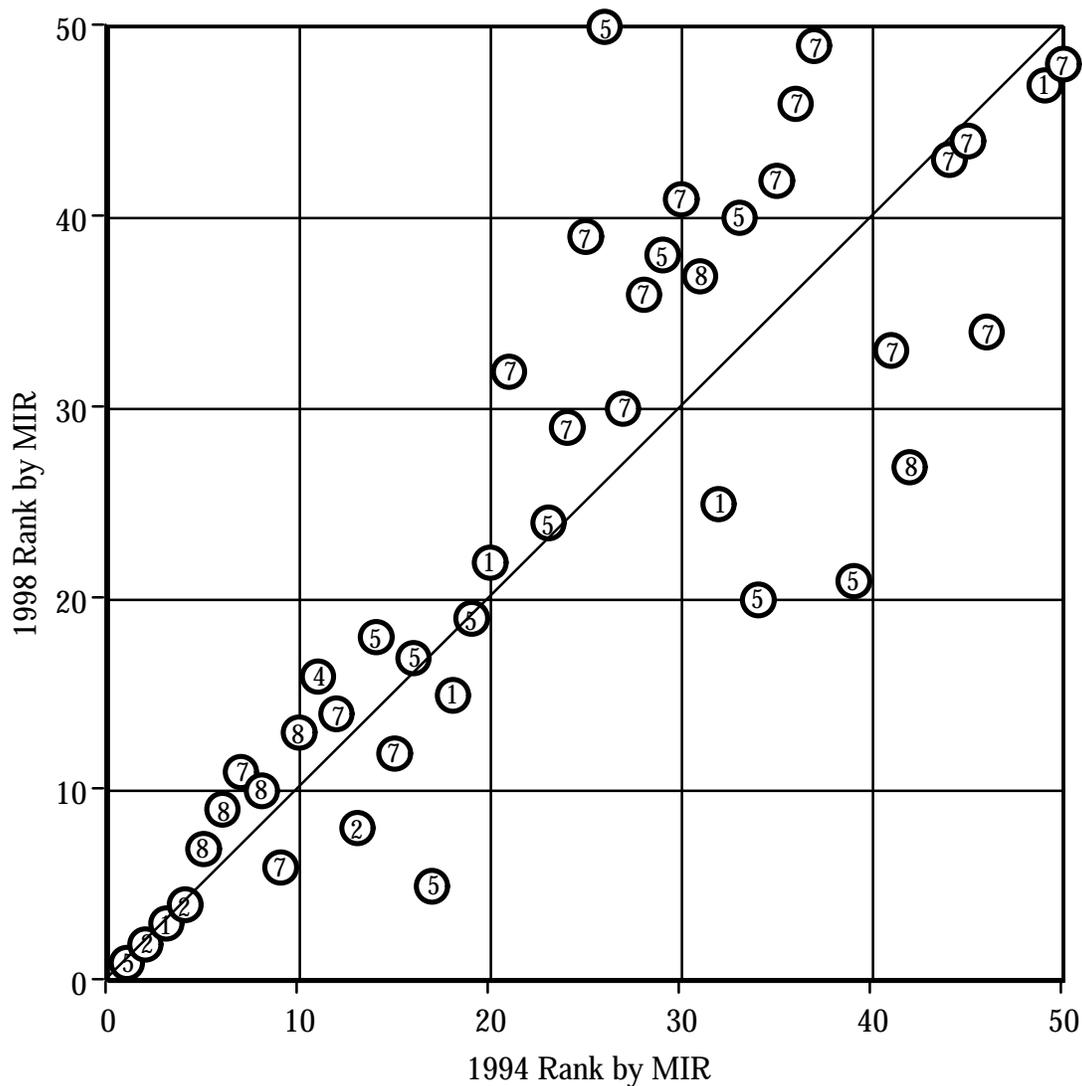
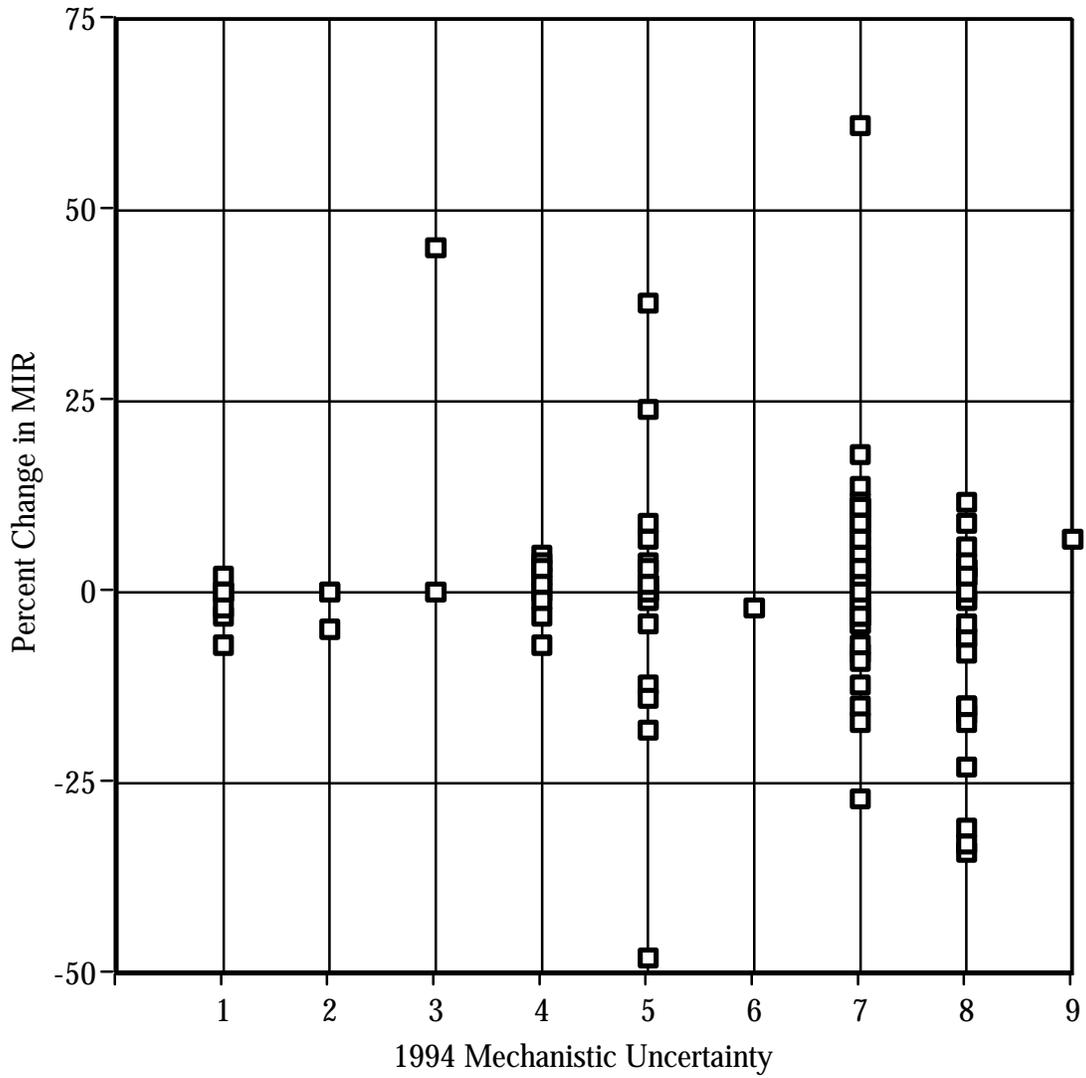


Figure 5-5. The percent change in the MIR values between 1994 and 1998 plotted as a function of the assigned uncertainty (Carter, 1994).



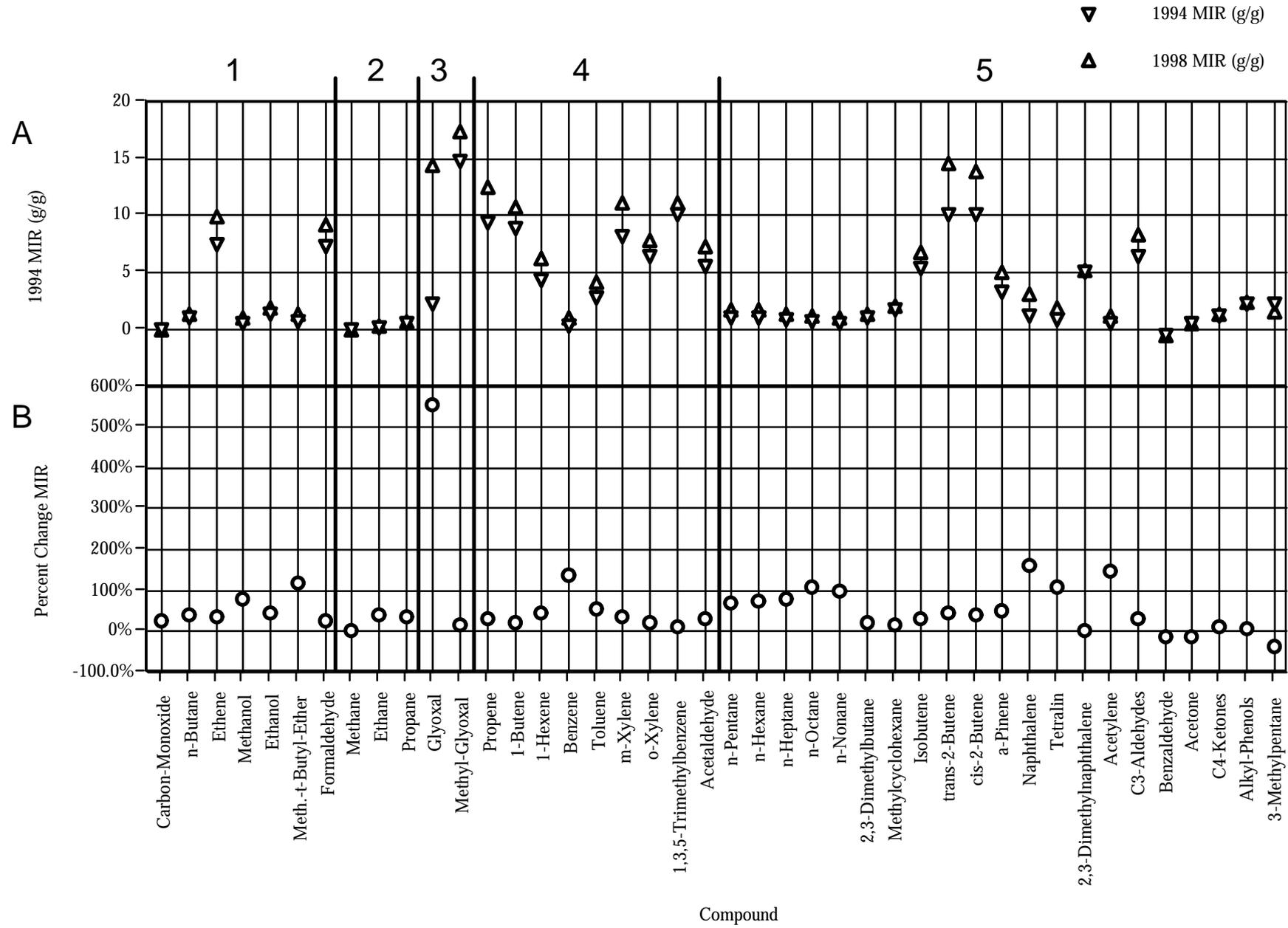
Figures 5-6 and 5-7 show a plot of the 1994 and 1998 MIR values, their percent change and the assigned uncertainty values from 1994 for each compound. Figure 5-7 is the same as Figure 5-6 except that the scales have been expanded to show better the less reactive compounds. Figures 5-6 and 5-7 show that the compounds in the higher uncertainty bins had a greater change in the MIRs as also seen in Figure 5-5. However there was not a sharp cutoff point where a higher assigned uncertainty was associated with a large percent change in the MIR values.

Conclusions

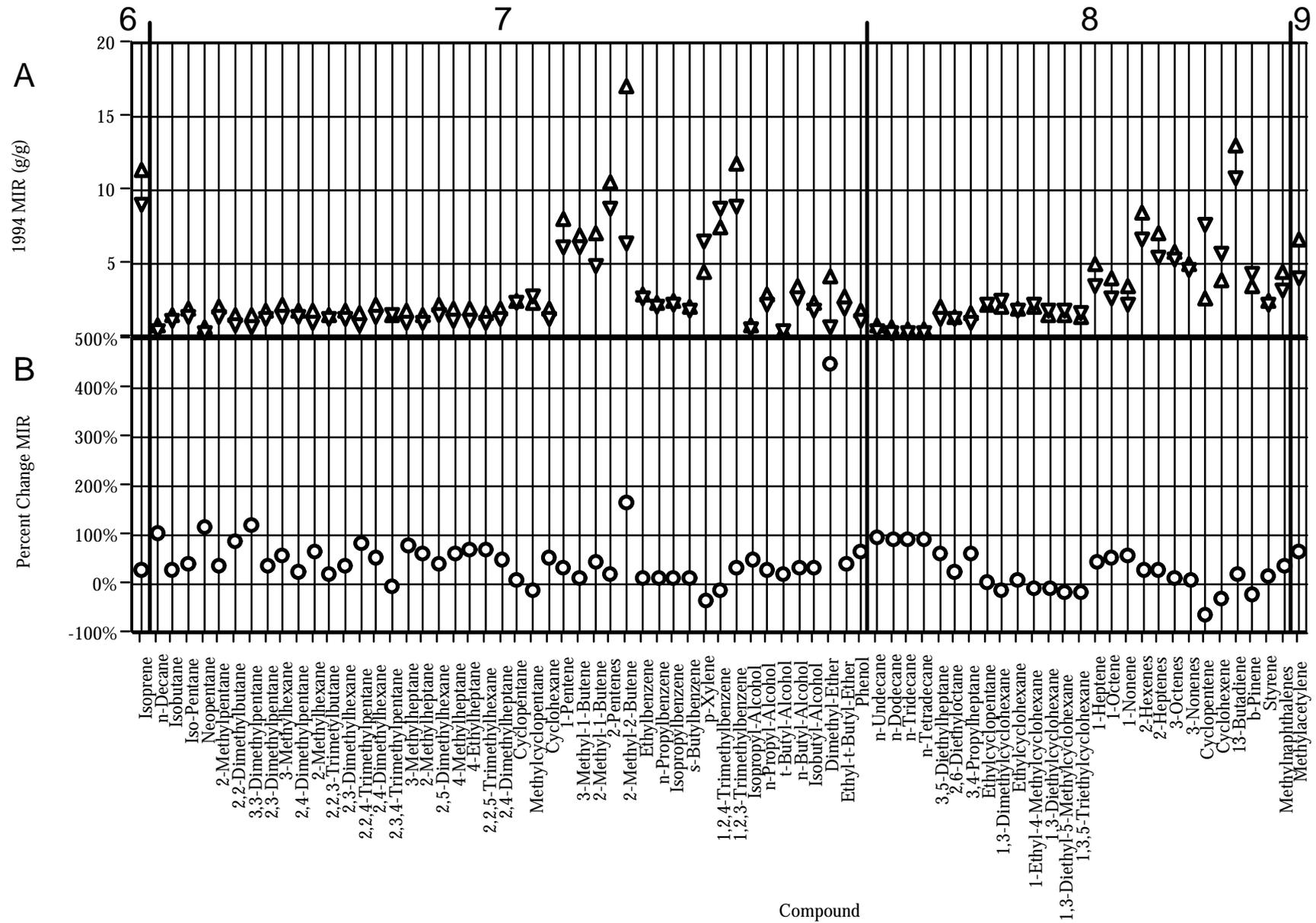
Carter's scheme of assigning organic compounds to 11 bins based on the compound's mechanistic uncertainty is reasonable. The assignments made by him appear to be reasonable in view of the current state of chemical knowledge.

A minimum multiplier of 1.5 should be used to estimate the uncertainty in all MIRs. This is based on the range of the average coefficient of variation being between 0.28 and 0.41 and on the fact that the MIRs increased between 1994 and 1998 by 47%. It would seem reasonable based on the past changes to assume that any MIR might vary by 50% in future calculations. Bins 1 to 4 should be adjusted by a factor of 1.5. Based on this analysis a factor of 2 is a large enough adjustment for bin 5 and higher bins. It is suggested that these new factors are a more reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity. Use of these proposed higher factors is a reasonable method of handling uncertainty in MIRs while minimizing the possibility of underestimating a product's reactivity.

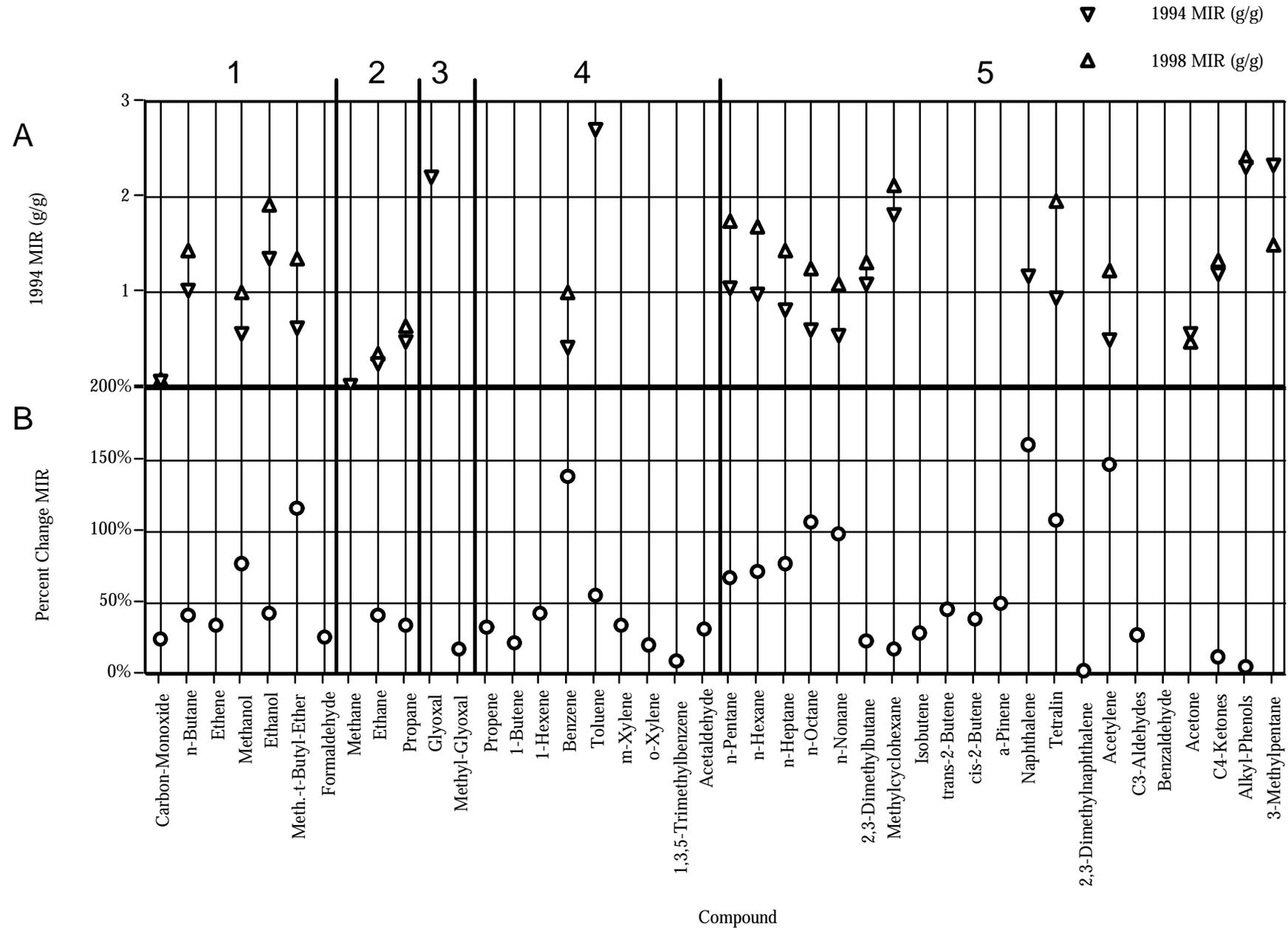
Figures 5-6. The 1994 and 1998 MIR values, their percent change and the assigned uncertainty values from 1994 for each compound.



Figures 5-6. Continued.



Figures 5-7. Expanded scale plot of 1994 and 1998 MIR values, their percent change and the assigned uncertainty values from 1994 for each compound.



Figures 5-7. Continued.

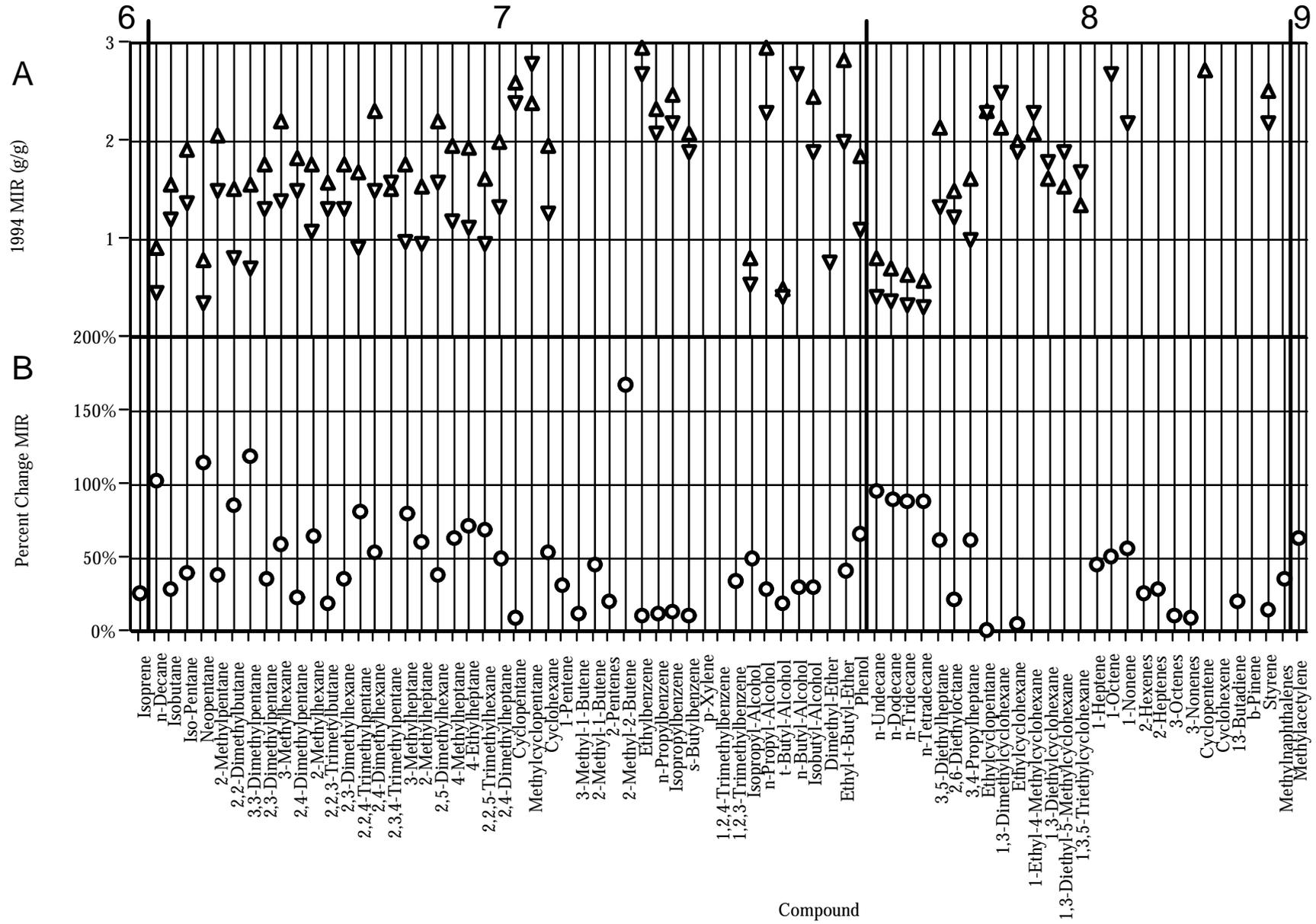


Table 5-5. The mechanistic uncertainty, MIR, the percent change in the MIR, the rank of the compounds MIR values estimated by Carter (1994) and by Carter (8/6/1998) and the change in the rank of the MIR between 1994 and 1998.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
Carbon-Monoxide	1	0.054	0.07	24.73	3	3	0
Methanol	1	0.56	0.99	77.23	18	15	-3
Meth.-t-Butyl-Ether	1	0.62	1.34	116.26	20	22	2
n-Butane	1	1.02	1.44	40.97	32	25	-7
Ethanol	1	1.34	1.92	43.15	49	47	-2
Formaldehyde	1	7.2	9.12	26.67	103	103	0
Ethene	1	7.4	9.97	34.77	104	104	0
Methane	2	0.015	0.01	-0.56	2	2	0
Ethane	2	0.25	0.35	41.90	4	4	0
Propane	2	0.48	0.64	34.24	13	8	-5
Glyoxal	3	2.2	14.39	553.92	69	114	45
Methyl-Glyoxal	3	14.8	17.37	17.40	117	117	0
Benzene	4	0.42	1.00	137.94	11	16	5
Toluene	4	2.7	4.19	55.10	80	82	2
1-Hexene	4	4.4	6.30	43.08	87	91	4
Acetaldehyde	4	5.5	7.27	32.15	94	97	3
o-Xylene	4	6.5	7.83	20.50	99	99	0
1-Butene	4	8.9	10.80	21.32	109	106	-3

Table 5-5. Continued.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
m-Xylene	4	8.2	11.06	34.88	106	107	1
1,3,5-Trimethylbenzene	4	10.1	11.10	9.87	115	108	-7
Propene	4	9.4	12.44	32.39	112	111	-1
Benzaldehyde	5	-0.57	-0.50	-12.02	1	1	0
Acetone	5	0.56	0.48	-13.91	17	5	-12
n-Nonane	5	0.54	1.07	98.68	16	17	1
Acetylene	5	0.5	1.23	146.48	14	18	4
n-Octane	5	0.6	1.24	107.09	19	19	0
2,3-Dimethylbutane	5	1.07	1.31	22.57	34	20	-14
C4-Ketones	5	1.18	1.32	12.19	39	21	-18
n-Heptane	5	0.81	1.43	77.02	23	24	1
3-Methylpentane	5	2.33	1.5	-35.63	74	26	-48
n-Hexane	5	0.98	1.69	72.24	29	38	9
n-Pentane	5	1.04	1.74	67.72	33	40	7
Tetralin	5	0.94	1.95	107.32	26	50	24
Methylcyclohexane	5	1.8	2.11	17.07	59	58	-1
Alkyl-Phenols	5	2.3	2.42	5.15	71	67	-4
Naphthalene	5	1.17	3.05	160.85	38	76	38

Table 5-5. Continued.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
a-Pinene	5	3.3	4.94	49.62	83	86	3
2,3-Dimethylnaphthalene	5	5.1	5.25	3.01	90	89	-1
Isobutene	5	5.3	6.81	28.41	92	93	1
C3-Aldehydes	5	6.5	8.30	27.72	100	101	1
cis-2-Butene	5	10	13.80	38.05	113	113	0
trans-2-Butene	5	10	14.52	45.24	114	115	1
Isoprene	6	9.1	11.47	26.10	111	109	-2
t-Butyl-Alcohol	7	0.42	0.50	18.56	9	6	-3
Neopentane	7	0.37	0.79	114.56	7	11	4
Isopropyl-Alcohol	7	0.54	0.81	50.26	15	12	-3
n-Decane	7	0.46	0.93	102.71	12	14	2
2,3,4-Trimethylpentane	7	1.6	1.52	-5.07	55	28	-27
2,2-Dimethylbutane	7	0.82	1.52	85.49	24	29	5
2-Methylheptane	7	0.96	1.54	60.21	27	30	3
3,3-Dimethylpentane	7	0.71	1.56	119.57	21	32	11
Isobutane	7	1.21	1.56	29.22	41	33	-8
2,2,3-Trimethylbutane	7	1.32	1.58	19.37	46	34	-12
2,2,5-Trimethylhexane	7	0.97	1.64	68.83	28	36	8

Table 5-5. Continued.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
2,2,4-Trimethylpentane	7	0.93	1.69	81.53	25	39	14
3-Methylheptane	7	0.99	1.78	79.92	30	41	11
2-Methylhexane	7	1.08	1.78	65.02	35	42	7
2,3-Dimethylhexane	7	1.31	1.78	36.10	44	43	-1
2,3-Dimethylpentane	7	1.31	1.78	36.24	45	44	-1
2,4-Dimethylpentane	7	1.5	1.85	23.51	52	45	-7
Phenol	7	1.12	1.86	65.76	36	46	10
Iso-Pentane	7	1.38	1.93	40.15	50	48	-2
4-Ethylheptane	7	1.13	1.94	71.28	37	49	12
4-Methylheptane	7	1.2	1.96	63.20	40	51	11
Cyclohexane	7	1.28	1.96	53.45	43	52	9
2,4-Dimethylheptane	7	1.33	2.00	50.21	47	53	6
2-Methylpentane	7	1.5	2.07	38.13	53	55	2
s-Butylbenzene	7	1.9	2.10	10.71	61	57	-4
2,5-Dimethylhexane	7	1.6	2.21	38.43	56	61	5
3-Methylhexane	7	1.4	2.22	58.64	51	62	11
2,4-Dimethylhexane	7	1.5	2.31	53.89	54	63	9
n-Propylbenzene	7	2.1	2.35	11.87	65	65	0

Table 5-5. Continued.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
Methylcyclopentane	7	2.8	2.40	-14.20	81	66	-15
Isobutyl-Alcohol	7	1.9	2.47	30.14	63	68	5
Isopropylbenzene	7	2.2	2.48	12.83	66	69	3
Cyclopentane	7	2.4	2.61	8.62	75	71	-4
Ethyl-t-Butyl-Ether	7	2	2.83	41.74	64	73	9
Ethylbenzene	7	2.7	2.97	10.03	77	74	-3
n-Propyl-Alcohol	7	2.3	2.97	29.29	73	75	2
n-Butyl-Alcohol	7	2.7	3.53	30.56	78	79	1
Dimethyl-Ether	7	0.77	4.21	446.96	22	83	61
p-Xylene	7	6.6	4.44	-32.72	101	84	-17
3-Methyl-1-Butene	7	6.2	6.92	11.64	96	94	-2
2-Methyl-1-Butene	7	4.9	7.14	45.73	89	96	7
1,2,4-Trimethylbenzene	7	8.8	7.49	-14.84	107	98	-9
1-Pentene	7	6.2	8.16	31.69	97	100	3
2-Pentenes	7	8.8	10.63	20.82	108	105	-3
1,2,3-Trimethylbenzene	7	8.9	11.90	33.72	110	110	0
2-Methyl-2-Butene	7	6.4	17.11	167.27	98	116	18
n-Tetradecane	8	0.32	0.60	88.93	5	7	2

Table 5-5. Continued.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
n-Tridecane	8	0.35	0.66	88.67	6	9	3
n-Dodecane	8	0.38	0.72	89.91	8	10	2
n-Undecane	8	0.42	0.82	95.91	10	13	3
1,3,5-Triethylcyclohexane	8	1.7	1.37	-19.55	57	23	-34
2,6-Diethyloctane	8	1.23	1.50	22.32	42	27	-15
1,3-Diethyl-5- Methylcyclohexane	8	1.9	1.55	-18.20	62	31	-31
1,3-Diethylcyclohexane	8	1.8	1.63	-9.45	58	35	-23
3,4-Propylheptane	8	1.01	1.64	62.25	31	37	6
Ethylcyclohexane	8	1.9	2.00	5.18	60	54	-6
1-Ethyl-4-Methylcyclohexane	8	2.3	2.10	-8.61	72	56	-16
1,3-Dimethylcyclohexane	8	2.5	2.15	-14.07	76	59	-17
3,5-Diethylheptane	8	1.33	2.16	62.29	48	60	12
Ethylcyclopentane	8	2.3	2.32	0.89	70	64	-6
Styrene	8	2.2	2.52	14.34	67	70	3
Cyclopentene	8	7.7	2.74	-64.44	105	72	-33
1-Nonene	8	2.2	3.45	56.97	68	77	9
b-Pinene	8	4.4	3.50	-20.47	86	78	-8
Cyclohexene	8	5.7	3.92	-31.29	95	80	-15

Table 5-5. Continued.

Compound	1994 Mechanistic Uncertainty	1994 MIR (O ₃ g / VOC g)	1998 MIR (O ₃ g / VOC g)	Change in MIR Value (Percent)	1994 Rank by MIR	1998 Rank by MIR	Difference in Rank
1-Octene	8	2.7	4.08	51.06	79	81	2
Methylnaphthalenes	8	3.3	4.47	35.39	82	85	3
3-Nonenes	8	4.6	5.01	8.95	88	87	-1
1-Heptene	8	3.5	5.07	44.89	84	88	4
3-Octenes	8	5.3	5.89	11.08	91	90	-1
2-Heptenes	8	5.5	7.07	28.63	93	95	2
2-Hexenes	8	6.7	8.46	26.30	102	102	0
1,3-Butadiene	8	10.9	13.09	20.09	116	112	-4
Methylacetylene	9	4.1	6.70	63.46	85	92	7

6. Evaluation of the Mechanism Documentation

The available documentation was examined. In general the documentation was adequate and reasonably well written. There were several places where it would be highly desirable for Dr. Carter to provide more detailed information in the documentation and these have been noted in the comments given above.

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Glossary of Acronyms

A	Arrhenius parameter, also called the pre-exponential factor. It is found in the Arrhenius equation for kinetic rate parameters: $k=A*\exp(E_a/T)$, where k is the rate parameter, E_a is the activation energy and T is the temperature
B	Exponent for the rate parameters of “third order reactions” and for the rate parameters of the high pressure limits of these reactions. For third order reactions: $k_0(T) =k_0^{300}(T/300)^{-B}$ and for their high pressure limits: $k_\infty(T) =k_\infty^{300}(T/300)^{-B}$
E_a	Activation energy, see definition of A, Arrhenius parameter, given above.
Falloff, F	A parameter used to interpolate between third order rate parameters (low pressure limit) and high pressure rate parameters to estimate reaction rate parameters at atmospheric pressure. See also the definition for “B”.
Falloff Expression	Equation used to interpolate between third order rate parameters (low pressure limit) and high pressure rate parameters to estimate reaction rate parameters at atmospheric pressure. See also the definition for “B”.
IR	Incremental reactivity, the change in the grams of ozone formed per change in grams of volatile organic compound present in the polluted atmosphere.
IUPAC	International Union of Pure and Applied Chemistry.
k_0	Third order reaction rate parameter. See also the definition for “B” and Falloff Expression.
k_∞	High pressure rate parameter. See also the definition for “B” and Falloff Expression.
$k(300)$	Rate parameter at 300 K for “third order reactions” and for the high pressure limits of these reactions. See also the definition for “B”.
MIR	Maximum incremental reactivity. An incremental reactivity calculated for a volatile organic mixture where the emissions of NO_x ($\text{NO} + \text{NO}_2$) have been adjusted to maximize the calculated MIR.

NASA	National Aeronautics and Space Administration.
Radical	A reactive chemical intermediate with an unpaired electron.
Rate Parameter	A parameter used to calculate the rate of a chemical reaction from the concentrations of the reactants. For example, the rate of a bimolecular reaction is: $R = k[A][B]$, where R is the rate, k is the rate parameter, [A] is the concentration of a reactant and [B] is the concentration of the second reactant.
Reactant	Chemical species lost in a chemical reaction.
Product	Chemical species formed by a chemical reaction.
VOC	Volatile Organic Compound.

Appendix A: Drafts of Dr. William P.L. Carter's Mechanism Used for this Review

January 9, 1999: [A listing of model species and kinetic parameters of base mechanism](#)

April 27, 1999: [Chemical mechanism components](#)

May 27, 1999: [Overview of mechanism generation system and discussion of initial reactions](#)

July 3, 1999: [Incomplete draft of documentation of the SAPRC99](#)

August 4, 1999: [Incomplete draft of documentation of the SAPRC99](#)

Appendix B: Dr. William P.L. Carter's Response to Comments Received from this Review

by

William P. L. Carter

August 3, 1999

The California Air Resources Board (CARB) has contracted Dr. William R. Stockwell to carry out a peer review of the updated SAPRC mechanism and its documentation, being prepared by the author under separate CARB contracts. As part of his efforts for this project, Dr Stockwell has prepared a draft final report, in which he gave some comments and recommendations concerning primarily the base mechanism and some of its current documentation. Since that time, some modifications have been made to the base mechanism and its documentation, in part as a response Dr. Stockwell's comments, and in part for other reasons.

Given below are summaries of various comments given in those reports that might be interpreted as criticisms or suggestions for change, and the authors responses to those comments. Note that in a number of cases the author agreed with the comments and has changed the mechanism accordingly, though there are some cases where the author does not completely agree with the comments or where changes could not be made.

Species Listing Format

Comment: The units for the defaults of the Constant Species should be defined. The units of O₂, M and H₂O appear to be ppm while the unit for light appears to be a multiplier of unity. HV, light, is listed under Constant Species and characterized as a Type "Con". Although HV is not a chemical species it is not a constant in the atmosphere. It is suggested that HV be moved to its own category for clarity. It is not clear how "Act*" differs from "Act"

Response: The tabulation that appears in the documentation report will not have default concentrations for constant species, since this is a function of the model scenario and not the mechanism. HV will be kept in the "constant" category because this is the way it is treated by the software, though it is recognized that it is not a chemical species. The model user should know the difference between HV and a chemical species. The "type" column, which contains the notation "Act*", etc., is used only by the macro producing the preparation input from the reaction listing spreadsheet, and will not be included in the documentation.

Comment: For complete clarity the R2O₂. radical could be described as "Peroxy Radical Operator representing NO to NO₂ conversion without HO₂ formation". It seems surprising that the radical character (nR) of R2O₂ is zero since it is a radical operator.

Response: As discussed in the report text, R2O2 isn't strictly speaking a radical. But this is a minor point because the "nR" assignments are used for internal checking only, and will not be in the documentation report.

Species Scope

Comment: H2 should be considered as either a constant species that reacts or as an active inorganic species because the reaction $H_2 + HO$ is a sink for HO that occurs with a rate that is 30% that of the reaction $CH_4 + HO$ for typical atmospheric conditions (Stockwell et al., 1997). Although H2 should be treated as a constant it is not unreactive. It is a sink for HO radicals that should not be ignored.

Response: Although the reaction of OH with H_2 may occur at a comparable rate as its reaction with methane, it is my understanding that the amount of H_2 in the atmosphere is much lower than the amount of methane, such that its reaction with OH is of no importance. Therefore, the effect of the OH + H_2 reaction is ignored, so H2 can either be included as a buildup species if there is any need to track H_2 , or it can be removed from the mechanism otherwise.

Comment: Dr. Carter may want to consider adding SO2 as an active species. Although SO2 is not greatly important for incremental reactivity applications the mechanism may be used for other applications, such as aerosol formation studies, where this chemistry can be important. The sulfate produced should be added as a Non-Reacting Species.

Response: This point is well taken. SO₂ and SULF have been added to the mechanism, as active and buildup species, respectively. The reaction of SO₂ with OH has been added, but its reactions with stabilized Crigee biradicals are assumed to be negligible.

Comment: Are there data that suggest that the average carbon number of higher organic peroxides, ROOH, is really as high as 3? I would guess that it is closer to 2.

Response: The model species is given the carbon number of 3 because its reactions are based on those estimated for a propyl hydroperoxide. It is being used to represent the hydroperoxides formed from all organic radicals, which in general would have a much higher carbon number. In the remote atmosphere methyl hydroperoxide may dominate, but there is already a separate model species for it.

Comment: I would expect the stabilized products from the Crigee biradicals to be too reactive to be treated as unreactive products. Would it be better to treat them as something at least like ketones?

Response: Stabilized Crigee biradicals are now assumed to be consumed primarily by reaction with H₂O to form the corresponding carboxylic acid. They are therefore removed from this version of the mechanism, and represented by the carboxylic acids themselves. These acids are represented as unreactive because they react relatively slowly, and it is expected that their loss by deposition would be more important than their loss by gas-phase reaction.

Comment: I can easily accept that CH₄ belongs in the category “Primary Organics Represented Explicitly” but given the relative complexity of isoprene chemistry it is not accurate to place it in this category.

Response: The complexity of the chemistry is not really relevant to the categorization. However, the reviewer has a point that it seems sort of strange to categorize isoprene with methane in this context. For organizational purposes isoprene itself (but not its unique products – which must be retained to allow isoprene to be accurately represented) has been removed from the base mechanism, being represented by a detailed model species like the other alkenes. The issue of whether it is represented explicitly will depend on the model application, but the recommendation concerning model implementation will be to represent isoprene explicitly. This will be discussed in a separate section which will concern lumping recommendations.

Comment: The definitions in “Biogenic Compounds in the EKMA Simulations” and “Lumped species used to represent the Base ROG mixture in the EKMA model simulations” are reasonable and within standard practice.

Response: These species are not part of the base mechanism, but will be given in a separate section on recommended lumped mechanisms for modeling.

Responses to comments on Reactions in Base Mechanism

Reaction 2: $O_3P + O_2 + M = O_3 + M$

Comment: The rate constant parameters are not computed correctly for the abundance of O_2 and N_2 in air. They should be: $A = 5.61e-34$, $B = -2.8$

Response: The rate constant in the original version was computed with O_2 and N_2 concentrations interchanged. This has been corrected. The corrected parameters are $A = 5.68e-34$ and $B = -2.8$. The reviewer made a slight miscalculation for the recommended A factor.

Reaction 21: $O_3 + HV = O(^1D) + O_2$

Comment: It seems that a higher base temperature could be chosen for the cross sections this may be important because recent data on the temperature dependence of ozone photolysis (Talukdar et al., 1998) leads to greater $O(^1D)$ formation rates. This could be a problem during the fall and spring because this may lead to more rapid photochemical loss of ozone and greater rates of HO formation.

Response: The reviewer has a good point, but I presently I do not have access to absorption cross section data at a higher temperature. Data are only given for $T = 273^\circ K$ in the evaluations.

Reaction 23: $O(^1D) + M = O_3P + M$

Comment: It would be somewhat more accurate to calculate the rate parameter as: $k = 1.80e-11 * \exp(107/T) * 0.791 * [M] + 3.20e-11 * \exp(67/T) * 0.209 * [M]$

Response: The difference between what the reviewer recommends and what is in the mechanism is insignificant and not worth the overhead of using a more complex expression in the mechanism.

Reaction 25: $HONO + HV = HO. + NO$

Comment: The IUPAC and the NASA evaluations favor the HONO cross sections given by Bongartz et al. (1991) over the values given by Stockwell and Calvert (1978). Although the IUPAC evaluations report the Bongartz et al. (1991) cross sections with a 5 nm resolution, the NASA evaluation reports them with the same resolution reported by Stockwell and Calvert (1978), 1 nm resolution. The cross sections of Bongartz et al. (1991) should be used because there are significant differences between the values of Stockwell and Calvert and Bongartz et al. (1991); the cross section reported by Stockwell and Calvert are 20% lower than the values of Bongartz et al. at 354 nm.

Response: The HONO absorption cross section data have been replaced by those in the NASA evaluation, as the reviewer recommended. The change in the calculated photolysis rate is non-negligible, though the impact on actual ambient simulations will probably be minor.

Reaction 32A: $HO. + CO = HO_2. + CO_2$

Reaction 32B: HO. + CO + M = HO2. + CO2 + M

Comment: The rate constant expression is consistent with the NASA recommendation but since the IUPAC evaluation provides a rate parameter with a temperature and pressure dependence it is suggested that the full expression be used.

Response: Although the form used in the mechanism (with the reaction split up into Reactions 32A and 32B) is no approximation, the expression has been re-formatted to the form used in the IUPAC evaluation as recommended by the reviewer. Thus, 32A and 32B have been combined into one reaction with the appropriate pressure and temperature dependence parameterization. The mechanism preparation program had to be modified to implement this. Note that this means that FCM and CALGRID mechanism preparation software will need to be updated to implement this mechanism.

Reaction 41: NO3 + HO2. = HO. + NO2 + O2

Comment: Although the mechanism is uncertain there probably is a significant radical termination and nitric acid production through the reaction: $\text{NO}_3 + \text{HO}_2 = \text{HNO}_3 + \text{O}_2$ that channel should not be ignored. The studies reported in the review by Le Bras (1997) find that the rate of the nitric acid channel is between 20 and 43% of the total reaction rate of NO3 with HO2. In fact there is one study by Hjorth that found the reaction channel represented by reaction 41 to be insignificant (Le Bras, 1997) although that study is probably not correct it still points to the possible importance of the HNO3 producing channel.

Response: The reviewer's recommendation to incorporate that channel is reasonable. The reaction has been changed to:



And the footnote documentation has been changed to:

Rate constant recommended by IUPAC (Atkinson et al, 1997b). Measurement of the branching ratios vary, so the mechanism is uncertain. The branching ratio assumed is approximately in the middle of the range given by IUPAC (Atkinson et al, 1997b) and NASA (1997) evaluations, which is 0.6 - 1.0 for the OH-forming channel.



Comment: The conclusion of note 30 was first proved by Stockwell and Calvert (1983:Stockwell, W.R. and J.G. Calvert, The Mechanism of the HO-SO2 Reaction, Atmos. Envir., 17, 2231 - 2235, 1983. That paper should be cited in Note 30 and the references.

Response: The existing draft documentation already incorporates this reference.

Reaction MER5: C-O2. + C-O2. = MEOH + HCHO + O2

Comment: There is some uncertainty in the temperature dependence of the ratio of the rate parameters for Reactions MER5 and MER6 and this affects the derivation of the individual rate parameters for the two reactions. But the fitted rate constant for Reaction MER5 yields a rate constant that is about 6% greater than the value calculated from the

simple difference between the IUPAC recommended values for the total rate parameter (MER5 + MER6) and the recommended value for the HCHO + HO2 forming reaction.

Response: No change was made because the difference is not considered to be significant.

Reaction RRME: RO2-R. + C-O2. = HO2. + #.75 HCHO + #.25 MEOH

Comment: The 0.25 yield of MEOH (CH3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Response: A somewhat more complete discussion of how the 0.25 yield was derived was added to the footnote.

Reaction RNME: RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PROD2} + #.75 HCHO + XC

Comment: The 0.25 yield of MEOH (CH3OH) is consistent with current knowledge of the rate of the H-atom transfer reaction; this assumption should be added to the footnote.

Response: The added discussion given in the footnote for RRME is considered to be sufficient, so no change was made to the footnote for this reaction.

Reaction RRR2: RO2-R. + RO2-R. = HO2.

Comment: The rate constant may be valid but the rationale seems weak. Atkinson recommends a rate constant of $5E-15 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for general secondary RO2 + secondary RO2 while for the rate parameter for the reaction of general primary is recommended to be $2.5e-13 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The geometric average of the primary and secondary rate parameters is $3.5E-14$ and that may be a bit better to use.

Response: The rate constant was changed to be the geometric average as recommended by the reviewer.

Reaction APNO: CCO-O2. + NO = C-O2. + CO2 + NO2

Comment: Although the temperature dependence of this reaction is not great the temperature dependence as given in IUPAC (Atkinson et al, 1999) evaluation should be included as $k = 7.8E-12 * \text{EXP}(300/T)$.

Response: The rate parameters in the mechanism were modified to be exactly the same as the IUPAC (1999) recommendation, though the effect of the change is small.

Reaction PPN2: RCO-O2. + NO2 = PAN2

Reaction PPNO: RCO-O2. + NO = NO2 + CCHO + RO2-R. + CO2

Comment: The reactants, products and rate parameters are reasonable for Reaction BPN2. The rate parameter is in agreement with the results of Seefeld (1997). If the rate constant is taken to be the same as $\text{CH}_3\text{CH}_2\text{CO}_3 + \text{NO}_2$. Seefeld (1997) the measured $k(\text{NO}_2)/k(\text{NO}) = 0.43 \pm 0.07$ over the temperature range of 249-302K. This leads to a rate constant of $1.2E-11 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ if the rate parameter for the reaction of $\text{CH}_3\text{CH}_2\text{CO}_3$ radicals with NO is assumed to be $2.8E-11 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in agreement with the value chosen by Carter.

Response: Although this was not noted by the reviewer, the rate constants used in the mechanism for PPN2 and PPNO are in fact not consistent with the data of Seefeld and Kerr (1997). The documentation for PPN2 was changed to note that the assumption that the rate constant was the same as the high pressure limit for the $\text{CCO-O}_2 + \text{NO}_2$ reaction was implicitly incorporated in the 1999 IUPAC evaluation when they gave their recommendation for the $\text{CH}_3\text{CH}_2\text{CO}_3 + \text{NO}$ rate constant. The rate constant for PPNO was changed to be consistent with this recommendation, which is based on the data of Seefeld and Kerr (1997). This is a 30% increase, and may result in a nonnegligible change in model predictions.

Reaction PAN2: PAN2 = RCO-O2. + NO2

Comment: The IUPAC Supplement IV (1999) reports a rate constant of 4.4E-4 (298K) and an expression $k = 2E15 * \exp(-12800/T)$ for PPN. Should that value be used for Reaction PAN2?

Response: The rate parameters in the mechanism are in fact exactly the same as the IUPAC (1999) recommendation. The footnote was changed to state simply that this IUPAC recommendation was used.

Reaction PPH2: RCO-O2. + HO2. = RCO-OOH + O2

Reaction BPH2: BZCO-O2. + HO2. = RCO-OOH + O2 + #4 XC

Reaction MPH2: MA-RCO3. + HO2. = RCO-OOH + O2 + XC

Comment: Note 57 is not exactly correct because while 25% of the acetyl peroxy radicals react with HO2 to produce O3 while, in contrast, 100% of the peroxy propionyl and higher peroxy acyl radicals are assumed to react with HO2 to produce higher peroxy organic acids.

Response: The mechanisms for these reactions were changed to be consistent with the mechanism used for acetyl peroxy radicals, i.e., to form 75% RCO-OOH + O2 and 25% RCO-OH + O3.

Reaction APME: CCO-O2. + C-O2. = CCO-OH + HCHO + O2

Comment: Although this choice is reasonable it must be noted that at 50 F the yield of CH3OOH may be near 25% if Horie and Moortgat (1992) as quoted in Atkinson et al. (1999) are correct. The uncertainty in the branching ratio represents a major uncertainty in this reaction.

Response: The discussion already notes that there is an inconsistency in the data, indicating that there is an uncertainty. No modifications were made.

Reaction APRR: CCO-O2. + RO2-R. = CCO-OH

Comment: The rate parameter is much closer to the IUPAC value for acetyl peroxy + methyl peroxy radical than for methyl peroxy + CH3C(O)CH2OO. The basis for the averaging should be given in Note 54. Given that these reactions involve operator radicals it is probably best to assume that the reactions proceed by disproportionation for simplicity. However, it is not clear that this choice is supported by the data for the acetyl peroxy + methyl peroxy reaction, see comments about Reaction APME

Response: The rate constant was changed to be the average of that for acetyl peroxy + ethyl peroxy and acetyl peroxy + CH3C(O)CH2OO. Although this is within the uncertainty of the value used, it is justification is more clear. The mechanism used is consistent with the assumptions used for APME.

Reaction TBON: TBU-O. + NO2 = RNO3 + #-2 XC

Comment: However the need to adjust the rate parameter to fit environmental chamber data raises concerns about the uncertainty of the rate parameter. Also since Atkinson

(1997) recommends an E_a of $-0.30 \text{ kcal mole}^{-1}$ it should be included in the rate parameter expression

Response: The temperature dependence is small compared to the uncertainty, so is not included. The comment that the rate constant “must be considered to be uncertain by at least this amount” was added to the footnote for this and the other adjusted rate constant.

Reaction BRH2: $\text{BZ-O} \cdot + \text{HO}_2 \cdot = \text{PHEN}$

Reaction BNH2: $\text{BZCO-O}_2 \cdot + \text{HO}_2 \cdot = \text{RCO-OOH} + \text{O}_2 + \#4 \text{ XC}$

Comment: It is not clear that the chosen rate parameter must be less than the actual rate parameter [as stated in the footnote documenting the estimated rate constant].

Response: The footnote was modified slightly to indicate why I suspected this to be the case. The footnote now reads: “Assumed to have the same rate constant as the reaction of HO_2 with peroxy radicals. This may underestimate the actual rate constant because alkoxy radicals tend to be more reactive than peroxy radicals.”

Reaction PAHV: $\text{RCHO} + \text{HV} = \text{CCHO} + \text{RO}_2\text{-R} \cdot + \text{CO} + \text{HO}_2$

Comment: Note 76 is not correct for Reaction PAHV because it discusses acetaldehyde and not propionaldehyde. Otherwise the reaction appears to be consistent with present knowledge.

Response: The note was changed to “Pathway forming molecular products is assumed to be negligible under atmospheric conditions, based on calculated rate for analogous reaction of acetaldehyde.”

Reaction PAN3: $\text{RCHO} + \text{NO}_3 = \text{HNO}_3 + \text{RCO-O}_2$.

Reaction GLN3: $\text{GLY} + \text{NO}_3 = \text{HNO}_3 + \#0.63 \text{HO}_2 + \#1.26 \text{CO} + \#0.37 \text{RCO-O}_2 + \#0.37 \text{XC}$

Reaction MGN3: $\text{MGLY} + \text{NO}_3 = \text{HNO}_3 + \text{CO} + \text{CCO-O}_2$.

Comment: This procedure [assuming the rate constant is the same as for acetaldehyde] may underestimate the rate parameter for this reaction. Figure 2 [of the Atkinson (1991) NO_3 review] suggests that there is a roughly log-linear relationship between k_{HO} and k_{NO_3} for HCHO and CH₃CHO. If the most recent values for k_{HO} and k_{NO_3} for HCHO and CH₃CHO are fit we get $k_{\text{NO}_3} = 2.78 * k_{\text{HO}} + 15.44$. This yields a k_{NO_3} of $5.0\text{E-}15$ for propionaldehyde if a k_{HO} of $2.0\text{E-}11$ for propionaldehyde is assumed.

Response: The estimated rate constants were changed according to the procedure suggested by the reviewer. Note that the estimated value we obtained for propionaldehyde is somewhat lower than that suggested by the reviewer, because we used only the OH rate constant for reaction at the -CHO group, which is slightly lower than the total rate constant. The footnotes were modified accordingly.

Reaction MeOH: $\text{MEOH} + \text{HO} = \text{HCHO} + \text{HO}_2$

Comment: The reactants and the rate parameter are in agreement with the Atkinson et al. (1999) recommendations. The CH₂OH reaction channel does represent 85% of the overall reaction at 298K. The products are reasonable if the CH₂OH produced mainly reacts through abstraction of the H atom attached to the OH group. The CH₃O reaction channel would be expected to produce almost all HCHO and HO₂.

Response: The footnote with the reaction needed to be modified because it appropriate for an earlier version of the mechanism, which represented methoxy radicals explicitly. In the present version of the mechanism, the value used for the branching ratio is irrelevant because the overall process after the reaction of the radicals with O₂ is the same. The footnote was modified to note the recommended branching ratios, but to point out that the overall mechanism is the same regardless.

Reaction BAHV: $\text{BACL} + \text{HV} = \#2 \text{CCO-O}_2$.

Comment: The absorption coefficients for biacetyl are based on glyoxal while the quantum yields are estimated.

Response: The footnote for this reaction mislead the reviewer, since in fact the absorption coefficients used are those measured for biacetyl. The footnotes were modified to clarify this.

Reaction CROH: CRES + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 MGLY + #4.87 XC

Comment: The rate parameter is consistent with the recommendations of Atkinson (1994) but it should be noted that o-cresol is assumed here.

Response: The footnote was changed to indicate that the rate constant is based on that for o-cresol..

Reaction D1OH: DCB1 + HO. = RCHO + RO2-R. + CO

Reaction D2OH: DCB2 + HO. = R2O2. + RCHO + CCO-O2.

Reaction D3OH: DCB3 + HO. = R2O2. + RCHO + CCO-O2.

Comment: The rate parameter of Bierbach et al (1994) does include a temperature dependence of $k = 2.8e-11 * \exp(175/T)$. This might be included in the mechanism.

Response: No change was made because the temperature dependence is negligible compared to the uncertainties involved.

Discussion of Mechanism Generation of NO₃ Radical Reactions

Comment: The discussion on the treatment of NO₃ radical reactions by the SAPRC automatic mechanism generation procedure needs to be clarified in places. The following needs to be said more clearly. The program considers only the abstraction of hydrogen atoms by NO₃ from aldehydes and the addition of NO₃ to alkenes. If rate constants for the abstraction of hydrogen atoms by NO₃ from aldehydes are estimated then the same rate parameter for the reaction of NO₃ from acetaldehyde is used. If the compound is an acid R-(CO)OH or a formate X⁺H(CO)O⁻ then the rate parameter is assumed to be zero.

Response: The discussion in the introductory paragraph in this section was modified slightly to hopefully clarify the matter. It now reads: "However, the current system assumes that rate constants for all abstraction reactions are negligible except for reaction at aldehyde -CHO groups. Therefore, only H abstraction reactions of NO₃ with aldehydes or additions to alkenes are considered in the current mechanism."