REVIEW OF THE SAPRC-90
CHEMICAL MECHANISM

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INTRODUCTION

This review was performed by Atmospheric Research Associates under contract to the California Air Resources Board. The intent of this report is to fulfill Task 1 of that contract; namely, to examine the principles and assumptions behind the SAPRC-90 Mechanism, pointing out areas of uncertainty and possible improvements. Operational evaluation of relative computer code was also to be included. Descriptions of both the operational and theoretical portions of that task are combined in this report.

The chemical details of the SAPRC-90 Mechanism were most recently presented by Dr. William Carter in an article of the journal *Atmospheric Environment* (Carter, 1990a). [That paper is referred to as CAR-90 throughout the remainder of this text.] Additional supporting materials necessary to understand and implement the mechanism exist in reports to the Air Resources Board (Carter, 1990a and Carter, 1988) and in references to those reports and CAR-90.

Besides presenting the theoretical support for SAPRC-90, the CAR-90 paper describes a method for deriving simulation-dependent kinetic and stoichiometric parameters for the different organic reaction sets of the mechanism. In essence, a knowledgeable user could select the degree of organic lumping or explicitness required for a particular simulation, provide a 'representative' VOC mixture, and available software would derive the mechanistic parameters to be used. Thus, given a different VOC mixture, a user could formulate a new organic reaction set to better represent it in the mechanism. This is considered an improvement because, previous to this work, all mechanisms (including earlier SAPRC versions, CBM-IV, and RADM) assumed one VOC mixture from which fixed mechanistic parameters were derived.

This report will analyze the SAPRC-90 Mechanism by focusing on each separate section of the mechanism, including all major organic reaction sets, inorganic reactions, operator chemistry, radical assumptions and some general and application aspects. Where applicable, operational character will also be evaluated. In each sub-section I will document, as applicable, needed updates, possible improvements, and areas of uncertainty and concern. The final section summarizes the most important findings.

DETAILS OF THE BASIC MECHANISM, SUGGESTED UPDATES, AND UNCERTAINTIES

1. INORGANIC REACTIONS

The inorganic reaction set is probably as complete as is possible given the current state of kinetic research. Some new details concerning individual reactions have become available since the formulation of the SAPRC-90 Mechanism, which is mostly based on the 1987 NASA review and later updates from the work of R. Atkinson (1990 and further references therein). However, in almost all cases the new measurements are within the ranges of uncertainty given in these reviews. Therefore, with the exception of a few points discussed below, no changes are recommended.

Necessary Updates:

\> The role played by water in the self reaction of hydroperoxy radicals is less than clear. Reactions A29C and A29D in CAR-90 are reasonable given what little is really known. [A note concerning the rate for A29C would be useful.] However, the assumption of similar water dependency in the reaction of HO_2 and NO_3 does not appear to be strongly supported or refuted by laboratory evidence. In addition, Mellouki et al. [J. Phys. Chem., 92:2229 (1988)] found that OH and NO_2 are the more likely products of this reaction.

The rate of reaction for HO_2 plus NO_3 is usually not significant. However, this reaction could produce some OH radical near the end of the day or immediately after sunset. I suggest that Dr. Carter review the above work and also that of Hall, et al. [J. Phys. Chem., 92:5049 (1988)]. I have no problem with the assumed rates as long as the assumption is clearly stated, but the product yields appear to require updating.

Uncertainties and Concerns:

\> The reaction rate constant for hydrolysis of dinitrogen pentoxide (reaction A10) is extremely uncertain because of the difficulty in eliminating laboratory surface interactions. This reaction converts gaseous NO_x to nitric acid during the mid-day period when both ozone and NO_x are available. On the time scale of a daily ozone episode, HNO_3 is relatively inert and serves as an important NO_x sink. In many smog chamber and ambient simulations, the reaction rate constant selected for this reaction has been shown to have an impact on maximum ozone concentration. I agree with Dr. Carter that the uncertainty in the rate constant of the homogeneous reaction is large and can be significant to the results of both smog chamber and ambient simulations. Because different VOCs will contribute reactivity at different times of day, it would seem useful to perform some simulations to determine the impact of this uncertainty on reactivity calculations.

2. THE REACTIONS OF SIMPLE (EXPLICIT) ORGANIC MOLECULES

The species formaldehyde (HCHO), acetaldehyde (CCHO), PAN, and acetone (ACET) are reviewed separately because, as far as I can tell, they are produced explicitly, not as surrogates for other species.

Necessary Updates:

> The formaldehyde absorption cross sections should be updated and photolysis rates re-calculated. A number of laboratory studies have now measured values in line with those presented by Moortgat and co-workers (1983). I suggest using the data published by Cantrell et al. (J. Phys. Chem., circa. 1990 - I have the pre-print only). I will discuss my concerns associated with this update below.

> New work has been done to clarify the reaction kinetics of the acetyl peroxy radical with NO and NO_2. This part of the mechanism should be updated. Dr. Carter is aware of the work of Tuazon in this regard and I am sure he was already planning the update. There are also measurements out of the LACTOZ project of the European Commission that should be reviewed prior to the update. These include the work of Kirchner et al. (1991) and Bridier et al. (1990). I have pre-prints of these papers if needed. I will also discuss the my concerns associated with this update below.

Possible Improvements:

> According to the CAR-90 text and notes, the chemistry of CCO-O2 and other RCO3s is almost completely based on acetyl peroxy kinetics and some assumptions of analogous chemistry with RO2 reaction. This is reasonable because the acetyl peroxy reactions are virtually the only acyl peroxy kinetics known. There are, however, additional improvements to the chemistry of CCO-O2 and other RCO3 that may not be critical, but bring into question some of the assumptions needed to formulate the lumped radical chemistry:

- The reactions of acetyl peroxy radical with HO_2 was investigated by Veyret et al. (1988). The results suggested:

  $$CH_3C(O)O_2 + HO_2 \xrightarrow{a} CH_3C(O)OOH + O_2$$
  $$\xrightarrow{b} CH_3C(O)OH + O_3$$

  with overall $k = 2.8 \times 10^{-13} e^{(1150/T)}$,

  and $k_b/(k_a + k_b) = 0.35 + 0.10$.

  The room temperature value of this rate is nearly three times that assumed in the mechanism by analogy with RO_2 reaction rates. In addition, far more stable products are formed and ozone was also measured as a product.

- Moortgat et al. (1989) investigated the reaction of acetyl peroxy radical with methyl peroxy radical:

  $$CH_3C(O)O_2 + CH_3O_2 \xrightarrow{a} CH_3C(O)O + CH_3O + O_2$$
  $$\xrightarrow{b} CH_3C(O)OH + CH_2O + O_2$$

  As noted in Dr. Carter's paper, Atkinson et al. (1989) reviewed this and recommended:

  with overall $k = 1.1 \times 10^{-11}$,

  and $k_b/(k_a + k_b) = 0.5$ at 298K.

  While the SAPRC mechanism utilizes the overall rate for RCO_3 + RO_2, the products of the individual reactions appear to assume an unusual and reactive product distribution for these data. This usage either requires a better explanation in note 46 (of CAR-90) or modification of the products in reaction C16.

- I believe that the way that the lumping of RCO3 is set up, these updates could potentially include changes to the rates of RCO3, CCO-O2, C2CO-O2, HCOCO-O2, BZ-CO-O2.

\> I do not understand the source of the temperature dependence for the NO_3 + HCHO reaction. Perhaps I have missed the rationale for this in the text.

Uncertainties and Concerns:

\> The update of formaldehyde absorption cross sections should cause the rate of radical production from formaldehyde photolysis (reaction C1 in CAR-90) to increase by about 15 percent. This reaction is a very important source of new radicals during the mid-day period and, if sufficient NO is available during this period, many of these new radicals could become OH. In the simulation of smog chamber experiments or ambient scenarios, the effect of increased mid-day OH formation would be to oxidize additional VOCs, creating extra chain-degradation cycles. As a result, the mechanisms could become more 'reactive' at this time. For smog chamber simulations, the calculated maximum ozone concentrations might increase somewhat and the time for the mechanism to reach the maximum ozone concentration (and other characteristic test points) might become faster than actual measurements.

The change in the ratio of NO and NO_2 reaction rates with acyl peroxy radicals will affect the storage of nitrogen for species that produce PAN-like compounds. This will, in turn, affect the mechanisms of different hydrocarbons in different ways. This change should also impact upon both the timing and maximum ozone concentrations calculated from different hydrocarbons.

My main concern is that, unlike most other anticipated mechanistic modifications, these two changes are far from trivial. The changes are not to the chemistry of one or two individual VOCs, but to formaldehyde and PANs. Formaldehyde is an oxidation product of almost every VOC and a significant governor of a chemical system's reactivity. PAN is formed by selected hydrocarbons and products and is a key governor of both the timing and magnitude of reactivity. After Dr. Carter makes these changes and re-simulates the smog chamber data, the statistics could indicate significant new 'mechanistic' reactivity characteristics during mid-day. If this occurs, it will be apparent that some other factors were inadvertently built into the chamber simulations to compensate for the reactivity that was lacking when the old chemistry was used. Whether the factors were in the mechanism or the assumed smog chamber characteristics will be difficult to determine, and there will probably be no simple adjustment that could immediately fix the mechanism.

My suggestion is to first make the changes, along with others discussed here, and to re-simulate the smog chamber experiments. The significance of these modifications should then be assessed by reviewing the smog chamber simulation statistics, particularly those of both PAN-forming organics and marginally-reactive organics that might be strongly affected by new, mid-day radicals. If results are significantly different, or if the statistics of only some groups of compounds are affected by the changes, it will be necessary to proceed with further modifications and chamber simulations to ensure that there are no chemical biases in the final mechanism.

3. REACTIONS OF AROMATIC HYDROCARBONS

The initial oxidation of aromatics by OH is represented with the general alkane/aromatic reaction set. A description of the aromatic oxidation mechanism is given in CAR-90. The mechanism is of the most basic structure that explains all major products observed:

OH + ARO --add---> α ARO-OH + β ARO-OH-OO
--abs---> ARO-CH2OO

ARO-CH2OO + NO -----> NO2 + BALD + HO2

ARO-OH -----> CRES + HO2
ARO-OH-OO + NO -----> NO2 + fragments + 1 radical (RO2R)

OH can either add or abstract a hydrogen atom. The abstraction path adds O_2, oxidizes NO to NO_2, and produces aromatic aldehydes (BALD) and HO_2. This is represented by BALD and RO2R products. The addition forms ARO-OH, which can either form CRES, PHEN, and HO_2, or add O_2 to oxidize NO to NO_2 and form one radical product (and non-radical ring fragments). This is represented by the production of RO2R and ring fragments (GLY, MGLY, AFG1, and AFG2).

The chemistry of these ring decomposition fragments is still very unclear after nearly two decades of investigation. Except for a few high-yield species of simple structure, the formation rates, chemical structure, individual yields, and subsequent reactions are unknown. In the SAPRC-90 Mechanism two idealized fragments with different chemical properties are assumed; the chemistry of AFG1 is designed to be less reactive than AFG2. Thus, one key means through which Dr. Carter could 'tune' the unknown chemistry to represent observations in smog chambers was by adjusting the yields of AFG1 and AFG2 (only one is selected for each individual aromatic).[*] The reactions of these product species are discussed in the next section.

To some degree, Dr. Carter has attempted to use laboratory-derived product yields for the formation of the initial, major products (BALD, CRES, GLY, and MGLY). Based on these yields and the above mechanism structure, he also derived initial HO_2 and RO2R yields. At this point, according to the text, smog chamber experiments for benzene, toluene, m-xylene, 1,3,5-trimethylbenzene, napthalene, and tetralin were simulated to derive the yields of the AFG1 and AFG2 ring decomposition fragments. Table 1 shows the values used in the general aromatic reaction set for all product species (from Table 7 of CAR-90).

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[*] This general reaction scheme varies somewhat from that used in other mechanisms. In the CBM, a similar mechanism was assumed except that the intermediate ARO-CH2OO radical was separated from the generalized peroxy radical lumping scheme and allowed to explicitly react with NO or decompose to a different set of products. This allowed a second method of 'tuning' to chamber results that is not available with the RO2R assumption.

Table 1. Product Parameters for the General Aromatic Oxidation Scheme

OH + AROn	= RO2R	+ HO2	+ CRES	+ BALD	+ GLY	+ MGLY	+ AFG2	+ AFG1	+ PHEN	+ RO2NP	- C
Toluene	0.74	0.26	0.26	0.08	0.12	0.13	0.41				2.76
Et-Benzene	0.74	0.26	0.26	0.08	0.12	0.13	0.41				3.76
i-Pr-Benzene	0.74	0.26	0.26	0.08	0.12	0.13	0.41				4.76
n-Pr-Benzene	0.74	0.26	0.26	0.08	0.12	0.13	0.41				4.76
s-Bu-Benzene	0.74	0.26	0.26	0.08	0.12	0.13	0.41				5.76
m-Xylene	0.82	0.18	0.18	0.04	0.11	0.37	0.67				3.12
o-Xylene	0.82	0.18	0.18	0.04	0.11	0.37	0.67				3.12
p-Xylene	0.82	0.18	0.18	0.04	0.11	0.37	0.67				3.12
1,3,5-TMBz	0.82	0.18	0.18	0.03		0.62	0.60				3.87
1,2,3-TMBz	0.82	0.18	0.18	0.03		0.62	0.60				3.87
1,2,4-TMBz	0.82	0.18	0.18	0.03		0.62	0.60				3.87
Benzene	0.76	0.24			0.21			0.49	0.24		3.16
Napthalene	0.69	0.17						0.32	0.17	0.14	7.50
Me-Napthalene	0.75	0.11	0.02			0.25		0.58	0.08	0.15	7.57
2,3-Di-Me-Napth	0.80	0.04	0.04			0.49		0.85		0.16	7.59
Tetralin	0.79	0.09						0.16	0.09	0.12	8.42

The product yields of toluene, m-xylene, 1,3,5-trimethylbenzene, and napthalene were then used directly to represent the products of other aromatic species that had less or no available smog chamber data.

<u>Necessary Updates</u>:

\> I suggest a few additional aromatic species be included in Table 7 of CAR-90; in particular, styrene, and the o-, m-, and p-isomers of ethyltoluene and methylstyrene.

\> In the case of the mono-functional aromatics (all compounds use toluene product yields), any carbon mass greater than C_7 is discarded to form '-C'. Thus, the only difference in chemistry for these species is the initial reaction rate constant with OH. The k_{OH} trend in Table 7 of CAR-90 shows decreasing rates with larger functional groups (presumably due to increased steric hindrance at the ortho carbons). However, in experiments at the University of North Carolina with equal amounts of different mono-functional aromatics added to synthetic mixtures, more ozone was produced for the compounds of higher molecular weight. This trend is opposite the k_{OH} trend of Table 7, suggesting that the mechanism would incorrectly predict lower reactivity for mono-functional aromatics with increasing molecular weight. Some method of including the added mass and reactivity should be devised to remove this problem.

Possible Improvements:

- The main concern that might be addressed is that the mechanism has very little 'detail' regarding some very important aromatic compounds. It is not difficult to argue that the group of eleven reactive single-ring aromatics (excluding benzene) in Table 7 of CAR-90 usually represents a significant fraction of both automobile exhaust and ambient organic content. However, the mechanism product yields are set to be identical to either toluene, m-xylene, or 1,3,5-trimethylbenzene. In effect, this ignores quite a bit of the laboratory data that is available concerning product yields of the multi-functional species (even though the paper indicates that these data were incorporated into the mechanism). Therefore, the only mechanistic difference between different species in any of these groups is the initial reaction rate with OH. In this sense, the mechanism underutilizes the advantages of its detailed formulation.

  The rationale for using the products of a few surrogate species to represent related aromatic compounds was based on the greater availability of smog chamber data for these compounds. In most cases, model developers do not supersede the use of laboratory measurements with smog chamber fits. In the case of most aromatics, where laboratory data is incomplete, fitting a mechanism may be as good as one can do at present. This was the basis for deriving the AFG1 and AFG2 yields as described in the text. However, I believe that where measured yields for important product compounds do exist, the information should be included in this mechanism to take advantage of its ability to provide chemical detail.

  I refer specifically to the identified dicarbonyl product data referenced in note 7 of CAR-90. A comparison of the mechanism and measured yields of GLY, MGLY, biacetyl (BIAC), and AFG2 for the multi-functional aromatics is:

Table 2. Mechanism and Observed Product Yields for some Aromatics

Aromatic	Percent Model Yield (Percent Observed Yield)			
	GLY	MGLY	BIAC	AFG2
m-xylene	11 (11)	37 (37)	0 (0)	67 (?)
o-xylene	11 (8)	37 (24)	0 (15)	67 (?)
p-xylene	11 (23)	37 (11)	0 (0)	67 (?)
1,3,5-TMBz	0 (0)	62 (62)	0 (0)	60 (?)
1,2,3-TMBz	0 (7)	62 (17)	0 (39)	60 (?)
1,2,4-TMBz	0 (7)	62 (36)	0 (8)	60 (?)

There are some significant differences here, especially because it is known that these products have very different chemical characteristics. AFG2 photolyzes rapidly to form new radicals. MGLY is rather reactive with OH and photolyzes. GLY is slower in both processes and BIAC, though photolabile, has no aldehydic hydrogen causing virtually no reaction with OH.

These different products and their chemical characteristics tend to link the structure of individual aromatics to the observed chemistry. For instance, ortho-oriented methyl groups tend to form high yields of BIAC, while meta (and sometimes para) orientation is very strongly associated with MGLY production. In the o-xylene-NO_x-air experiments performed at UNC, the ozone profiles show unique characteristics related to high PAN formation and later decay. PAN is a high yield product in these experiments because BIAC photolyzes to form two acetyl peroxy radicals (PAN precursors). However, there is no way to represent these characteristics with any of the ring fragmentation products now used in the SAPRC-90 Mechanism.

At the very least, I would suggest the following attempts to improve the mechanism:

- Analysis to determine if the inclusion of biacetyl in the aromatic mechanisms of ortho-substituted aromatics would be useful. [The representation of biacetyl, a known product of significant yield, might add detail to the mechanism. Since biacetyl has a k_{OH} nearly 2 orders of magnitude slower than the AFG species, I see no way that products such as biacetyl could be included in the present product surrogates.]
- Inclusion of <u>all</u> significant product yields that have been measured in the laboratory. These molecules could be substituted for AFG2 yields.
- Analysis of a larger set of chamber experiments than those noted in Table 7 to investigate ways of including the above data. Perhaps, the newest toluene, xylene, and other aromatic-containing experiments from UNC would be useful in the 'tuning' process. I will discuss more on AFG tuning below, however, because this chemistry is so speculative, I strongly suggest updating the model data base by including these experiments.

<u>Uncertainties and Concerns</u>:

> I must reiterate that all aromatic mechanism development is presently done under conditions of high uncertainty. Only the initial rates of reaction and the yields of relatively stable products are known. Key pieces of the

mechanistic puzzle are obviously missing. In addition, while smog chamber experiments can be of some aid, they too require improvement. Further, it is not clear that ongoing research will be able to uncover a significant amount of additional details. Therefore, the information that Dr. Carter had to work with was very limited. This extreme uncertainty translates into application uncertainty. In some cases, we may not yet have the ability to use chemical mechanisms to make intricate calculations.

> A detailed mechanism cannot simply ignore significant fractions of reactive carbon. Table 1 shows the 'lost' carbon yields for the aromatics given in Table 7 of CAR-90. Although some of the ring carbon may end up in unreactive products like acids and CO_2, the 'lost' carbon represents too large of a fraction to ignore. I wonder if ignoring a high percentage of parent carbons, instead of putting them in slower reacting species (like biacetyl), necessitates compensation by creating too high a yield of overly reactive AFG products. This may seem like a reasonable choice in either direction, but if fewer reactive carbon are produced instead of more carbon of less reactivity, the system being simulated may also be ignoring carbon products that could be transported and react on a second simulation day.

> The current aromatic lumping scheme utilizes the RO2R operator (to be discussed below) and assumes the immediate formation of oxygenated products from the RO2 + NO reaction. In situations where a large fraction of the initial organic is not consumed in the late afternoon and where the products 'promptly' produced are relatively reactive, difficulties related to the breakdown of the lumping assumptions can occur as NO and sunlight decrease. For the aromatics listed in Table 7, such conditions could occur for the mono-functional aromatics due to their slower OH loss rates. Because of this and the fact that the chemistry of the aromatic-O_2-radical intermediate currently appears to be rather mysterious, I believe it would be useful to perform sensitivity studies to determine whether the aromatic RO2 radical should not be represented explicitly.

4. REACTIONS OF AROMATIC PRODUCTS

There are two important sets of aromatic products: those arising from H-abstraction from a functional group (maintaining aromatic ring structure) and those arising from OH addition to the ring. The abstraction products are of much lower yield, forming benzaldehyde analogs (BALD) and subsequent nitrophenols (NPHE). Addition of OH to the ring is the major pathway, resulting in both ringcontaining products (CRES and PHEN) and ring-decomposition products (GLY, MGLY, AFG1, and AFG2).

The effort to describe the reactions of the minor pathway is reasonable. Much of these kinetics have been known for over a decade. [It is unfortunate that we are more confident concerning only the least important chemistry of aromatics.] Given the low saturation vapor pressure of nitrophenols and the extreme uncertainty associated with the major portion of the aromatics oxidation mechanism, I am not convinced that chamber simulations could yield any useful evidence for deciding whether or not to include the NO_3 + NPHE reaction. [Nitrophenols are third level products of a minor reaction channel.] Nevertheless, I have no problem with including the chemistry. It just seems that if an additional species were to be included in the mechanism it would be far more useful as a major aromatic product or an additional alkane or alkene surrogate product.

For the major pathway products, the principal area of uncertainty is in the AFG1 and AFG2 chemistry (and the missing carbon described above). As CAR-90 clearly points out, AFG1 and AFG2 are 'tuned' entities needed to allow the mechanisms to fit chamber data. This need is real, based on the extremely empirical nature of the aromatic mechanism. The 'tuning' process that was used is clearly described in the text and notes. It was quite innovative and adds a degree of versatility to the aromatics mechanism. First, AFG1 was given the k_{OH} of GLY and AFG2 was given the k_{OH} of MGLY. Chamber simulations were then performed to adjust the photolysis values of the AFG species so that observations gathered under the different, artificial lighting conditions of the SAPRC-ITC and -EC could both be adequately simulated.

Necessary Updates:

> The assumption of a constant absorption cross section for AFG1 and AFG2 is physically inappropriate. First, there is no basis for extending the assumed values to wavelengths shorter than the spectra of the artificial lights in the SAPRC-EC and ITC. Second, a more reasonable spectrum shape should be assumed.

> Since the two SAPRC chambers used in the AFG tuning are indoor chambers using different artificial light sources, while the ultimate goal is ambient simulation, I recommend that the tuning simulations be extended to include data from chambers using ambient light. There are a reasonable amount of experiments that have been performed in the UNC chambers that should allow verification or adjustment of the present AFG values.

Possible Updates:

> Reaction G7 of CAR-90 has a typo. It is missing the "OH +".

Uncertainties and Concerns:

> The AFG2 chemistry should be investigated in ambient light. It's extreme photolysis rate in natural light makes it a potential source of predictive inaccuracy.

5. REACTIONS OF ALKANES

The initial oxidation (and some subsequent reactions) of alkanes by OH is represented by the general alkane/aromatic reaction set. The kinetic and stoichiometric parameters used in that scheme are given in Table 6 of CAR-90 for some individual alkanes. The parameters for methane and ethane were calculated from explicit chemistry and kinetic formulas. For alkanes with greater than two carbons, the Dr. Carter's ALKANE program was used to determine the parameters for the general reaction (rate constants, product yields and NO to NO_2 conversions). Therefore, the details of the alkane chemistry lie within the ALKANE program.

Dr. Carter provided the source code, input files, and preliminary documentation for the ALKANE program. Since this is a key portion of the mechanism, I have reviewed the code in detail, compiled and implemented the program, analyzed the input files, executed the program, and examined the results. A rather detailed discussion of these tasks follows.

Operational Characteristics of the Alkane Program

> Given the molecular structure of each alkane, the techniques and mathematical algorithms developed by Atkinson (1987) are used to estimate the probabilities of various hydrogen abstraction sites on each compound. From this it is possible to estimate the OH reaction rate constants.

> For each possible alkyl peroxy radical arising from the hydrogen abstractions and assuming available NO, the program calculates the yields of alkyl nitrates and alkoxy radicals which result after oxidation of the NO.

> For each alkoxy radical created, the probabilities of RO decompositions, reactions with O_2, and isomerizations are determined using additional mathematical relationships derived by Carter and Atkinson (1985). Stable products, radical products, and new RO2 radicals are counted. In the case of new RO2 radicals, it is necessary to repeat the process, again assuming available NO. As Dr. Carter says, "since many of the initially-formed organic radicals are predicted to form other organic radicals, which in turn frequently form yet other radicals, this process is repeated for each of the radicals predicted to be formed until the reactions and products of all of the organic radical intermediates have been accounted for."

> When all radicals are reacted to products that can be represented in the mechanism, the program calculates the products 'promptly' formed, the number of NO-to-NO2 conversions, and the number of NO-to-nitrate conversions. Organic products are either apportioned into explicit species (HCHO, CCHO, CO, and ACET) or lumping surrogates (MEK and RCHO). Also, radical operators (RO2R, R2O2, RO2N, RO2XN, and RO2) are determined from the number of specific types of conversions counted.

> The program output delineates each radical's reaction probabilities and yields, and summarizes the products and operators produced. One optional file can be input directly into the PREPEMIT program for airshed model emissions lumping. This file was the source of information in Table 6 of CAR-90.

Analysis of the ALKANE Program

The computer code is very detailed and indicates a great deal of thought and ingenuity. It appears to have gone through a few development iterations before achieving its present state. This was probably due to improvements to parameters, logic, and kinetics data. The code is generally good and, except for a few minor 'bugs', appears to be error free. I have verified that the kinetic algorithms and parameters previously referenced have been correctly implemented. In terms of comments regarding implementation, use, and content, a few specific algorithms could be referenced better and a few hidden assumptions exist. However, most aspects are commented adequately in either CAR-90, the implementation notes, or in the source code itself.

The following list contains <u>coding and operational items</u> that have emerged during my analysis of the program and its operations. Only a few require immediate action.

Necessary Updates:

> When inputting the structural formula for a cyclic alkane, the program expects that the first carbons numbered are the ring carbons. This was a problem in the current methylcyclopentane inputs and should be changed in the ALKANE.ALL file. In addition, this characteristic should either be eliminated or included in the program documentation.

> There is a bug in the KISO calculations of subroutine ALKSUB. The program currently allows calculation of a rate for isomeric hydrogen abstraction from quaternary carbons. Since there is no H on such a carbon, the program calculates five-bonded carbon products. This causes discrepancies in at least 2,2,5-trimethyl hexane products and yields. The existence of a quaternary carbon must be trapped in the ISOM subroutine, and the KISO calculation for 'normal' isomerizations should only occur with (NN.LE.3.) in ALKSUM.

Possible Improvements:

> The logical NPNO3 is used in the program but never given a value. Initial comments for the variable are very confusing. It's initial value appears to be set .TRUE. by the initialization of Leahy F77L. However, this is not the case with other compilers and it should be formally given a value. At present, its value of .TRUE. causes the program to ignore RONO2 formation if an RO2 radical has any O-substituted carbons. Also, the comments output by the program should be changed. RONO2 from O-substituted RO2's is not "negligible," it is "ignored".

> The HO_2 formed upon isomerization termination is counted in the final product yields, but not listed in the step by step product lists. This should be corrected at some time to eliminate the appearance of neglecting this product.

> There are some variables with values that are calculated, but the variable is never used again. Among these are FTISO, FTDEC, and YIELD(1).

> I believe that isomerization was at one time a 'FAST' RO radical reaction (as certain decompositions are). However, I can find nowhere in the code where the KISO and KIND variables would get values for this to now occur. Therefore, there are at least three sections of code (where the calculations for 'FAST' isomerizations are calculated) that are never accessed.

> In subroutine LMPSUM, the information dumped at the end of the program execution incorrectly indicates that RONO2's contain 5.5 carbon atoms. This should be updated.

> The note concerning the TYP radical should be fixed and expanded. Types 2 and 3 are mixed and there is no mention of types 0 and 4.

> I am not sure why the many 'NO_x absent' variables exist or why these calculations are performed and reported on. I assume that this is code from an older version of the program. This code should really be eliminated if it is not used in the present mechanism formulation. At the least, the output should be modified if these values are not presented.

> The last update to the RO reaction algorithms and other reaction parameterizations appears to have been done in March of 1988. I wonder if there is any new data that would improve our confidence in these formulations.

With the exception of the first three items noted above, most are not serious. The program will calculate the same product fractions without the minor changes.

ALKANE Program Inputs

I compiled the ALKANE program sent by Dr. Carter and used the ALKANE.ALL file as input to determine product fractions at 300K. There were a number of typographical and logical errors that I corrected and include in an updated ALKANE.ALL file. In addition, I have added a number of alkanes to the file based on published inventories of hydrocarbons measured in Los Angeles and across the country. Some of the update items are (most already included in new ALKANE.ALL file):

Necessary Updates:

> The structural listing for Me-CYC5 was modified. This is because the program assumes the first numbered carbons are the ring carbons. The modification caused some changes to the Me-CYC5 mechanism parameters.

> Documentation should be improved to indicate that the first numbered carbons must be the ring carbons.

> The equivalence lists for Me-CYC5, 4-ME-C7 (BR-C8), and 4-PR-C7 (BR-C9) were improved. Only the speed of calculation would be affected.

> The IUPAC name for CYC-C11 was fixed.

> The ALKANE.ALL file was re-arranged in groups of straight chain, branched chain, and cyclic alkanes. Duplicates were removed. The primary names were changed to IUPAC nomenclature. The original generic names are included as comments.

> Based on reported observations for the Los Angeles Basin and across the United States, I have included some new alkanes on the list. these are:

Alkane	C#	Label
2-methyl hexane	7	2-ME-C6
3,3-dimethyl pentane	7	33-DM-C5
2,2,3-trimethyl butane	7	223-TM-C4
2-methyl heptane	8	2-ME-C7
3-methyl heptane	8	3-ME-C7
2,3-dimethyl hexane	8	23-DM-C6
2,4-dimethyl hexane	8	24-DM-C6
2,5-dimethyl hexane	8	25-DM-C6
2,3,4-trimethyl pentane	8	234-TM-C5
2,4-dimethyl heptane	9	24-DM-C7
2,2,5-trimethyl hexane	9	225-TM-C6
1,3-dimethyl cyclopentane	7	13-DM-CY-C5
ethyl cyclopentane	7	ET-CY-C5
1,3-dimethyl cyclohexane	8	13-DM-CY-C6

The product parameters for these and all other alkanes in the new ALKANE.ALL file are given in Table 3. [The 'bug' which affects quaternary carbons was not fixed when generating Table 3.]

Table 3. Product Yields Calculated by the ALKANE Program for 300K and 1 atm.

Name	C#	RNO3	-N	HO2	R2O2	HCHO	CHO	ACET	RCHO	MEK	CO	CO2	-C
NORMAL ALKANES													
PROPANE	3	0.000	0.039	0.961	0.000	0.000	0.000	0.658	0.303	0.000	0.000	0.000	0.116
N-C4	4	0.076	0.000	0.924	0.397	0.001	0.571	0.000	0.140	0.533	0.000	0.000	-0.076
N-C5	5	0.120	0.000	0.880	0.544	0.007	0.080	0.000	0.172	0.929	0.000	0.000	0.001
N-C6	6	0.185	0.000	0.815	0.738	0.000	0.020	0.000	0.105	1.134	0.000	0.000	0.186
N-C7	7	0.267	0.000	0.733	0.727	0.000	0.000	0.000	0.056	1.241	0.000	0.000	0.535
N-C8	8	0.333	0.000	0.667	0.706	0.000	0.000	0.000	0.002	1.333	0.000	0.000	0.998
N-C9	9	0.373	0.000	0.627	0.673	0.000	0.000	0.000	0.001	1.299	0.000	0.000	1.934
N-C10	10	0.397	0.000	0.603	0.659	0.000	0.000	0.000	0.001	1.261	0.000	0.000	2.969
N-C11	11	0.411	0.000	0.589	0.654	0.000	0.000	0.000	0.001	1.241	0.000	0.000	3.975
N-C12	12	0.420	0.000	0.580	0.644	0.000	0.000	0.000	0.001	1.223	0.000	0.000	5.004
N-C13	13	0.427	0.000	0.573	0.638	0.000	0.000	0.000	0.001	1.211	0.000	0.000	6.022
N-C14	14	0.431	0.000	0.569	0.634	0.000	0.000	0.000	0.001	1.202	0.000	0.000	7.033
N-C15	15	0.434	0.000	0.566	0.631	0.000	0.000	0.000	0.001	1.196	0.000	0.000	8.044
BRANCHED ALKANES													
2-ME-C3	4	0.027	0.000	0.973	0.744	0.744	0.000	0.744	0.229	0.000	0.000	0.000	0.202
2-ME-C4	5	0.064	0.002	0.933	0.734	0.000	0.614	0.611	0.133	0.303	0.000	0.000	0.007
22-DM-C3	5	0.051	0.000	0.949	0.019	0.019	0.000	0.010	0.939	0.000	0.000	0.000	1.878
2-ME-C5	6	0.122	0.005	0.873	0.749	0.006	0.023	0.223	0.545	0.724	0.000	0.000	0.137
3-ME-C5	6	0.112	0.000	0.888	0.860	0.005	0.523	0.000	0.089	1.003	0.000	0.000	0.110
22-DM-C4	6	0.153	0.000	0.847	0.960	0.295	0.303	0.295	0.372	0.542	0.000	0.000	0.164
23-DM-C4	6	0.061	0.039	0.901	0.944	0.000	0.000	1.584	0.128	0.096	0.000	0.000	0.177
2-ME-C6	7	0.196	0.000	0.803	0.858	0.030	0.037	0.036	0.118	1.265	0.000	0.000	0.393
3-ME-C6	7	0.182	0.002	0.815	0.842	0.000	0.127	0.000	0.329	1.119	0.000	0.000	0.369
23-DM-C5	7	0.128	0.011	0.860	1.101	0.036	0.253	0.390	0.185	0.960	0.000	0.000	0.252
24-DM-C5	7	0.131	0.002	0.867	0.844	0.000	0.000	0.257	0.772	0.682	0.000	0.000	0.531
33-DM-C5	7	0.231	0.000	0.769	0.940	0.040	0.289	0.145	0.237	0.907	0.000	0.000	0.453
223-TM-C4	7	0.107	0.000	0.893	1.581	0.637	0.000	1.291	0.255	0.255	0.000	0.000	0.165
2-ME-C7	8	0.260	0.000	0.740	0.839	0.022	0.025	0.018	0.118	1.360	0.000	0.000	0.779
3-ME-C7	8	0.245	0.000	0.755	0.867	0.000	0.072	0.000	0.066	1.425	0.000	0.000	0.733
4-ME-C7	8	0.244	0.002	0.753	0.803	0.000	0.000	0.000	0.352	1.204	0.000	0.000	0.906
23-DM-C6	8	0.175	0.008	0.817	1.051	0.006	0.010	0.125	0.241	1.363	0.000	0.000	0.548
24-DM-C6	8	0.178	0.000	0.822	0.968	0.045	0.122	0.027	0.339	1.257	0.000	0.000	0.698
25-DM-C6	8	0.188	0.000	0.812	1.731	0.422	0.000	0.518	0.165	1.008	0.000	0.000	0.563
224-TM-C5	8	0.188	0.001	0.811	0.942	0.111	0.000	0.251	0.747	0.643	0.000	0.000	1.380
234-TM-C5	8	0.128	0.016	0.855	1.312	0.066	0.037	0.518	0.332	1.075	0.000	0.000	0.368
24-DM-C7	9	0.223	0.001	0.776	0.933	0.033	0.020	0.015	0.385	1.257	0.000	0.000	1.586

Table 3. (Concluded).

Name	C#	RNO3	-N	HO2	R2O2	HCHO	CHO	ACET	RCHO	MEK	CO	CO2	-C
BRANCHED ALKANES (continued)													
4-ET-C7	9	0.271	0.002	0.727	0.804	0.002	0.059	0.000	0.303	1.167	0.000	0.000	1.949
225-TM-C6	9	0.248	0.000	0.466	0.843	0.038	0.000	0.074	0.171	0.740	0.000	0.000	4.030
4-PR-C7	10	0.301	0.002	0.696	0.775	0.000	0.004	0.000	0.328	1.139	0.000	0.000	2.945
35-DE-C7	11	0.246	0.000	0.754	1.273	0.021	0.054	0.000	0.090	1.862	0.000	0.000	1.922
36-DE-C8	12	0.267	0.000	0.733	1.351	0.002	0.422	0.000	0.012	1.647	0.000	0.000	3.192
37-DE-C9	13	0.285	0.000	0.715	1.226	0.002	0.008	0.000	0.111	1.819	0.000	0.000	3.943
38-DE-C10	14	0.298	0.000	0.702	1.122	0.002	0.000	0.000	0.003	1.820	0.000	0.000	5.223
39-DE-C11	15	0.310	0.000	0.690	1.103	0.001	0.000	0.000	0.003	1.790	0.000	0.000	6.285
CYCLIC ALKANES													
CY-C5	5	0.127	0.000	0.873	1.745	0.000	0.000	0.000	0.873	0.218	0.873	0.000	0.000
CY-C6	6	0.193	0.000	0.807	0.352	0.003	0.000	0.000	0.333	0.816	0.000	0.003	0.765
ME-CY-C5	6	0.153	0.000	0.847	1.978	0.284	0.000	0.000	0.697	0.490	0.564	0.189	0.153
ME-CY-C6	7	0.216	0.000	0.784	0.928	0.092	0.001	0.000	0.466	0.987	0.003	0.046	0.432
13-DM-CY-C5	7	0.160	0.000	0.840	2.118	0.517	0.000	0.000	0.478	0.825	0.284	0.344	0.320
ET-CY-C5	7	0.207	0.000	0.793	1.849	0.009	0.340	0.000	0.523	0.674	0.336	0.261	0.410
13-DM-CY-C6	8	0.215	0.000	0.785	1.386	0.170	0.001	0.000	0.499	1.131	0.002	0.084	0.646
ET-CY-C6	8	0.265	0.000	0.735	1.282	0.186	0.293	0.000	0.347	0.811	0.010	0.185	1.425
1E-4M-CY-C6	9	0.247	0.000	0.753	1.782	0.278	0.250	0.000	0.457	1.022	0.000	0.264	1.263
13-DE-CY-C6	10	0.267	0.000	0.733	1.596	0.211	0.370	0.000	0.175	1.151	0.006	0.208	2.370
13-DE-5-M-CY-C6	11	0.238	0.000	0.762	1.890	0.226	0.368	0.000	0.159	1.530	0.001	0.184	2.068
135-TE-CY-C6	12	0.251	0.000	0.749	1.722	0.202	0.392	0.000	0.136	1.408	0.001	0.166	3.550
13-DE-5-P-CY-C6	13	0.267	0.001	0.732	1.469	0.129	0.216	0.000	0.250	1.391	0.001	0.107	4.682
13-DP-5-E-CY-C6	14	0.281	0.001	0.718	1.277	0.077	0.097	0.000	0.329	1.359	0.001	0.066	5.835
135-TP-CY-C6	15	0.293	0.002	0.705	1.128	0.041	0.023	0.000	0.380	1.312	0.001	0.038	7.020

The Alkane Mechanism

The ALKANE program is a model of the general alkane mechanism. Therefore, the methods used to calculate various parameters in the program actually represent the essential features of the alkane mechanism. Many of the details as to how various calculations are performed were noted above. Many of the mechanistic assumptions used in the general alkane oxidation mechanism are stated either in CAR-90 documentation or in the ALKANE results file.

The following items discuss these and other assumptions and uncertainties related to program content; and therefore, alkane mechanism content:

Necessary Updates:

> Reaction rates of alkanes with OH are calculated by the program instead of using the measured k_{OH} values. These are shown in comparison with measured rates in Table 4. In general, the method appears to work very well in estimating k_{OH} for a variety of alkane types (the comparison may indicate a possible bias trend for the n-alkanes). I wonder, however, why the actual k_{OH} values are not used when they are known, as was the rate for 2-butoxy decomposition.

Possible Improvements:

> The potential reactions of alkoxy radicals are unimolecular decompositions, H-atom isomerizations, and reaction with O_2. In the case of the unimolecular processes, a number of different reaction paths are often possible. Different α-carbon sigma bonds may decompose and different hydrogen atoms may be internally abstracted. The program calculates the rate for each potential process and considers all processes that are at least one percent of the total rate. Thus, it is possible for an alkoxy radical to undergo two or three different decompositions or isomerizations. The overall rate of decomposition or isomerization is merely the sum of all individual processes.

It seems to me, however, that there is a fundamental difference between the decomposition and isomerization processes and that this should be reflected in the calculation of total process rates. Decompositions are more or less likely because of the configuration of atoms in each molecule. The rate of decomposition can be calculated for each specific bond of a radical carbon. On the other hand, isomerization abstractions occur if an intramolecular alkoxy radical can find an appropriate leaving group (H-atom) somewhere else in the molecule. This occurs if the molecule is in the proper

Table 4. Carbon Apportionment and Rate Constants for Alkanes.

	CARBON NO.		-C (%)			k_{OH} x 1E12		
Name	React.	Prods. w/o -C	Total	RNO3	Prods.	Calcd.	Meas.	Delta
NORMAL ALKANES								
PROPANE	3	2.88	3.9%	3.9%	0.0%	1.22	1.15	6.3%
N-C4	4	4.08	-1.9%	-1.9%	0.0%	2.55	2.54	0.6%
N-C5	5	5.00	0.0%	0.0%	0.0%	3.96	3.94	0.4%
N-C6	6	5.81	3.1%	3.1%	0.0%	5.36	5.61	-4.5%
N-C7	7	6.47	7.6%	7.6%	0.0%	6.76	7.15	-5.5%
N-C8	8	7.00	12.5%	12.5%	0.0%	8.16	8.68	-6.0%
N-C9	9	7.07	21.5%	16.6%	4.9%	9.56	10.20	-6.2%
N-C10	10	7.03	29.7%	19.8%	9.8%	10.97	11.60	-5.4%
N-C11	11	7.02	36.1%	22.4%	13.7%	12.37	13.20	-6.3%
N-C12	12	7.00	41.7%	24.5%	17.2%	13.77	14.20	-3.0%
N-C13	13	6.98	46.3%	26.3%	20.1%	15.17	16.00	-5.2%
N-C14	14	6.97	50.2%	27.7%	22.5%	16.57	19.00	-12.8%
N-C15	15	6.96	53.6%	29.0%	24.7%	17.98	22.00	-18.3%
BRANCHED ALKANES								
2-ME-C3	4	3.80	5.1%	-0.7%	5.7%	2.39	2.34	2.0%
2-ME-C4	5	4.99	0.1%	0.0%	0.1%	4.00	3.90	2.5%
22-DM-C3	5	3.12	37.6%	0.0%	37.6%	0.75	0.85	-11.1%
2-ME-C5	6	5.86	2.3%	2.0%	0.2%	5.40	5.60	-3.6%
3-ME-C5	6	5.89	1.8%	1.9%	-0.0%	5.76	5.70	1.1%
22-DM-C4	6	5.84	2.7%	2.6%	0.2%	1.84	2.32	-20.6%
23-DM-C4	6	5.82	2.9%	1.0%	1.9%	5.44	6.30	-13.6%
2-ME-C6	7	6.61	5.6%	5.6%	0.0%	6.80		
3-ME-C6	7	6.63	5.3%	5.2%	0.1%	7.16		
23-DM-C5	7	6.75	3.6%	3.7%	-0.1%	7.21		
24-DM-C5	7	6.47	7.6%	3.7%	3.8%	6.84	5.10	34.2%
33-DM-C5	7	6.55	6.5%	6.6%	-0.1%	3.12		
223-TM-C4	7	6.83	2.4%	3.1%	-0.7%	3.29	4.23	-22.3%
2-ME-C7	8	7.22	9.7%	9.7%	-0.0%	8.20		
3-ME-C7	8	7.27	9.2%	9.2%	-0.0%	8.57		
4-ME-C7	8	7.09	11.3%	9.2%	2.2%	8.57		
23-DM-C6	8	7.45	6.8%	6.6%	0.3%	8.61		
24-DM-C6	8	7.30	8.7%	6.7%	2.1%	8.61		
25-DM-C6	8	7.44	7.0%	7.0%	-0.0%	8.25		
224-TM-C5	8	6.62	17.2%	7.1%	10.2%	4.69	3.68	27.4%
234-TM-C5	8	7.63	4.6%	4.8%	-0.2%	8.65	7.00	23.5%

Table 4. (Concluded).

	CARBON NO.		-C (%)			k_{OH} x 1E12		
Name	React.	Prods. w/o -C	Total	RNO3	Prods.	Calcd.	Meas.	Delta
BRANCHED ALKANES (continued)								
24-DM-C7	9	7.41	17.6%	9.9%	7.7%	10.01		
4-ET-C7	9	7.05	21.7%	12.0%	9.6%	10.52		
225-TM-C6	9	4.97	44.8%	11.0%	33.8%	6.09		
4-PR-C7	10	7.06	29.4%	15.1%	14.4%	11.92		
35-DE-C7	11	9.08	17.5%	13.4%	4.0%	14.28		
36-DE-C8	12	8.81	26.6%	15.6%	11.0%	15.69		
37-DE-C9	13	9.06	30.3%	17.6%	12.8%	17.09		
38-DE-C10	14	8.78	37.3%	19.1%	18.2%	18.49		
39-DE-C11	15	8.72	41.9%	20.6%	21.3%	19.89		
CYCLIC ALKANES								
CY-C5	5	5.00	0.0%	0.0%	0.0%	5.62	5.16	8.8%
CY-C6	6	5.24	12.7%	3.2%	9.5%	8.41	7.49	12.3%
ME-CY-C5	6	5.85	2.5%	2.5%	0.0%	8.03		
ME-CY-C6	7	6.57	6.2%	6.2%	0.0%	10.22	10.40	-1.7%
13-DM-CY-C5	7	6.68	4.6%	4.6%	-0.0%	8.58		
ET-CY-C5	7	6.59	5.9%	5.9%	-0.1%	8.88		
13-DM-CY-C6	8	7.35	8.1%	8.1%	0.0%	12.02		
ET-CY-C6	8	6.58	17.8%	9.9%	7.9%	12.17		
1E-4M-CY-C6	9	7.74	14.0%	11.0%	3.1%	13.98		
13-DE-CY-C6	10	7.63	23.7%	13.3%	10.3%	15.94		
13-DE-5-M-CY-C6	11	8.93	18.8%	13.0%	5.8%	17.74		
135-TE-CY-C6	12	8.45	29.6%	14.6%	14.9%	19.70		
13-DE-5-P-CY-C6	13	8.32	36.0%	16.4%	19.6%	21.10		
13-DP-5-E-CY-C6	14	8.16	41.7%	18.1%	23.6%	22.50		
135-TP-CY-C6	15	7.98	46.8%	19.5%	27.3%	23.90		

conformation to bring the oxygen and hydrogen into proximity. However, unlike decomposition, where the molecule is always configured to have all possible decomposing bonds attached to the radical carbon, the molecule may have only one isomerization conformation at any time. Therefore, the summing of all possible isomerization rates to determine the total rate seems to be an overestimate. Perhaps, only the fastest rate or some normalized sum of all possible rates should be used.

> The ALKANE program utilizes a number of 'FAST' processes that supersede the calculation of normal RO rates (decomposition, isomerization, and O_2 reaction). For instance, the production of an α-hydroxy radical immediately reacts further with O_2 to form HO_2 and a more stable product. If a decomposing RO is a β-hydroxy radical, this is the exclusive RO reaction. If not, β-carbonyl decomposition and cyclic ring opening can both occur exclusive of other processes, and are equally as fast. These assumptions should be documented.

> Based on the above-noted assumptions, the dominant reaction of the β-hydroxy RO, CH_2OH-CH_2O, will be decomposition in the ALKANE program. In reality, however, hydroxy acetone appears to form about 25 percent of the time (Atkinson, 1990).

Uncertainties and Concerns:

> The ALKANE program is a well-conceived implementation of the mathematical algorithms used to describe our current understanding of the alkyl peroxy and alkoxy chemistry for different alkanes under NO-rich conditions. However, the primary basis for that understanding is a few experimental measurements extended to encompass large groups of molecules through thermochemical calculations. In addition, most of the existing experimental evidence is restricted to small molecules. Hence, the formulations used in the ALKANE program (and mechanism) are forced to assume chemical similarity as a basis for including most alkane molecules in the scheme.

In his review of alkoxy chemistry and the algorithms used to describe these processes, Atkinson (1990) indicated significant uncertainty in all alkoxy radical rate constants. Because of uncertainties in thermochemical estimates of heats of reaction, the calculations of rate ratios between alkoxy decomposition and O_2 reaction are expected to have minimum uncertainties of a factor of 5. In particular, the 2-butoxy radical has been measured to decompose approximately four times faster than the rate determined by the general decomposition algorithm used in the ALKANE program. [Hence, the measured rate is used instead of calculating a rate with the program's RO decomposition algorithm.]

In the case of alkoxy H-shift isomerizations, the algorithms describing this process are based on thermochemical estimates, with only one radical (n-butoxy) having been studied experimentally. CAR-90 states that, "the estimates of the processes occurring following the 1,5-H shift isomerizations of long chain alkoxy radicals have never been verified by product studies." Nevertheless, the program assumes that H-shift isomerization is a very significant alkoxy radical reaction pathway for larger alkanes. "These estimates, however, must still be considered to be highly uncertain," (Atkinson, 1990).

Therefore, although the ALKANE program can utilize the referenced algorithms to very precisely determine the assumed reaction pathways and provide a detailed product distribution, the uncertainty in our current understanding of these processes does not yet provide confidence in either the content of the algorithms or the accuracy of the calculated product distributions. Further, since different processes are assumed to dominate in certain radicals because of molecular structure, the differing amounts of uncertainty for various processes may not be uniformly applied across all alkanes. For instance, H-shift isomerization is assumed to be the dominant process in many long-chain alkoxy radicals. The process and resulting products are very uncertain. Further, many of the reaction products of H-shift isomerization are predicted to be quite different from those of decomposition or O_2 reaction. Hence, *the chemistry of larger alkanes must be considered far more uncertain than for smaller molecules because the program must assume that this very unstudied area is significant.*

\> In the calculation of isomerization rates, hydrogen abstraction from a TYPE 3 (C=O) group is given a rate equal to that of hydrogen abstraction from -CH(OH)-. Since I cannot find documentation on this I wonder: (1) the nature of the C=O group [I assume it is an aldehyde], and (2) the rationale for setting the rate equal to that of -CH(OH)-.

\> The yields of alkyl nitrates are calculated for the reactions of each alkyl peroxy radical with NO (Carter and Atkinson, 1989). Based on chemical modeling of smog chamber observations (Carter and Atkinson, 1985), alkyl nitrate formation for OH- or -CO- substituted peroxy radicals is assumed to be negligible. For other alkyl peroxy radicals, nitrate yield is determined depending on the number of carbons on each radical, the type of peroxy radical (factors for primary:secondary:tertiary = 0.3:1.0:0.4) and temperature (Atkinson, 1990). The mathematical algorithm used to derive alkyl nitrate yields in this mechanism would benefit from more experimental data but appears to be far less uncertain than many of the alkoxy radical algorithms discussed above. In addition, Dr. Carter has taken the precaution of creating alkyl nitrate operators instead of 'promptly' producing nitrates as products. Therefore, nitrates will only be produced in situations of available NO.

This nitrate algorithm appears to handle the kinetics of alkyl nitrate molecules better than any other available mechanism. Unfortunately, though better, the method is still limited because the mechanism must assume a fixed structure for the RNO3 species. In this case, RNO3 chemistry is derived using "the average of the reactions of the lumped C_4 nitrate and the lumped C_7 nitrate used in the mechanism of Carter et al. (1986)." However, "the lumped alkyl nitrate species in this mechanism is represented as having five carbons, not 5.5 as would be the case for the average of C_4ONO_2 and C_7ONO_2" (CAR-90). This type of representation causes two problems.

(1) The 5-carbon RNO3 is a surrogate of constant chemistry that must be used to represent the different chemistries of a number of nitrates. Given the current inability of chemical mechanism solvers to track specific product characteristics, the choice of the lumped RNO3 characteristics described above is reasonable. In addition, the measured OH reaction rates of C_4 through C_9 nitrates only vary by about a factor of 1 from the specified RNO3 rate.

(2) The use of a RNO3 with a fixed number of carbons causes carbon mass inconsistencies in the secondary chemistry. For example, C_3 nitrates are assumed to be negligible, with the carbon and nitrogen saved as '-C' and '-N'. C_4 and greater nitrates are saved as RNO3, a 5-carbon molecule. In the case of C_4 radical precursors, carbon mass must artificially be created to form a 5-carbon nitrate product (see Tables 3 and 4). C_6 and greater precursors lose carbon to '-C' at increasing rates to create the 5-carbon RNO3. The increasing trend of carbon loss is best shown for the normal alkanes in Table 4. Although the ALKANE program can account for the lost carbon, it places it in an unreactive species (-C) to do so. When the product RNO3 reacts to deliver products back into the radical-oxidation system, only 5 carbons return. Therefore, *as the molecular weight of alkane precursors increases, the oxidation process represented in this mechanism tends to misplace greater amounts of carbon.*

\> A problem similar to the above inconsistencies associated with alkyl nitrate formation arises because of the necessary use of fixed-structure surrogates as products in the alkane reaction scheme. For most small alkanes, decompositions and reactions of RO with O_2 result in monofunctional products that can be reasonably represented using explicit and surrogate product species. However, since larger alkoxy radicals are assumed to frequently undergo H-shift isomerization, large multi-functional (hydroxyl and carbonyl) products are predicted to be formed. A mechanism using fixed structure surrogates has difficulty apportioning such products into the mechanism surrogates.

In this mechanism, some non-radical, organic products are represented by explicit species (HCHO, CCHO, and ACET). However, the carbon mass in larger products must be apportioned between surrogate species (RCHO and MEK). For all large ($>C_2$) mono-functional products and all bi-, and poly-functional products, aldehyde functional groups are first identified, and counted as 3-carbon RCHO. The remaining product carbons are then apportioned as MEK or -C in the following way:

(1) The number of remaining product carbons are counted.

(2) Ketone (-C(O)-) and alcohol (-CH(OH)-) functional groups are counted.

(3a) If there are enough carbons to allow each functional group four carbons, each functional group is represented as an MEK and the remaining carbons are -C.

(3b) If there are more functional groups than the remaining carbon x 4, the MEK yield is calculated by dividing the remaining carbon by 4, with no -C produced.

This method is mass conservative in the sense that all carbons are accounted for somewhere. However, the logic used is really a partial, carbon-bond type of approach that disregards molecular integrity. It counts and apportions only carbons and functional groups, irrespective of unique structures or relationships. In addition, it is only a partial carbon-bond type of approach in that some reactive carbon must be thrown away if the product carbons are not exactly 4 x the number of product functional groups.

It is possible that these assumptions may yield biases with respect to the eventual product reactivity of different parent alkanes. There are four issues that require, at the least, further documentation.

(1) The lack of detail that results from the distribution of individual oxidation products into mechanism surrogate species (only RCHO and MEK) leads to poorly resolved product chemistry. For almost all alkanes, MEK is the major reaction product (compare the MEK yields in Table 3 to those of the smaller aldehydes and ACET). *This placement of a large fraction of product mass into one, fixed-chemistry surrogate will cause poor resolution of transported products*, and seems to be an unnecessary limitation given the highly resolved product chemistry calculated by the ALKANE program. Although very little of the ALKANE program is verified by experimental observations, the effort to consolidate this plausible set of theoretical estimates into

detailed product projections seems rather futile given that a large percentage of the product mass is lumped into one surrogate species.

(2) The use of '-C' to accumulate mass that does not fit into (3a) of the above product distribution logic may produce a bias depending on the size of the parent alkane. From inspection of the program output (Table 3), there appears to be a trend of increasing production of 'lost' carbon as the number of carbons in the parent alkane increases. However, this only begins to be significant above about C_8. The bulk of the 'lost' carbon is due to the assumption of 5-carbon RNO3. Conversely, the alternate product distribution logic (3b) requires that, when there are not enough product carbons to produce enough MEK surrogates, some carbonyl function must be eliminated to produce the correct number of MEK products. This creates an artificial limit to the amount of functional groups that can be produced in the oxidation products. That is, if there is more than one functional group for every four carbons, some carbonyls are converted to alkyl carbons.

(3) There is no explanation as to why a ketone surrogate is used to represent alcohol products. This approximation can be very important for larger alkanes that are predicted to undergo significant H-shift isomerization. Isomerization products typically have one carbonyl and one or more alcohol groups. The representation of subsequent chemistry of alcohols by assigning product mass to MEK surrogates should produce excessively reactive product chemistry.

To demonstrate this, the most obvious comparison is with the alcohol analog to MEK. One would expect 2-butanol to react with OH faster than 2-butanone, to produce some potentially less reactive acid products and to photolzye at an insignificant rate. Hence, production of new radicals would be far less important for such an alcohol. Although there certainly is very little experimental evidence to use as a guide, it seems that the product distribution in Table 3 is too reactive for the larger alkanes that are expected to predominantly isomerize to poly-functional, hydroxy-containing products. For normal alkanes above C_7, MEK is virtually the only organic species produced.

(4) Following the same arguments as in (1), I also question whether the poly-functional products predicted for larger alkanes would long exist in the gas phase. If these products actually condense, the use of MEK surrogates for each functional group would again overestimate reactivity of products.

\> The immediate formation of products, due to the assumed, immediate reaction of alkyl peroxy radicals with NO, is a necessary assumption used to condense the extensive RO2 chemistry into a set of radical operator processes. The theory and limitations will be discussed in the operator chemistry section below. However, there are a few aspects specific to the ALKANE program that should be noted here:

(1) The program totally depends on the assumption that NO is available to immediately reduce alkyl peroxy radicals to alkoxy radicals.

(2) Because of this assumption, the reactions of alkylperoxy radicals with NO_2 must be ignored, even though the reaction rate of alkyl peroxy radicals with NO2 is comparable to that of NO. [It is assumed that the alkylperoxy nitrate products rapidly decompose to the original reactants. This is probably reasonable, although it is difficult to gauge the impact of this assumption because experimental data on alkylperoxy nitrate decay does not exist.]

(3) The ALKANE program proceeds through as many NO oxidations by RO2 as are necessary to produce a product distribution that can be represented by mechanism species. Sometimes 3 or 4 conversions occur for one oxidation pathway (for H-shift isomerization). As will be discussed below, the chemical bookkeeping that is necessary to implement such a method requires that stable products be formed immediately, along with creation of operator species that eventually react to complete the chemical changes that actually formed the stable products. Since these 'prompt' products are those that would form with available NO, this decoupling of product mass and chemical function can cause problems in the absence of sufficient NO. For instance, if HO_2 reaction dominates over NO reaction, the -OOH function is formed, but promptly-formed MEK and other alkane products are free to react in other ways, perhaps forming more -OOH. This discrepancy will become fairly significant for alkanes in low NO situations, because the products promptly formed are more reactive than the original alkane.

\> The reactions of peroxy acyl radicals are handled by creating CO_2, RO2, and an NO-->NO_2 conversion operator. This eliminates the ability to address the competing peroxy acyl reaction with NO_2. However, this is relatively unimportant. Calculated peroxy acyl yields are low, mainly from cycloalkane oxidations.

6. REACTIONS OF ALCOHOLS, ETHERS AND ACETYLENE

These species are included in the mechanism through the parameterized, general alkane/aromatic oxidation scheme. Parameters and rate constants are given in Table 8 of CAR-90.

Necessary Updates:

\> The parameter table should be expanded to include values for methyl-*tert*-butyl ether. In addition, observations from recent measurement programs should be reviewed to identify and any other compounds found to be important.

Possible Improvements:

\> It might be useful to add reactions of NO_3 and alcohols to the mechanism. However, since there is no generalized NO_3 oxidation scheme, and the NO_3 reactions are almost always secondary to OH reaction, this is only a suggestion if the mechanism is to be expanded.

\> I have some questions concerning the alcohol reaction mechanisms and products listed in Table 8 of CAR-90:

- If isobutyl alcohol is 2-methylpropanol, I see no way for either MEK or CCHO to form as products. I would think that the major product 2-methylpropanal, would be better represented by RCHO.
- The propylene glycol mechanism should be amended. It is inappropriate to form a 4-carbon product from a 3-carbon reactant. At present, there is a net gain of 0.686 carbons for every propylene glycol molecule reacted.
- Mono-functional alcohols below C_3 include all reacted carbons in the products. However, C_4 alcohols lose 0.60, 0.16, and 0.00 carbons for n-, iso-, and tert-butanol.

\> The k_{OH} value for acetylene seems slightly low compared to the value recommended by Atkinson (1989).

\> For acetylene, 0.6 initial carbons are missing in products. I believe that 0.3 is in HCOOH, which is ignored based on slow further reactions. However, it seems that 0.3 should be in CO products. I believe that this was overlooked.

Uncertainties and Concerns:

\> The oxidation mechanism of acetylene by OH ignores the pathway of isomerization of the OH-acetylene adduct to vinoxy radical (CH_2CHO). This is acceptable based on the fact that the fraction of reaction through this pathway is unknown. However, this pathway is somewhat unique in that it produces glyoxal and OH without oxidation of NO to NO_2. Hence, it will be operative at low or no NO. This is an example of the breakdown of the RO2R method, similar to what may occur for aromatics.

7. REACTIONS OF ALKENES

Except for ethene (see below), alkene reactions are also represented with a set of generalized reactions. However, alkenes react rapidly with OH, O_3, NO_3, and $O(^3P)$. Therefore, a generalized representation of kinetics and products is far more complicated than for the above VOCs that mainly react with OH. This extra dimension of multiple alkene oxidation pathways exposes many limitations of current chemical mechanism solution schemes and forces the mechanism developer to make assumptions so that the chemistry can fit into the constraints of the solver. Dr. Carter has done a good job focusing on the key chemical aspects of alkene chemistry and developing a reaction scheme that allows those points to be solved. The following comments apply to the mechanism in general:

Necessary Updates:

\> It would be useful to expand Table 9 of CAR-90 to include some other alkenes. Some suggestions are:

cis-2-pentene
trans-2-pentene
cis-2-hexene
trans-2-hexene
2-methyl-2-pentene
cis-4-methyl-2-pentene
trans-4-methyl-2-pentene
Δ-3-carene
d-limonene

\> Table 9 contains a compound listing for 'Unspeciated C≥5 internal alkenes'. I believe the substituent codes are incorrect for this, since one is code number 1 ($=CH_2$), a terminal alkene bond.

Possible Improvements:

\> The method of substituent coding and product formation for cycloalkenes seems to unnecessarily ignore half of the product mass and chemical function.

Uncertainties and Concerns:

\> The method of substituent coding is unable to account for more than one functional group on a molecule. Therefore, secondary groups like long alkyl chains, allylic carbons, or a second alkene bond in dialkenes, must be ignored. This becomes a problem in both apportioning carbon into the proper products and counting product mass as discussed in detail below.

> Given the inability of the mechanism to completely describe diene chemistry and the significant amount of lost carbon in the pinene species (see below), I would expect significant inaccuracies in the mechanistic representation of biogenic compounds. Such problems would also occur if α-pinene or isoprene were used to represent terpenes in general.

The following are specific notes related to each alkene oxidation scheme.

OH-Alkene Reaction Scheme

The product distribution for the OH-alkene reaction scheme is given in Table 5. The following items are relevant to that oxidation scheme.

Table 5. Product Parameters for OH + Alkenes.

ALKENE + OH =	RO2R	+ HCHO	+ CCHO	+ RCHO	+ ACET	+ MEK	+ RO2N	-C
Propene	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000
1-Butene	1.000	1.000	0.000	1.000	0.000	0.000	0.000	0.000
t-2-Butene	1.000	0.000	2.000	0.000	0.000	0.000	0.000	0.000
c-2-Butene	1.000	0.000	2.000	0.000	0.000	0.000	0.000	0.000
Isobutene	1.000	1.000	0.000	0.000	1.000	0.000	0.000	0.000
2-Me-1-butene	1.000	1.000	0.000	0.000	0.000	1.000	0.000	0.000
2-Me-2-butene	1.000	0.000	1.000	0.000	1.000	0.000	0.000	0.000
3-Me-1-butene	1.000	1.000	0.000	1.000	0.000	0.000	0.000	1.000
2,3-DiMe-2-butene	1.000	0.000	0.000	0.000	2.000	0.000	0.000	0.000
1-Pentene	0.900	0.900	0.000	0.900	0.000	0.000	0.100	0.900
1-Hexene	0.775	0.775	0.000	0.775	0.000	0.000	0.225	1.775
Cyclohexene	1.000	0.000	0.000	1.000	0.000	0.000	0.000	3.000
Cyclopentene	1.000	0.000	0.000	1.000	0.000	0.000	0.000	2.000
1,3-Butadiene	1.000	1.000	0.000	1.000	0.000	0.000	0.000	0.000
Isoprene	1.000	1.000	0.000	1.000	0.000	0.000	0.000	1.000
a-Pinene	1.000	0.000	0.000	1.000	0.000	0.000	0.000	7.000
b-Pinene	1.000	1.000	0.000	1.000	0.000	0.000	0.000	6.000

<u>Necessary Updates</u>:

> Based on the assumptions of Ohta (1983) as reported by Atkinson (1990), the rate constant ratio for OH radical addition to the $CH_2=CH-$ and $CH_2=C<$

bonds of isoprene are calculated to be 34/66 at room temperature. However, the substituent code for isoprene are 1,3. Based on the rule of using the most reactive double bond, the code should be changed to 1,5 for the $CH_2=C<$ bond.

Possible Improvements:

> The issue of nitrate formation through reaction of NO with the OH-adduct-peroxy radical is very confusing. CAR-90 notes the observation of a 1.6% yield of RNO3 for propene. There is also discussion of the need to use a value of 23% for 1-hexene simulations in the SAPRC-ITC (note 13), and a value of 0% for α-pinene simulations in the UNC chamber (notes 19 and 20). Obviously, good laboratory measurements are lacking for almost every alkene. The use of simulation results may indicate that some organic nitrates are formed, but not very confidently.

The text and notes [to Table 9] of CAR-90 are very confusing with respect to nitrate yields. Following a description of the above points, CAR-90 suggests a organic nitrate formation estimate based on the calculated nitrate yields for alkane RO2 radicals. Apparently, for C_{6+} alkenes, the nitrate yield is somehow based on the nitrate yield for an alkane of equal chain length (note 22). However, the text explains that, for 1-hexene, the n-pentane yield would be relevant had not an estimate for 1-hexene been made from chamber simulations. In addition, when dealing with this 1-hexene example, the paper refers to a value in its own Table 6 that does not exist [perhaps the table was updated after the text was written]. The alkene table (Table 9) includes only two non-zero nitrate yields, 0.23 for 1-hexene and 0.10 for 1-pentene. The minor yields in propene are ignored, and it is unclear where the 1-pentene value originated.

I understand the extreme uncertainty that will exist in any scheme used to estimate organic nitrate yields. However, the current values are internally inconsistent and it is not clear what they are based on. Accepting great uncertainty, some coherent scheme should be put forth and new values should be calculated. [Even though the value is not very significant, I would feel better if the measured propene yields were put into the pN value instead of assuming a yield of 0].

> For cycloalkenes, the product scheme is difficult to apply. Only one half of the products are accounted for in cycloalkenes, even though there are two aldehyde functional groups formed. I would suggest updating the substituent codes from 3,0 to 3,3, since the RCHO groups formed are joined at the alkyl group anyway.

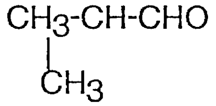
Uncertainties and Concerns:

- The OH product distribution is based on the assumption of no hydrogen abstraction occurs on long side chains and no abstraction from allylic hydrogens. This is acceptable based on the need to generalize. A worst case scenario might have 20% of an individual alkene reacting through these two paths combined.

- As with other product schemes, the OH scheme assumes available NO and instantaneous product formation. In addition, the assumption is made that scission of β-hydroxy alkoxy radical to form carbonyl-containing decomposition products is the exclusive product-forming reaction.

- Non-cyclic mono-alkenes are fairly well represented by the general OH-alkene product scheme. These schemes produce either explicit products (HCHO, CCHO, and ACET) or long-chain aldehydes or ketones that are represented by surrogates (RCHO and MEK) and 'lost' carbon. However, as noted above, carbon chains longer than $-C(CH_3)(CH_2CH_2-)$ or $-CH(CH_2CH_2-)$ have more carbons in the alkyl groups than can be included in MEK or RCHO surrogates (4 and 3 carbons respectively). In such cases, these carbons are thrown away. For instance:

  For 3-methyl-1-butene:

  $CH_3-CH(CH_3)-CHO$ is represented by CH_3-CH_2-CHO

  For 1-hexene:

  $CH_3-(CH_2)_3-CHO$ is represented by CH_3-CH_2-CHO

  These surrogate placements lose 1 and 2 carbons respectively.

- For dienes, the kinetics of both bonds are included in the k_{OH} value but the products of only one alkene bond can be addressed. The guidance in CAR-90 advises creation of substituent codes for the most reactive bond, although there is no method referenced to show which bond is the most reactive. The products created by only one bond effectively convert the second alkene bond into an alkyl, sigma bond. Thus, both 1,3-butadiene and 2-methyl-1,3-butadiene (isoprene) form HCHO and RCHO upon reaction with OH (an additional carbon is lost for isoprene). Based on experimental observations, this provides an incorrect product distribution. For instance, in the case of isoprene, the observed products of methylvinyl ketone and methacrolein are far more reactive than MEK and can produce products from reaction at the second alkene bond that cannot even be represented with MEK.

> The inability to include product carbon in further reactions has been addressed above. The values for lost carbon in the OH-alkene oxidation scheme are given in Table 5. Note that this is particularly prevalent for cyclic alkenes for the reasons discussed above: a-pinene, b-pinene, and cyclohexene ignore 70%, 60% and 50% of their reacting carbon.

O_3-Alkene Reaction Scheme

The kinetics of the initial oxidation of alkenes by O_3 are fairly well known and adequately represented in the mechanism. Unfortunately, the reaction of ozone with alkenes forms energetic, biradical intermediate products. The chemistry of these products has only been studied in any depth for the smallest molecules. Dr. Carter has had to employ a number of approximations and assumptions to complete this alkene oxidation scheme. The projected distribution of products for various alkenes is given in Table 6. There are a few items that should be pointed out:

Possible Improvements:

> As noted many times in CAR-90, the chemistry of the biradical intermediates is very uncertain. In this and other cases, Dr. Carter utilizes the simulation of smog chamber observations to supplement the laboratory kinetic data. For the biradical chemistry this is done in at least two situations: the [CCHO2*] and [C(C)COO*] biradicals. In the first case, model simulations of propene-NO_x-air experiments (Carter et al., 1986) are used to support reducing the radical yield from 68% (Atkinson, 1990) to 30%. The remaining carbon mass is put into an MEK surrogate or '-C'.

For the [C(C)COO*] biradical, CAR-90 utilizes an isobutene-NOx-air experiment for determining stabilization and decomposition yields of radicals. Niki et al., (1987) and Martinez and Herron (1987) have since looked at this reaction. Dr. Carter assumed no stabilization although 25 to 30% has now been reported. Also, the principal decomposition pathway produces OH whereas CAR-90 assumed only 50% through this path. Therefore, the mechanism's radical production again appears to be lower than expected from the laboratory data. The following are a few notes related to these reaction schemes.

Table 6. Product Parameters for O_3 + Alkenes.

ALKENE + O3 =	HO2	+ OH	+ RO2R	+ R2O2	+ CCO3	+ C2CO3+	HCHO	+ CCHO	+ RCHO	+ ACET	+ MEK	+ CO	+ MGLY	-C	Real -C
Propene	0.165	0.060	0.135	0.000	0.000	0.000	0.650	0.500	0.000	0.000	0.140	0.295	0.000	0.435	0.495
1-Butene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	0.565
t-2-Butene	0.210	0.120	0.270	0.000	0.000	0.000	0.300	1.000	0.000	0.000	0.280	0.150	0.000	0.430	0.430
c-2-Butene	0.210	0.120	0.270	0.000	0.000	0.000	0.300	1.000	0.000	0.000	0.280	0.150	0.000	0.430	0.430
Isobutene	0.060	0.100	0.100	0.000	0.000	0.000	0.500	0.000	0.000	0.500	0.400	0.220	0.100	-0.180	-0.120
2-Me-1-butene	0.060	0.100	0.000	0.150	0.050	0.050	0.550	0.050	0.000	0.000	0.900	0.220	0.000	0.220	0.280
2-Me-2-butene	0.105	0.160	0.235	0.000	0.000	0.000	0.150	0.500	0.000	0.500	0.540	0.075	0.100	-0.185	-0.185
3-Me-1-butene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	1.565
2,3-DiMe-2-butene	0.000	0.200	0.200	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.800	0.000	0.200	-0.800	-0.800
1-Pentene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	1.565
1-Hexene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	2.565
Cyclohexene	0.105	0.060	0.135	0.000	0.000	0.000	0.000	0.150	0.500	0.000	0.210	0.075	0.000	0.285	3.285
Cyclopentene	0.105	0.060	0.135	0.000	0.000	0.000	0.000	0.150	0.500	0.000	0.210	0.075	0.000	0.285	2.285
1,3-Butadiene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	0.565
Isoprene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	1.565
a-Pinene	0.105	0.060	0.135	0.000	0.000	0.000	0.000	0.150	0.500	0.000	0.210	0.075	0.000	0.285	7.285
b-Pinene	0.165	0.060	0.135	0.000	0.000	0.000	0.500	0.150	0.500	0.000	0.210	0.295	0.000	0.505	6.565

- Dr. Carter may want to update the [C(C)COO*] mechanism based on the work of Niki (1987) and Martinez and Herron (1987).

- Only a few alkene-NO_X-air experiments appear to have been used to determine the stabilization yields (in the case of [C(C)COO*], only one). Mechanisms developed using chamber simulations are subject to offsetting errors. It is possible that the need for less reactivity in the biradical schemes may actually be offsetting another mechanism estimate that is over-reactive. Therefore, the schemes are still highly uncertain and it may be wise to try the schemes on alkene-NO_X-air experiments of other chambers.

Uncertainties and Concerns:

> For all biradicals larger than [$HCHO_2$*], the products include yields of MEK as an arbitrary surrogate for many non-radical carbons. This includes 2- and 3-carbon products. For example, acetic acid is represented by MEK at 1/2 the yield to account for 2 times the carbons. MEK is used to represent acids, esters, and other unspecified biradical products. I am concerned about both the lack of resolution in the product chemistry and the use of a 4-carbon product to represent smaller molecules.

The guidance in the text of CAR-90 for [C(C)CO_2*] biradical decomposition is to create negative '-C' as a product; in effect, to create mass from somewhere because the product MEK originates from a 3-carbon biradical. Beyond being undefinable from a chemical point of view, this type of mechanism can cause solvers to carry negative concentrations (or abort simulation). As shown in Table 6, the calculated yields of '-C' for any alkene with a substituent group of 4 (-$CH(CH_3)_2$) produces this effect. In the case of 2,3-dimethyl-2-butene, the 6 original carbons produce 6.8 product carbons. Although it is distasteful, perhaps the better solution would be the carbon-bond type of approach taken in the ALKANE program, where the yield of MEK surrogates was lowered to conserve mass.

> Even given the amount of '-C' to be calculated in the biradical decompositions, the scheme still appears to lose and create carbon that is unaccounted for in either the products or '-C'. This is shown in Table 6.

NO_3-Alkene Reaction Scheme

The kinetics of NO_3-alkene reactions are established for a number of important alkenes at room temperature. However, there are a few items concerning the kinetics and mechanism that are less certain:

Necessary Updates:

> Some reaction rate constants in Table 9 of CAR-90 do not appear to agree with those recommended by Atkinson (1990). These are for 2,3-dimethy-2-butene, cyclohexene, and cyclopentene.

Uncertainties and Concerns:

> The temperature dependence must be assumed, in this case, based on OH kinetics.

> The NO_3 reaction scheme exclusively follows decomposition of the RO radical, ignoring the O_2 reaction and its products (which have been found by Shepson (1985) for propene). This would yield nitrate-containing carbonyl products and HO_2.

> Because the product carbonyls are apportioned into mechanism species much like the OH-alkene scheme, my above-noted concerns about lost

carbon and the appropriateness of exclusively using MEK as the product surrogate apply for NO_3 as well.

> The reaction of NO_3 and alkenes may be significant during high ozone events, especially near evening. Under these conditions, ozone concentration is sufficient to convert most NO_x to the more oxidized states of NO_2, NO_3, and N_2O_5. Therefore, NO concentration is probably low and the assumption of prompt product formation, because of rapid NO reaction, may be poor.

$O(^3P)$-Alkene Reaction Scheme

> If these reactions are unimportant in the atmosphere and the mechanism is known to be a gross approximation (because it is difficult to generalize), why include it at all?

> The kinetics of the $O(^3P)$ plus alkene reactions are reasonable. Perhaps the review of Cvetanovic (1987) should be consulted for an update.

8. REACTIONS OF ETHENE

The chemistry of ethene is represented explicitly because there is often a significant fraction of ethene in the atmospheric mixture and because the chemistry of the OH-adduct differs somewhat from the generalized alkene schemes.

> Of concern is the fact that CCHO is used to represent glycolaldehyde. Glycolaldehyde forms products of different reactivity compared to acetaldehyde. In addition, the chemistry for the glycolaldehyde analog of PAN is highly uncertain. Because of the high fraction of ethene in many atmospheric mixtures, these uncertainties not only affect ethene chemistry, but that of the entire mixture.

9. LUMPED (SURROGATE) ORGANIC PRODUCTS

Methylethyl ketone (MEK) is by far the most used organic surrogate product in the SAPRC-90 Mechanism. Therefore, even though the chemical reactions of the mechanism explicitly describe MEK chemistry, the actual application is to represent general oxidation for a wide variety of organic product mass, very little of which would actually be MEK. With this in mind, the OH oxidation and photolysis reactions of MEK are reasonable,* although somewhat irrelevant.

Uncertainties and Concerns:

> As noted in various sections above, MEK is used to represent almost all non-explicit carbonyl and alcohol functional groups (not molecules) formed in alkane oxidation (including one MEK for each carbonyl or alcohol on bi- and tri-functional molecules) and various products of alkene oxidation (stabilized biradicals and products, acids, esters and ketones). A high percentage of these products are not ketones.

As would be expected, the chemistry of many of these products, including larger ketones, differs from that of MEK. For example, many species do not photolyze in ambient light. Therefore, representation of product mass with an MEK surrogate allows the photolytic formation of new radicals that would not normally occur. Also, the range of k_{OH} values for the actual species will vary by at least two orders of magnitude, with the surrogate rate (k_{OH+MEK}) about an order of magnitude slower than most large ketones and alcohols. In addition, inclusion of vastly different types of products as MEK eliminates the mechanism's ability to represent unique aspects of individual products from different VOCs. Instead, the use of MEK chemistry will cause a large fraction of products to react somewhat more slowly than expected, consuming OH and producing peroxy acyl radicals (and potentially PANs).

I suggest a study be made to determine how resolved different aspects of product chemistry are. My feeling is that a large number of product species are used to represent a relatively unimportant pathway in aromatic chemistry, while MEK is used as a surrogate for a vast amount of alkane and alkene products. At some point in many VOC oxidation schemes, the structures of individual products were known, but that knowledge is thrown away by representing the products as MEK. Perhaps the number of surrogates should be expanded to allow for more resolution of the alkane and alkene products. I suggest at least the inclusion of an alcohol product. This will not eliminate the mass loss issue, but could at least improve the resolution of product chemistry for alkanes and alkenes.

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* The photolysis reaction is somewhat uncertain with respect to explicitly representing MEK because of the poor quality of quantum yield information available. Dr. Carter had to base the assumed quantum yield on one UNC chamber experiment. In addition, that simulation probably utilized older (somewhat questionable) light data for the UNC chamber. Nevertheless, the OH reaction usually dominates over photolysis.

Aldehyde products of 3 carbons or greater are represented by RCHO. The chemistry of RCHO is based on propanal, as best as can be done given current measurements. This representation is not unreasonable, but there are a number of associated minor problems:

> In some cases the creation of an RCHO product results in ignoring the additional alkyl chain carbons, which appear as 'lost' carbon.

> The k_{OH} values for larger aldehydes can increase by about 50% over that of propanal.

> Higher molecular weight PAN chemistry (PPN) is assumed to have the same kinetics as PAN. This is very uncertain.

Organic nitrates are represented by RNO3. The fixed-carbon nature of this species is an important source of lost product carbon. This and other RNO3 uncertainties are discussed in the alkane and alkene sections above.

10. LUMPED REPRESENTATION OF PEROXY RADICALS

In all tropospheric photooxidation mechanisms, it is necessary to aggregate the chemistry of the hundreds of different organic peroxy radicals that originate during reaction of the various compounds found in complex organic mixtures. One of the central parts to the SAPRC-90 Mechanism is a method used to calculate organic peroxy radical concentrations and chemical effects. Originally devised around 1985, it is described in CAR-90 and in more detail by Carter and co-workers (1986) and Lurmann et al. (1987).

While some peroxy lumping methods are rather simplistic and attempt to describe only the gross character of peroxy radical chemistry, the SAPRC method attempts to reach a more detailed level. The method conserves carbon mass and can approximate concentrations of total RO2, RCO3, and organic products. This is done by employing an extensive series of mathematical/chemical operator species in the mechanism. The added detail, however, requires a number of assumptions to be made concerning generalized reaction schemes and a set of conditions for which the formulation is optimized. Many of these assumptions have already been described because they are an inherent part of the ALKANE program. The following discussion is not as concerned with updates to the kinetic parameters as it is with recognizing limitations of the lumping method and understanding the subsequent range of application and predictive uncertainty.

Possible Improvements:

\> Based on the uniqueness of individual RCO3/PAN-type species and the mathematical inconsistencies of RCO3 self-reactions (noted below), it may be advisable to eliminate calculation of total RCO3 in favor of more explicit representation of individual RCO3 species. The reasons for this are discussed below. The change would allow different rate constants and products for individual RCO3/PAN analogs.

Uncertainties and Concerns:

\> As noted above, a necessary assumption is that all products and reaction rate constants are identical for all peroxy radicals and operators when reacting with NO, HO_2, RO2, or RCO3. This is particularly difficult to accept for the RO2 + RO2 radical termination reactions, which have room temperature rate constants ranging from about 1.0×10^{-13} $cm^3 molec^{-1} sec^{-1}$ (primary RO2s) to about 2.0×10^{-17} $cm^3 molec^{-1} sec^{-1}$ (tertiary RO2s), and also, different activation energies.

\> Contrary to what is implied on page 506 of CAR-90, there are some mathematical inaccuracies in the calculation of total organic peroxy radical (RO2 and RCO3) concentrations.

(1) The peroxy radical self-reactions must be formulated in a way that is mathematically inconsistent with the actual kinetics of individual peroxy radical reactions. As discussed in Carter et al. (1986), the "representation of the radical + radical reactions tends to underestimate the overall rate of removal of radicals by this route [self-reaction] since it does not take into account the fact that when a given radical reacts with itself, two radicals of that type are removed via this reaction route, not one." I hasten to add, that this is an unavoidable problem that is due to limitations in the types of solvers presently employed by all simulation models. It was identified and noted in earlier works and, to my knowledge, cannot be improved upon by any simple adjustment to the RO2 and RCO3 reaction parameters.

In the case of alkyl peroxy radicals (RO2), the reaction rates for the self reactions appear to be a few orders of magnitude less than the NO rate, and this approximation seems to hold reasonably well under urban conditions. However, the self reaction of RCO3 radicals proceeds at the rate of the NO reaction. In simulations performed during a recent implementation of a condensed version of the SAPRC-90 Mechanism in an airshed model, the approximation was found to break down during low NO situations (either low NO_x or high O_3 and NO_2 in the late afternoon). In that implementation, the RCO3 lumped peroxy radical was removed in favor of explicit reactions of all acyl peroxy radicals.

(2) As noted, the use of RO2 and RCO3 as total peroxy radical operators requires that all individual (RCO3) radicals and minor (RO2) radical operators utilize identical reactions, product types, and reaction rate constants to achieve mathematical closure. Nevertheless, in the case of the acyl peroxy radicals of RCHO and BZCHO, different rates are used for the reaction with NO_2. This is somewhat justified by various laboratory and smog chamber evidence that indicates different formation and destruction rates for larger PAN analogs. However, the different rates again cause mathematical inaccuracies in the calculation of RCO3. [Dr. Carter points this out in mechanism note 51.] While I agree that the effect should be small if most RCO3 is acetyl peroxy radical, I am not sure to what extent this is always true.

> To enact the peroxy radical lumping method, the individual peroxy radicals produced in organic oxidation reactions are replaced by a set of oxygenated products plus a set of peroxy radical operators. The products are those expected after subsequent peroxy radical reactions, while the operators provide the chemical effects of the peroxy radicals on the system while forming the products. At least two important approximations are necessary to implement this method:

(1) In reality, the stable products do not form immediately, but upon reaction of the peroxy radicals. However, to complete the mathematical implementation, the products of the subsequent peroxy radical reactions must be included in the original, radical-forming reaction (see CAR-90, pages 506-507). This procedure is often referred to as 'prompt' product formation. The use of this method is acceptable as long as the steady-state approximation holds for peroxy radicals. As I discuss below, this is usually the case provided there are high enough NO concentrations. However, the method does have the effect of mathematically decoupling the chemistry (the operators formed) from the mass (the stable products) of the original peroxy radical.

(2) Because the type of stable products formed depend on the chemical conditions, there is not one ideal set of products. Therefore, *the mechanism developer must select a 'representative' set of products for each reaction.* In the SAPRC-90 Mechanism (and others) it is assumed that the products of the NO reaction with the specific peroxy radicals are the most appropriate. This is reasonable, since NO is generally present in high enough concentrations throughout much of the day to dominate over peroxy-peroxy reactions. Again, this assumes that steady-state conditions exist for the peroxy radicals.

The weakness of these assumptions arises when the conditions necessary to sustain the peroxy radical steady-state approximation break down. For different reasons, this can occur for both low-NO situations and low light conditions. In low-NO conditions, particularly in late afternoons of NO_x-poor ambient scenarios, HO_2, RO2s, and RCO3s can compete with NO for peroxy radicals. The chemistry under these conditions is radical terminating. The lumping scheme will recognize this by terminating the radical operator. That is, the RO2R formed in the initial oxidation reaction will react with HO_2, RO2 or RCO3 instead of with NO. However, the mass that would ordinarily be contained in the peroxy radical exists elsewhere (in stable products of the expected NO-peroxy reaction). Therefore, the peroxy + NO products that were 'promptly' formed in the initial reaction cannot be eliminated or changed to peroxy + HO_2 or + RO2 products. For example:

(1) If the products of an oxidation reaction are MEK and RO2R (based on NO oxidation) but the system is radical terminating, MEK is formed anyway but the RO2R could more easily react with HO_2 to form -OOH. -OOH is the organic peroxide function, which reacts with its own set of rates to re-adjust radical chemistry. Coincidentally, MEK actually holds the mass of the intended peroxide and is free to again photolyze or react with OH with a different set of rates to produce additional (unintended) -OOH. That is, once the peroxide function and mass are decoupled, the peroxide operator loses control of its mass. [The need to include various HO_2 yields in the RO2 and RCO3 termination reactions of peroxy radical operators is a similar process that is needed to adjust the chemical functionality of the system during non-steady-state conditions.]

(2) Besides potentially incorrect products, the peroxy lumping method will poorly represent the timing of product formation in low-NO and low-light situations. Again, this is because the oxygenated products of the NO-peroxy radical reaction are formed instantly. In many cases (mostly with alkanes and alkenes), successive oxidation steps must be lumped together, producing a cascade of NO oxidations, stable products, and radical operators. The R2O2 operator "is used to represent the net effect of the additional NO to NO_2 conversions resulting from multi-step photooxidation mechanisms involving second- and subsequent-generation peroxy radicals [note 41]." In conditions where the steady-state approximations breaks down, the oxygenated products and some operators could be formed 'out of time'. This could affect individual VOCs differently depending on their products and the assumed scenarios.

It should be emphasized that these peroxy radical, steady-state assumptions are not unique to the SAPRC Mechanism. Similar assumptions had to be made to formulate the CBM-IV and RADM Mechanisms. The key issue to understand is that all of these mechanisms have been optimized for specific conditions; namely, one-day urban ozone episodes with available NO_x. The formulation of a lumped peroxy radical reaction scheme that could focus on multiple conditions is overdue, but mainly delayed by limitations to mechanism solvers, not the mechanisms. The SAPRC-90 Mechanism approximates the complete set of peroxy radical reactions as well or better than any other available mechanism. My concern is not with the chemistry implemented in the SAPRC-90, but with acknowledging the limitations of application due to these necessary approximations. In particular,

> *it is unwise to perform any reactivity calculations for a set of scenarios where the conditions of any scenario used in the calculation will be NO-limited.*

Such conditions, however, are not common. Note especially that NO-limited conditions should not be confused with NO_x-limiting scenario conditions. A NO_x-limited scenario occurs when the sum of NO and NO_2 concentrations and emissions are sufficiently low such that the VOC/NO_x ratio is below the EKMA ridge line. In such a case, more NO_x in the scenario would be expected to lead to higher ozone concentrations.

NO-limited conditions occur in a simulation if the NO concentration is sufficiently low, with respect to peroxy radical concentrations, that peroxy radical termination reactions become more important than reaction with NO. At this point the peroxy radical steady-state assumptions begin to fail. Based on comparison of the reaction rate constants used in the SAPRC-90, one might consider such a situation to exist if NO concentrations drop below either HO_2 or RCO3 concentrations. Thus, NO concentrations would have to decline to near the ppt range. There are only two ambient periods where I can think of such conditions possibly occurring: (1) in the late afternoon of a very reactive day, where high levels of ozone are transported to regions of virtually zero NO_x emissions, or (2) similar but less extreme conditions occurring after sunset. The second scenario is far more likely to be NO-limited because the key chemical source of NO (NO_2 photolysis) would be inoperative at night while rapid depletion of NO by O_3 would still occur. Hence,

> *NO-limited conditions are most likely to occur in the evenings of high ozone days where the air is transported to regions of low NO_x emissions.*

If scenarios are to be run for multiple days or in the afternoons of very low NO_x conditions, the NO concentration profile should be compared with HO_2 and RCO3 profiles to ensure that the steady-state approximation for peroxy radical chemistry is still operative. If this is not the case, one may find that reactivity calculations for slow reacting species that form products late in the day may be biased because of the above problems. In theory, this problem could be exacerbated by 'prompt' formation for products that are more reactive than the original species, or by multiple levels of oxidation as is assumed in the alkane oxidation assumptions. In both cases, the decoupling of mass and chemistry could be rather significant, and would be better served by implementing better product chemistry in the mechanism.

11. GENERAL MECHANISM COMMENTS

> Some reactions in the mechanism explicitly produce H_2O and CO_2 while others ignore these products. For example, the biradical reactions of ethene and alkenes accumulates the CO_2 produced as 'lost' carbon. I suggest that the mechanism either ignore or account for all H_2O and CO_2 production in a consistent manner.

> I have a serious concern as to the strength of the smog chamber data set used in devising the mechanism. There is very little discussion as to the experiments used. In particular, few UNC experiments are referenced and none of those are recent. Simulation of chamber observations is still our best way of evaluating a mechanism in conditions as near to ambient application as possible. I am not suggesting that the mechanism be exclusively based on UNC data, but that chamber is by far the largest source of ambient-light experiments. In addition, different, linked sets of experimental have been specifically carried out to evaluate particular chemical aspects and allow focused tuning of mechanisms. Merely analyzing the statistics of individual experiments will not access this information.

12. REPRESENTATION OF COMPLEX MIXTURES WITH SAPRC-90

An important aspect of CAR-90 mechanism is its ability to represent chemical details for a large number of individual hydrocarbons. The structure is set up such that new laboratory information can be easily included into the parameter tables, provided that data fits into the existing system and assumptions. The parameter tables are then used to derive various degrees of lumped mechanisms, based on VOC composition characteristics provided by the user. It is a solid step in the direction of providing composition-specific lumped mechanisms.

For use in ambient situations where complex mixtures of VOCs exist, the SAPRC-90 and associated software can provide lumped, operational mechanisms. Unfortunately, a significant amount of detail is lost in this process. This loss of detail is primarily caused by solver and computer limitations, not by choices made by Dr. Carter. Assumptions such as fixed-carbon-number surrogates, lost carbons, averaged reaction rate constants, and chemical operators are often formulations chosen to conform with constraints limiting the number of species and the mathematical functions they can perform. Nevertheless, it is difficult to call this mechanism 'detailed' if much of the detail is eliminated during practical applications.

Uncertainties and Concerns:

> Quite a bit of the chemical detail associated with individual compounds seems to be lost when individual VOCs are included in the lumped species (represented by different general reaction schemes).

  - Averaging of the individual rates and product yields will cause lost detail. As fewer aggregation groups are used, less detail is conveyed. Practical guidance is needed so that users understand the limits of this type of aggregation.

  - The guidelines as to how to lump individual hydrocarbons into groups are rather vague. Three methods of weighting the individual fractions of each group are given, depending on whether a species reacts with OH rapidly, very slowly, or somewhere in the middle. All methods appear to be k_{OH}-based. This is reasonable for species that only react with OH but adds uncertainty to other species that can be oxidized through different paths (at least for alkenes + O_3).

  - Only one 'representative' mixture can be used to derive the kinetic and product parameters for a simulation. This is because mass transported between cells that used different chemical parameters for the same lumped species would artificially change its chemical characteristics. Unfortunately, the reality is that different VOC compositions will occur in every cell. Only one composition can be selected to derive the mechanistic parameters. Thus, all cells with other conditions will be represented by a mechanism that is, to some degree, out of tune. Transport dominated cells with low emissions and many oxidized products will be especially poorly represented by a mechanism tuned to primary emissions.

> The method of using the SAPRC-90 for reactivity calculations of individual VOCs is not explained in CAR-90 or any of the CARB reports on implementing the mechanism in air quality models. [These reports preceded most of Dr. Carter's reactivity work.] However, it seems to me that the proper way to calculate relative reactivities between individual compounds would be to simulate each scenario with a mechanism using explicit chemistry for each compound under consideration and a lumped mechanism for the remaining mixture minus each compound. This is a grand undertaking and I find it hard to believe that it has ever been attempted.

The degrees of chemistry uncertainty and application limitations discussed in this report are mainly based on individual measurements and mechanism formulations. The uncertainties associated with specific VOCs and classes would translate well to relative reactivity calculations if they are made in the rather explicit manner just stated. However, if additional assumptions are employed in the reactivity calculations, additional uncertainties will emerge. Such uncertainties are not considered in this report, but may be large.

SUMMARY

1. CONCLUSIONS AND RECOMMENDATION

Provided that a few major improvements are adequately implemented (see below) and uncertainties and limitation are acknowledged, I conclude that the SAPRC-90 Mechanism is a reasonable choice for proceeding with reactivity calculations at this time. My recommendation is based on the fact that kinetic and mechanistic data is current and because the theoretical formulation is as sound and comprehensive as can be expected (given current gaps in chemical knowledge and the limitations of chemical solvers). As noted in the following sections, however, there are a few difficult updates and concerns that must yet be accomplished.

2. MAJOR IMPROVEMENTS AND UPDATES

The SAPRC-90 Mechanism contains basic information dating from about 1989, with many significant updates based on 1990 publications and pre-prints. In that sense, it is probably the newest mechanism available for use. Most of the above sub-sections include a discussion of 'Necessary Updates.' These updates are all important but there are only a few that require immediate attention (noted below). Immediate attention is warranted because data now available is significantly different from that included in the present SAPRC-90. As I discuss below, however, inclusion of this information in the SAPRC-90 could cause different ambient simulation characteristics.

The needed updates are:

\> Update formaldehyde absorption cross section.

\> Update kinetics of acetylperoxy radical reactions with NO and NO_2. [Based on the logic of CAR-90, this probably will also include updates to the chemistry of larger acyl peroxy radicals.]

\> Improve the AFG1 and AFG2 photolysis assumptions. Remove the constant absorption cross section and evaluate the radical generating characteristics in ambient light.

> Address the apparent inconsistency in mono-functional aromatic kinetics and observed chamber reactivity. This may best be done through improved product yields.

> Include new species in the product parameter tables for various VOC groups. Some new species have been suggested for aromatics, alkanes (included in the new, enclosed ALKANE.ALL file), ethers, and alkenes. Of course, the main concern at this time is to be able to accurately represent all important species in the scenario mixtures. Thus, some suggestions can be ignored for now if they are not important, while any VOCs that I have missed should be included.

> Verify the updates I have made to the new ALKANE.ALL file.

> Fix the coding 'bug' in ALKSUB subroutine of the ALKANE program and re-run the program to generate new product parameters.

3. MINOR UPDATES

Because of time constraints, I suggest only those additional updates that appear to be simple be performed at this time. However, all updates in the 'Possible Improvements' sections should be reviewed. In my opinion, the minor updates that could now be performed include:

> Improve the nitrate formation algorithm for alkenes.

> If available, measured k_{OH} values for alkanes should supersede estimates.

> Check and update if necessary the substituent code for 'Unspeciated $C\geq5$ internal alkenes'.

> Check and update if necessary the substituent codes for cycloalkenes. [It seems that the codes should sum to 2.]

> Check and update if necessary the substituent codes for isoprene. According to the logic in CAR-90, it seems that the codes are based on the wrong bond.

> Check and update if necessary the reaction rate constants for NO_3 plus 2,3-dimethyl-2-butene, cyclohexene, and cyclopentene.

> Update products of HO_2 + NO_3 reaction.

> Include minor updates to the ALKANE program as noted above.

4. SIGNIFICANT CONCERNS, UNCERTANTIES, AND LIMITATIONS:

These issues may not be able to be completely addressed within the current time frame. However, at the least they should be recognized as significant uncertainties and, in the case of the next point, the changes must be made and evaluated.

Present Concerns:

> The effects of major kinetic and product updates on the predictive capacity of SAPRC-90 is very uncertain. *The combination of these and the other updates suggested above could affect SAPRC-90 predictions in unanticipated ways. The continued accuracy of mechanism predictions must be verified before the mechanism is used.*
>
> I am particularly concerned that the process of correctly performing these needed updates may require more than simple changes of mechanistic parameters. The changes will probably affect the smog chamber simulation statistics, indicating that some other (as yet unidentified) mechanistic errors were inadvertently included to compensate for the original inaccuracies in the updated parameters. At this point, the best circumstance would be if Dr. Carter could identify a few changes (hopefully, in the way the chamber processes were described) that would allow the new formulation to again fit the chambers. However, if the statistical divergence is significant and no simple improvements are found, credible remedial action could potentially be extensive and well beyond the time constraints of this project. In such a case, it may be necessary to select the 'best' mechanism available, and acknowledge the limitations. As far as I can see, the choices would then be to use: (1) the old formulation with known inaccuracies in key mechanistic parameters, or (2) the updated formulation, assuming that the compensating errors are in the chamber portion of the mechanism, which will be discarded for ambient simulation. Given the intricate chemical calculations required of this project, I am uncomfortable with either choice.

> Product resolution is poor. This significantly affects the quality of calculations once a scenario changes from emissions-dominated to transport conditions. For aromatics, the measured yields of dicarbonyls are ignored for many species. In addition, for alkenes, alcohols, and alkanes, MEK is used for an extremely high fraction of the reactive product carbon that is not

determined to be one of the explicit products (HCHO, CCHO, or ACET). For alkanes, this represents almost all remaining product carbon. In general, for alkenes, alcohols, and alkanes, such products as alcohols, acids, ketones, stabilized biradicals and products (esters and acids) are all represented by MEK. The use of multiple MEKs to represent multiple carbonyls and alcohols on difunctional products becomes a carbon-bond type of approach, since molecular integrity is lost in favor of representing functional groups. At some point (probably the afternoon of the first day of a simulation), a significant amount of product resolution will be lost in favor of generic, MEK chemistry. It would seem useful to devise some additional product surrogate species, such as an alcohol, to address this issue.

> Significant amounts of reactive product carbon is ignored ('lost') for some individual compounds or classes. This is because the surrogate product molecules (RCHO, MEK, and RNO3) must assume a fixed structure. Extra carbons are discarded. This could also lead to predictive biases between individual compounds. The tables given in the report show significant losses for some species in all classes. Aromatics, alkanes, and alkenes lose carbons when the chain length of alkyl groups is too long to be represented by these fixed-length products. In addition, some alcohols and acetylene also apportion product carbons incompletely.

> In a few cases, product mass is created by some rather strange product algorithms. As far as I can tell, these cases are limited butane (must create 1 carbon for every 5-carbon RNO3 formed), propylene glycol (forms 4-carbon MEK as a product), and a few alkenes using the $[C(C)CO_2^*]$ biradical product algorithm.

> Given the inability of the mechanism to completely describe difunctional chemistry and the significant amount of lost carbon in the terpene species, I would expect significant inaccuracies in the mechanistic representation of biogenic compounds. Such problems would also occur if α-pinene or isoprene were used to represent terpenes in general.

Later Concerns:

These and the above items should be considered during the next stage of mechanism improvement.

> It may be necessary to expand the peroxy operator mechanism, at least in the case of RCO3. This is because: (1) approximations associated with peroxy + peroxy representation in SAPRC-90 may require more explicit RCO3 chemistry, and (2) new data (products and kinetics) on peroxy + peroxy

radical reactions does not appear to conform with any simple organic operator scheme like the one used in the SAPRC-90.

> The number, types, and quality of smog chamber data experiments used in mechanism development and evaluation must be improved.

> Chemistry solvers should be improved to allow more detailed and intricate organic lumping schemes. The limitations to mechanism representation should always be in the experimental data, not solver constraints.

> While mechanism rate constants and stoichiometry are based on a 'representative' emissions profile, transported mixture compositions will differ significantly from that profile and are not well-represented.

5. GENERAL UNCERTAINTY SCALES

Below are a few scales of predictive uncertainty for the SAPRC-90 Mechanism. These are based solely on my subjective assessment of the mechanism content. The scales span from most uncertain to more certain.

Hydrocarbon Class:

1. Aromatics. The large uncertainty is due to a general lack of critical experimental data. In addition, SAPRC-90 neglects measured dicarbonyl yields, cannot easily differentiate between products of similar aromatic groups, and has significant questions concerning AFG2 photolysis in ambient light.

2. Alkanes. The product yields of these species are based on a rather extensive set of radical chain-degradation assumptions. The assumptions seem sound, but are not yet well-verified by experimental data. For larger alkanes, both the kinetic assumptions and the product apportionment are more uncertain. In addition, because alkanes are relatively less reactive than alkenes and aromatics, there are far fewer smog chamber experiments available that are useful in verifying mechanism formulation.

3. Alkenes. At least parts of the alkene chemistry are reasonably well established. However, significant concerns still exist regarding biradical chemistry and biogenic (difunctional) chemistry.

Scenarios:

1. High ozone concentrations at night. Under these conditions, it is quite possible that the peroxy steady-state approximation will not hold due to low NO concentrations. Thus, product yields will be incorrect for RO2s. Also, if NO_x is available, additional uncertainties will arise because of: (1) the uncertainty associated with the N_2O_5 + H_2O reaction, (2) the fact that the products of alkene oxidation by NO_3 assume NO is available, and (3) the 'out-of-time' problems associated with decoupling RO2 chemistry (operators) and mass (stable products).

2. Transport conditions. By definition, transport conditions lack significant new emissions and are driven by VOC product chemistry. Therefore, at least three problems become important: (1) the above-noted poor product resolution, (2) the issue of lost carbon, and (3) the fact that the mechanism kinetics and stoichiometry are based on one 'representative' profile of emissions unlike the transported oxidation products. All three problems significantly limit the mechanism's range of focus. *With respect to reactivity assessment calculations, I believe any scenario beyond a single-day, daytime, urban-like, emissions-dominated environment will enter conditions for which the calculations will be highly uncertain.*

3. Afternoon transport conditions with high O_3 and low NO_x. VOC species that have not reacted rapidly in the mid-day period will be reacting in conditions approaching those stated in 1 and 2 above. Therefore, some problems associated with those scenarios may begin to occur. The reactivity calculations of such species could be biased because the chemical environment of the model is very uncertain. Specifically, I refer to the uncertainties in: (1) the N_2O_5 + H_2O reaction, (2) poor product detail and lost carbon, and (3) inappropriate mechanism stoichiometry and kinetics.

Mechanistic Uncertainty:

1. Multi functional VOCs, such as biogenic alkenes, cannot be easily represented in the lumping scheme of SAPRC-90. Only one functional group can be addressed. Thus, only mono-functional products are formed (for isoprene, MEK must be formed instead of the much more reactive methacrolein and methylvinyl ketone

products). This category also includes aromatics with long or multiple alkyl side chains.

2. The chemistry of longer chain VOCs is generally more uncertain that for smaller molecules. This is because: (1) less is known about product chemistry, especially H-shift isomerization, (2) multifunctional products cannot be represented well, (3) carbon in large products must be 'lost' to produce fixed-carbon surrogates, and (4) there are fewer or no smog chamber experiments available for more complex VOCs.

3. Slower reacting VOCs have a much smaller range of experimental conditions under which meaningful oxidation can be observed in a one-day smog chamber experiment. Hence, chamber simulation is less helpful in 'tuning' a mechanism for these species. In particular, alkanes and some aromatics suffer in this regard.

4. The 'detail' of the mechanism is overstated. Although it is possible to create a set of reactions for every VOC in a mixture, the products are often generic (RCHO, RNO3, and MEK) and quite a bit of potentially reactive product carbon mass is ignored. In addition, because of aggregation of individual VOCs with different reaction rates into a few groups, much detail is lost due to averaging. Further, as the dynamics of a VOC mixture changes, the rates and stoichiometries remain fixed.

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