CONDENSED ATMOSPHERIC PHOTOOXIDATION MECHANISMS FOR ISOPRENE

by

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February 22, 1996

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ABSTRACT

Two condensed mechanisms for the atmospheric reactions of isoprene, which differ in the number of species used to represent isoprene's reactive products, have been developed for use in ambient air quality modeling. They are based on a detailed isoprene mechanism that has recently been developed and extensively evaluated against environmental chamber data. The new condensed mechanisms give very close predictions to those of the detailed mechanism for ozone, OH radicals, nitric acid, H_2O_2, formaldehyde, total PANs, and for incremental effects of isoprene on for ozone formation in one day simulations. The effects of the condensations become somewhat greater in multi-day simulations, particularly in cases where NO_3 reactions are important at nighttime, but the ozone predictions are still very close. On the other hand, the SAPRC-90, RADM-2, and Carbon Bond IV isoprene mechanisms give quite different predictions of these quantities. It is recommended that the new mechanisms replace those currently used in airshed simulations where isoprene emissions are important.

INTRODUCTION

Isoprene is emitted from certain types of vegetation, and is believed to play an important role in both urban and rural ozone formation (Trainer et al, 1987; Chameides et al, 1988; Sillman et al, 1990). For this reason, its reactions are represented in most of the currently used urban or regional air quality models. For example, the Carbon Bond IV (CB4) (Gery et al, 1988), RADM-2 (Stockwell et al (1990), or SAPRC-90 (Carter, 1990; Lurmann et al, 1991) chemical mechanisms, which are widely used in airshed models, all include separate reactions for isoprene. However, to avoid adding new species to the model to represent speculative reactions of isoprene's products, these isoprene mechanisms are all highly condensed. In addition, in recent years there has been substantial improvements in our understanding of the atmospheric chemistry of isoprene (Paulson and Seinfeld, 1992, Carter and Atkinson, 1996, and references therein), and this new information is not reflected in these mechanisms.

Recently, Carter and Atkinson (1996) developed a detailed mechanism for isoprene which incorporates the recent progress in our understanding of isoprene's atmospheric reactions. This was

evaluated using results of NO_x-air irradiations of isoprene and its two major products, methacrolein and methyl vinyl ketone (MVK), in five different environmental chambers at two different laboratories. In most cases the mechanism simulated the experimental data to within the uncertainty of the data and the chamber and run characterization model, although it tended to underpredict PAN yields in the isoprene runs, despite giving good simulations of this product in the methacrolein and MVK runs. This discrepancy for PAN might be due to uncertainties in the mechanism developed to represent the reactions of the C_5 unsaturated carbonyl products, though the possibility that it is due to interferences in the experimental measurements of PAN have not been ruled out.

In any case, this new mechanism gives substantially better simulations of the data than the mechanism of Paulson and Seinfeld (1992), the most up-to-date and comprehensive isoprene mechanism prior that work. In addition, as shown in Figure 1, the new mechanism also gives substantially better predictions of ozone formation and NO oxidation in representative environmental chamber experiments than do the condensed mechanisms currently used in airshed models. [Ozone formation and NO oxidation is measured by the quantity $d(O_3$-NO), the change in $[O_3]$-$[NO]$, since the start of the experiment. See Carter and Atkinson (1996), for a discussion of the chamber modeling approach, and results of simulations of other experiments and measurements.] While the $d(O_3$-NO) data from some of the runs are reasonably well predicted by some of the condensed mechanisms, the new mechanism consistently gives the best predictions for the largest number of experiments. Therefore, this can be considered to represent an advance in our ability to model the atmospheric reactions of isoprene.

In view of this, the Carter and Atkinson (1996) isoprene mechanism ideally should be used in airshed model applications where the reactions of this compound might be important. However, it is much more detailed than most would consider to be necessary or appropriate for current airshed model applications. In particular, it requires adding to the general mechanism a total of 19 new species, listed in Table 1, to represent isoprene's various primary and secondary products. This is far greater than the number of species currently used for any of the other VOCs present in the atmosphere, and this level of detail is not necessary in most current applications cases where the primary interest is in simulating the major air quality features such as ozone, overall radical levels, total nitrate or oxidant formation, etc.

In this paper we present two condensed versions of the Carter and Atkinson (1996) isoprene mechanism that might be more suitable to current model applications. Since isoprene's products are sufficiently different in reactivity characteristics from other product species already in the mechanisms, a minimum level of chemical realism requires the addition of at least one new species to the model to

represent these compounds. However, a mechanism where all isoprene's products are lumped together would not be useful for applications where isoprene product data are available for comparison with model predictions. For example, atmospheric measurements of methacrolein and MVK, the major isoprene oxidation products whose yields have been quantified (Carter and Atkinson 1996, and references therein) have been reported in certain ambient air studies (Pierotti, et al., 1990; Martin et al., 1991; Montzka et al., 1993, 1995; Yokouchi, 1994). Therefore, we also developed a second version of the mechanism where methacrolein and MVK are represented explicitly.

DESCRIPTION OF MECHANISMS

The starting point for this work is a version of the detailed SAPRC mechanism (Carter, 1990, 1995; Carter et al, 1993). This is "detailed" in the sense that it explicitly represents a large number of different types of emitted compounds, but it uses a condensed representation for most of their reactive products. The reactions of inorganics, CO, formaldehyde, acetaldehyde, peroxyacetyl nitrate (PAN), propanal, peroxypropionyl nitrate (PPN), glyoxal and its PAN analog, methylglyoxal, and several other product compounds are represented explicitly. A "chemical operator" approach is used to represent peroxy radical reactions. Generalized reactions with variable rate constants and product yields are used to represent the primary emitted alkane, alkene, aromatic, and other VOCs (with rate constants and product yields appropriate for the individual compounds being represented in each simulation). Most of the higher molecular weight oxygenated product species are represented using the "surrogate species" approach, where simpler molecules such as propanal or 2-butanone (MEK) are used to represent the reactions of higher molecular weight analogues that are assumed to react similarly. The major characteristics of this mechanism are described by Carter (1990), and the updates in the current version are given by Carter et al (1993) and Carter (1995).

The SAPRC-90 mechanism represented isoprene by a single model species with its OH radical, O_3, NO_3 radical and $O(^3P)$ atom reactions represented explicitly, but with the products formed being represented as if they were the same as those formed from internal monoalkenes such as trans-2-pentene (Carter, 1990). Carter and Atkinson (1996) replaced this with a mechanism that explicitly represents most of isoprene's reactive products, using a total of 19 new model species, listed in Table 1, for this purpose. This mechanism incorporated significant new laboratory data, was evaluated against a variety of environmental chamber experiments, and was found to perform quite well in simulating not only ozone formed and NO oxidized in isoprene - NO_x experiments (shown on Figure 1), but also the formation of

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methacrolein and methyl vinyl ketone (MVK) from isoprene, and of O_3 and PAN from methacrolein and MVK. A complete listing of that mechanism is given by Carter and Atkinson (1996).

Although this mechanism is detailed in many respects, it does use a condensed and approximate method to represent the peroxy + peroxy and peroxy + HO_2 radical reactions that can become important at nighttime or in the absence of NO_x [see Carter (1990)]. Using a more detailed representation of these processes would significantly increase its size and complexity and, because of the uncertainties in the processes involved and the lack of chamber data suitable for evaluating this aspect of the mechanism, may not necessarily improve its predictive capability. But this approximation means that the mechanism does not incorporate available information concerning the reactions of peroxy radicals formed in the isoprene system, and that its predictions under low NO_x conditions where these reactions may be important may not be reliable. However this mechanism, and condensed mechanisms derived from it, can serve as the starting point for development of mechanisms that use a more detailed representation of these processes.

In this work, two condensed versions of the mechanism have been developed, differing in the number of model species used to represent isoprene's unique reactive products. The model species used, and the compounds they represent, are listed in Table 1. Table 2 lists their reactions and documents in footnotes the derivations of parameters and rate constants that differ from those in the detailed mechanism. Their major features are summarized below.

Four Product Mechanism
This is the less condensed of the two mechanisms and is intended for applications where explicit representation of isoprene's major identified products, methacrolein and MVK, are desired. The model species ISOPROD represents the other products that are not already in the general mechanism, as indicated on Table 1, and its product yield parameters and rate constants are derived as discussed below. MEK (methyl ethyl ketone) is used to represent hydroxyacetone and CCHO (acetaldehyde) is used to represent glycolaldehyde, consistent with the lumping approach used in the general mechanism (Carter, 1990). The various unsaturated PAN analogues formed from isoprene's products or the isoprene + O_3 reaction are represented by MA-PAN, the PAN analogue formed from methacrolein, because this is the unsaturated PAN analogue formed in the highest yield. The species HOMA-PAN, NA-PAN, HO-PAN, and HET-UNKN are not formed in this mechanism because their precursors are not the mechanism.

The model species ISOPROD represents highly reactive compounds that are formed in fairly high yields, so model predictions would be expected to be sensitive to its reactions. The most important

compounds it represents are hydroxymethacrolein (HOMACR) and the two C_5 unsaturated aldehydes IP-MHY and IP-HMY. The product yield parameters and the rate constant for the OH reaction were derived by weighted averages of those for these species, as indicated in Footnote 3 and 4 to Table 2. The O_3 reaction rate constant was derived by optimization to minimize the discrepancy between the condensed and detailed model simulations in the one-day isoprene-NO_x test calculations, as indicated in Footnote 5 to Table 2 (see also "Test Calculations", below). The NO_3 radical reaction rate constant was the same as that for the C_5 unsaturated aldehydes in the detailed mechanism, since these make up ~75% of the lumped ISOPROD and react much more rapidly with the NO_3 radical than does hydroxymethacrolein. The photolysis absorption cross-sections and quantum yields for ISOPROD are the same as used for all the unsaturated aldehydes in the detailed mechanism, which was based on those for methacrolein.

One Product Mechanism

This is the most condensed isoprene mechanism that we feel would be chemically realistic. It uses only a single species, ISOPROD, to represent the reactions of isoprene's unique products. Methacrolein and MVK are thus lumped with the other species represented by ISOPROD, and ISOPROD's mechanistic parameters are modified to reflect this fact. In addition, the model species MA-PAN, used in the four-product mechanism to represent the unsaturated PAN analogues formed by methacrolein and the other unsaturated aldehydes, is replaced by PPN, the model species used in the general mechanism to represent most of the higher PAN analogues.

The mechanistic parameters for ISOPROD are derived analogously to those for this species in the four product mechanism, except that the contributions of METHACRO and MVK are also taken into account (see Footnote 6 to Table 2). The OH radical and O_3 rate constants are derived by simultaneously optimizing them to minimize differences between the condensed and detailed mechanisms in the one-day isoprene-NO_x test calculations, as indicated in Footnote 9 to Table 2. The ISOPROD absorption cross-sections and quantum yields are the same as those in the four product mechanism. Results of multi-day simulations, discussed below, indicated that HO_2 and H_2O_2 predictions under nighttime conditions in scenarios where NO_3 reactions were important were significantly different from the detailed mechanism unless a relatively low rate constant was used for the ISOPROD + NO_3 reaction. Therefore, this mechanism uses a low ISOPROD + NO_x rate constant (see footnote 10).

Base Mechanism

The mechanism for species in the general mechanism not listed in Table 2 is the updated version of the SAPRC-90 mechanism summarized by Carter (1995), and listed by Carter et al (1993). It is very

similar to the SAPRC-90 mechanism of Carter (1990) except that photolysis absorption cross-sections for formaldehyde and rate constants involving PAN have been updated, changes have been made to the O_3 + alkene mechanisms based on new laboratory data, and updates have been made for reactions of several VOCs (Carter, 1995).

Other Mechanisms

Calculations using the SAPRC-90 (Carter, 1990), RADM-2 (Stockwell et al., 1990; Carter and Lurmann, 1990), and Carbon Bond 4 (Gery et al, 1998) are presented in this work for comparison purposes. The SAPRC-90 isoprene mechanism represents isoprene reacting with its appropriate rate constants, but has it forming the same products as internal olefins (Carter, 1990). For more straightforward comparisons of the condensation approach, the mechanisms for the species other than isoprene were updated to be the same as the base mechanism employed in this work. The RADM-2 isoprene mechanism uses a very similar condensation approach as SAPRC-90; its main difference is that it excludes the $O(^3P)$ + isoprene reaction, which is generally negligible in the atmosphere but can be important in chamber experiments. This mechanism is given by Carter and Lurmann (1990) and Stockwell et al, (1990). The Carbon Bond IV isoprene mechanism also has isoprene reacting with its appropriate rate constants, but it uses a peculiar mix of product species already in the model, including ethylene, to represent some of the unique reactivity characteristics of isoprene's expected products, derived from modeling University of North Carolina (UNC) outdoor chamber experiments (Gery et al, 1988). The version used here is that incorporated in version 6.21 of the Urban Airshed Model (UAM), as provided to us by the staff of the California Air Resources Board (Woodhouse, private communication, 1994). The photolysis rates for the chamber simulations were derived using absorption cross-section and quantum yield data used in the development of the Carbon Bond IV mechanism (Gery, private communication, 1990), adjusted to duplicate the ambient photolysis rates hardwired into the UAM.

TEST CALCULATIONS

The most sensitive type of scenario to assess mechanism differences for reactive compounds are those where the compound and NO_x are the only reactive constituents present, so most of the test cases employed in this study are of this type. However, since isoprene is usually emitted in the presence of other pollutants, the effects of the mechanism condensations on incremental reactivity calculations, which measure the effects of adding isoprene to an already polluted scenario, are also examined. The specific types of test simulations employed are summarized below.

Static Isoprene - NO$_x$ Simulations

The major set of test cases were isoprene-NO$_x$ calculations under simulated atmospheric conditions, with both static and continuous emissions scenarios. In the static scenarios, varying amounts of isoprene and NO$_x$ were present at the beginning of the simulation, and allowed to react without subsequent emissions or dilution. Although this is not a particularly "natural" situation because other reactive pollutants are almost always present in ambient atmospheres, we found that introducing other pollutants decreases the sensitivity of the calculation to differences in the isoprene mechanisms. It also complicates comparisons with other mechanisms that have differences in their representations of other organic pollutants besides isoprene.

Nine sets of initial NO$_x$ and isoprene levels were used in the static simulations, though results of only a representative subset are shown here. These were as follows (given as ppm NO$_x$, ppm isoprene): (0.03, 0.01); (0.03, 0.03); (0.03, 0.1); (0.1, 0.03); (0.1, 0.1); (0.1, 0.3); (0.3, 0.1); (0.3, 0.3); and (0.3, 1). The NO$_x$ consisted of 75% NO and 25% NO$_2$. The temperature was constant at 300 K. Two types of static simulations were conducted. For the derivations of the ISOPROD rate constants and mechanistic parameters, the simulations were at constant light intensity for 12 hours duration, with photolysis rates being those calculated using the actinic fluxes given by Peterson (1976) for direct overhead sun, corresponding to an NO$_2$ photolysis rate of 0.54 min^{-1}. For mechanism comparison purposes, the second set of simulations were for two days (36 hours), and employed diurnally-varying photolysis rates calculated using the zenith-angle dependent actinic fluxes used in the calculations of Carter (1994a), with the time dependence of the zenith angle being appropriate for Atlanta, GA, at the time of the solar equinox. These simulations started at 8AM EDT and ended at 6PM EDT on the following day.

Continuous Emissions Isoprene - NO$_x$ Simulations

The continuous emissions test cases employed the same conditions as the two-day, diurnally-varying light intensity static cases except that the NO$_x$ and isoprene were not present initially, but were introduced at constant rates throughout the duration of the simulations. The emission rates were such that if no chemical reactions occurred the concentrations at the end of 12 hours would be the same as the initial concentrations in the static simulations.

Environmental Chamber Simulations

The environmental chamber experiments used in the evaluation of the detailed mechanism was also used to assess mechanism differences, though in this case the objective is not for the condensed mechanisms to fit the chamber data as closely as possible, but to test whether they give the same

predictions as the detailed mechanism. (To adjust condensed mechanisms to fit chamber data better than the detailed mechanism amounts to in effect ignoring the fundamental mechanistic information in the detailed mechanism and instead deriving a parameterization of the chamber data.) The run conditions (chamber effects model parameters, light intensity and spectra, etc.) used when assessing the alternative mechanisms were the same as in the evaluation of the detailed mechanism (Carter and Atkinson, 1996; Carter et al, 1995).

Incremental Reactivity Simulations

To assess effects of mechanism differences on simulations of ozone under conditions more representative of polluted urban atmospheres, incremental reactivities, defined as the change in O_3 caused by adding small amounts of a compound to the emissions, were calculated for isoprene for various simulated atmospheric pollution scenarios. The scenarios included the 39 "base case" and 3 "averaged conditions" scenarios used by Carter (1994a) in the development of various VOC reactivity scales. The base case scenarios consisted of single-day EKMA box model scenarios (EPA, 1984) derived by the EPA to represent 39 different urban ozone exceedence areas around the United States (Baugues, 1990). The averaged conditions scenarios were derived by averaging the inputs to the base case scenarios except for the total amounts of NO_x emissions (Carter, 1994a). Since NO_x is the most important factor affecting incremental reactivity (Carter and Atkinson, 1989; Carter, 1991, 1994a), three different were derived to represent different NO_x conditions: a "maximum reactivity" scenario with NO_x inputs adjusted such that the final O_3 level is most sensitive to changes in VOC emissions; a "maximum ozone" scenario with NO_x inputs adjusted to yield the highest maximum O_3 concentration; and an "equal benefit" scenario with NO_x inputs adjusted such that relative changes in VOC and NO_x emissions had equal effect on ozone formation. As discussed by Carter (1994a), these represent the range of NO_x conditions where VOC reactivity is of relevance when assessing O_3 control strategies.

RESULTS

Comparisons of Predictions of the Detailed <u>vs</u> Previously Published Condensed Mechanisms

Figure 1 shows the differences between the detailed mechanism of Carter and Atkinson (1996) and the condensed isoprene mechanisms of SAPRC-90, RADM-2, and Carbon Bond IV in simulating ozone formed and NO oxidized in representative isoprene - NO_x environmental chamber experiments. The new detailed mechanism gives reasonably good simulations of the results of these experiments, which were carried out using different light sources and conditions. On the other hand, the SAPRC-90 isoprene

mechanism tends to overpredict the initial rate of NO oxidation and O_3 formation, while usually underpredicting the final ozone yield. The RADM mechanism also tends to underpredict final ozone yields, but, because it neglects the radical initiation caused by the $O(^3P)$ reaction, which is non-negligible in most of the chamber experiments, it predicts slower initial NO oxidation and O_3 formation rates than does SAPRC-90. Since RADM-2 uses essentially the same condensation approach as SAPRC-90 but ignores a non-negligible reaction, its superior performance in simulating initial rates of NO oxidation and O_3 formation is due to compensating errors. The Carbon Bond mechanism, which uses a different approach to represent isoprene's products, performs somewhat differently. While it tends to overpredict final O_3 yield and initial NO oxidation and O_3 formation rates in some runs, in general it performs somewhat better in simulating the chamber data than SAPRC-90 and RADM-2. This can be attributed to the fact that, unlike the other condensed mechanisms, it is parameterized to improve fits to chamber data. However, it does not perform as well as the detailed mechanism in simulating the UNC outdoor chamber runs, despite the fact that such data were used in its development (Gery et al, 1988).

Figure 2 shows concentration-time plots of selected species calculated using the detailed mechanism and the various published condensed mechanisms in three representative 2-day static or continuous emissions simulations. The results of the other 15 simulations we carried out are reasonably well represented by the range of results for these three and are thus not shown. Note that total PAN analogues is shown rather than PAN because most of the condensed mechanisms do not represent PAN explicitly, and also because the detailed mechanism does not perform well in predicting PAN measurements in the chambers (Carter and Atkinson, 1996). The figure shows that the mechanisms do not give very close simulations in many cases. For example, relative to the detailed mechanism, the Carbon Bond mechanism predicts a significantly different dependence of O_3, OH radicals, HNO_3, and PANs on NO_x conditions, and tends to predict significantly higher H_2O_2 levels. It also predicts much greater OH radical levels under moderate and high NO_x conditions in the continuous emissions scenarios. The RADM-2 mechanism tends to predict less O_3 under higher NO_x conditions, predicts a different dependence of HNO_3 on NO_x, and generally predicts lower H_2O_2 levels. The SAPRC-90 mechanism tracks the detailed mechanism somewhat better than the others, perhaps because it uses the same base mechanism. However, it predicts higher O_3 yields under low NO_x conditions and tends to overpredict HNO_3 when NO_x is low, particularly between days 1 and 2 in some continuous emissions scenarios.

These simulations of isoprene - NO_x mixtures are designed to be particularly sensitive to the isoprene mechanism, and the effects of the mechanisms differences in actual urban and regional modeling applications may be different. However, these results indicate that it cannot be assumed that the effects

of these mechanism differences are small. Although the differences in O_3 predictions are not large (except for the highest NO_x conditions), the differences in HNO_3 predictions may be of significance in regional modeling applications where predictions of acid deposition are of importance.

An indication of the effects of the mechanism differences on ozone predictions in urban scenarios can be obtained from the results of the incremental reactivity calculations. Table 3 shows the incremental reactivities calculated for the three averaged conditions scenarios. The table gives the incremental reactivities of isoprene relative to the incremental reactivities of the base ROG mixture (the mixture of reactive organic gases used to represent the total of all VOCs emitted into the scenarios). This is referred to as the "relative reactivity" of isoprene (Carter, 1994a), and normalizes out, at least to some extent, effects of mechanism differences related to other VOCs and effects of scenario conditions that affect absolute incremental reactivities. For comparison purposes, the incremental reactivities of the base ROG mixture is also shown.

Table 3 shows that the three mechanisms are within ±25% of each other in their predictions of the incremental reactivities of the base ROG mixture. In addition, despite their differences in the isoprene - NO_x simulations, the detailed, SAPRC-90 and RADM-2 mechanisms give similar relative reactivities of isoprene, with the isoprene relative reactivities for SAPRC-90 being ~25% higher and those for RADM-2 being ~25% lower, than those for the detailed mechanism. On the other hand, the Carbon Bond IV isoprene relative reactivities are almost twice those for the detailed mechanism, regardless o NO_x level. This may be related to the greater sensitivity of the Carbon Bond mechanism to radical inputs in general, as indicated by the fact that it also predicts ~40% higher relative reactivities for formaldehyde (Carter, 1994b), despite the fact that its mechanism is based on similar mechanistic assumptions and environmental chamber data (Gery et al, 1988). Thus one cannot always use results of compound - NO_x simulations alone as a guide to how mechanisms may differ in their predictions of relative reactivity.

Comparisons of Predictions of the Detailed _vs_ the New Condensed Mechanisms

Figures 3 and 4 show the effects of the mechanism condensations on the predictions of selected species in representative two-day isoprene - NO_x simulations. For easier comparison, the scenarios shown on Figures 2 and 3 are the same, while Figure 4 shows some additional scenarios that are of interest. Results of other the other simulations are generally similar and are not shown. These figures show that the condensed and detailed mechanisms give reasonably close predictions, with a few exceptions as noted below. The day 1 results are almost indistinguishable for all species shown except formaldehyde, which the 1-product mechanism tends to underpredict slightly compared to the other mechanisms. The

mechanism differences become greater for the second simulated day, as expected since these would be more affected by differences in the representations of the products. However, the day 2 O_3 predictions are still very close except for the high NO_x, low isoprene/no_x continuous emissions scenario shown on the left side of Figure 4. The condensed mechanisms generally perform well in matching the detailed mechanism's predictions of H_2O_2, after appropriate adjustments are made to the NO_3 + ISOPROD rate constant, as discussed below. The worst discrepancy for H_2O_2 is the second day of the same high NO_x, low isoprene/NO_x continuous emissions scenario that gives the worst day 2 ozone discrepancy, as shown on Figure 4. Both condensed mechanisms give quite good agreement to the detailed mechanisms in simulations of OH radical levels, with the notable exception of the second day in the continuous emissions scenarios with similar levels of isoprene and NO_x (right side of Figure 3), where both condensed mechanisms predict almost half the maximum OH radical levels as the detailed one. However, in general the differences between these mechanisms are extremely minor, especially when considering the much larger differences between the previously published mechanisms, as discussed above.

The underprediction, by almost a factor of 2, of OH radicals on the continuous emissions scenario shown on Figure 3 is of concern given the importance of OH radicals in the photooxidation system, and the fact that all three condensed mechanisms perform equally poorly in this case. This discrepancy is attributed to the NO_3 + isoprene reaction being particularly important at nighttime in this scenario, which accounts for almost half of the total isoprene reacting. (This situation occurs when both NO_x and isoprene are emitted at nighttime when O_3 is present at sufficient levels to react with NO_2 to form NO_3, but not at such high levels that isoprene is consumed primarily by reaction with O_3.) The detailed mechanism has model species RCHO-NO3 formed in 80% yield in the isoprene + NO_3 reaction (Carter and Atkinson, 1996); this is represented in the condensed mechanisms by the general higher aldehyde and alkyl nitrate species (see Table 1). If RCHO-NO$_3$ and its PAN analogue NA-PAN are added back to the mechanism, then the model gives much closer predictions of the day-2 OH radical levels in this simulation. This is shown on the right side of Figure 3, where the continuous emissions plots includes a calculation with RCHO-NO3 and NA-PAN added back to the 1 product mechanism (shown as "ISOPROD + RCHO-NO3"). Note that adding RCHO-NO3 but still lumping NA-PAN with MA-PAN does not solve this problem, indicating that the reactions of the NO_3-substituted PAN analogue is apparently the significant factor. Adding RCHO-NO3 has no significant effect on results of any of the one-day simulations or any of the two-day static simulations.

These results suggest that it might be appropriate to retain RCHO-NO3 and NA-PAN in the condensed mechanisms, since this would give predictions more closer to that of the detailed mechanism

in simulations where both NO_x and isoprene are emitted into the atmosphere in the presence of moderate amounts of O_3 at nighttime. However, this was not done because this is probably a fairly unusual situation in real atmospheres, and also because the NO_3 + isoprene mechanism is highly uncertain (Carter and Atkinson, 1996) and thus the detailed mechanism may not necessarily have greater predictive capability than the condensed versions. The day 2 OH levels are reasonably well simulated in most of the static and continuous emissions scenarios in the condensed mechanisms without adding this species. However, it would be of interest to assess the sensitivity of regional and urban model simulations to the level of condensation employed for this reaction.

The two condensed mechanisms give almost identical simulations in most cases, indicating that the more condensed version would probably be satisfactory for most applications except when explicit predictions of methacrolein, MVK, or total unsaturated PAN analogues are required. Other than those compounds, the main difference between the two are predictions of formaldehyde and (in a few cases at nighttime or on day 2) total PAN analogues. The differences in the formaldehyde predictions appear to be due primarily to lumping the unsaturated PAN analogues (MA-PAN) with PPN in the one product mechanism, since adding MA-PAN back to the one product mechanism gives much closer formaldehyde predictions to those of the 4-product mechanism. This is shown on the left and middle plots for the static simulations on Figure 3, where simulations using 1-product mechanism with MA-PAN added back ("ISOPROD + MA-PAN") are also included.

When the 1-product mechanism was first derived, it was assumed to be appropriate to use a ISOPROD + NO_3 rate constant which is somewhere between that for methacrolein and the C_5 unsaturated carbonyls in the detailed mechanism, since these are the main species ISOPROD represents that react with NO_3 radicals. However, if this was assumed, certain low isoprene/NO_x static simulations gave predictions of nighttime H_2O_2 formation rates that were far greater than those predicted by the more detailed mechanisms. This is shown, for example, the left hand plots on Figure 4, which include a calculation assuming the ISOPROD + NO_3 rate constant is the same as that for methacrolein. This problem does not occur in the higher isoprene/NO_x simulations or in any of the continuous emissions scenarios, as shown on the other plots on Figure 4 The high nighttime H_2O_2 production in this low isoprene/NO_x static calculation is due to the NO_3 + ISOPROD reaction, which has increased importance in the one product mechanism because of the higher ISOPROD yields combined with lower rate constant for competing reactions. Using a much lower NO_3 + ISOPROD rate constant in the one product mechanism, as indicated in Footnote 10 to Table 1, solved this problem without having any adverse effects on the other test simulations.

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Figure 1 shows that the one product mechanism gives predictions of NO oxidized and O_3 formed in the environmental chamber experiments that are almost identical to those of the detailed mechanism. Simulations of $d(O_3-NO)$ using the 4-product mechanism are similar. The small differences in O_3 predictions of these mechanisms are well within experimental or chamber characterization uncertainty.

Table 3 shows that the condensed mechanisms give almost exactly the same incremental reactivity of isoprene in the maximum reactivity averaged conditions scenario as does the detailed mechanism, but give ~5% higher relative reactivities in the lower NO_x scenarios. Similar levels of agreement are obtained for the base case scenarios, as shown in Figure 5, which plots the discrepancies in incremental reactivities between condensed and detailed mechanisms in all the scenarios, as a function of relative NO_x levels. [As discussed by Carter (1994a), the ratio of total NO_x emissions to those that give maximum O_3 yields in the scenario provides a useful measure of relative NO_x levels for reactivity assessment.] For comparison purposes, Figure 5 also shows the discrepancies for the reactivity predictions of the SAPRC-90 mechanism, which gives the best correspondence to reactivities in the detailed mechanism of all the previously published condensed mechanisms. These data show that the isoprene reactivities predicted by the condensed mechanisms developed in this work agree closely with those of the detailed mechanisms for relatively high NO_x conditions, but tend to be ~7% higher when NO_x is low. However, these differences are well within the uncertainties and variabilities of incremental reactivity simulations.

DISCUSSION AND CONCLUSIONS

The new detailed isoprene - NO_x mechanism of Carter and Atkinson (1996), which reflects results of recent laboratory studies and gives good predictions of results of environmental chamber experiments, often gives significantly different predictions of isoprene - NO_x simulations in the atmosphere than do the mechanisms currently used in most ambient air quality models. For example, the Carbon Bond IV mechanism, which actually simulates isoprene environmental chamber data somewhat better than the other previously published condensed mechanisms (though not as well as the new mechanisms), predicts the incremental ozone reactivities of isoprene in urban-like scenarios to be almost twice those predicted by the new detailed mechanism. How significant these differences would be in actual urban and regional air quality modelling applications was not investigated, but clearly the possibility that the differences are important cannot be discounted. Given this, and the fact that the new detailed mechanism represents our current state of knowledge of isoprene chemistry, one must conclude that the predictions of effects of isoprene emissions on air quality by the previous mechanisms must be considered to be suspect.

One approach for dealing with this is simply to incorporate the new detailed mechanism directly in airshed models. However, this work shows that much more condensed mechanisms can give almost identical predictions of major species in one-day isoprene - NO_x simulations, and fairly close predictions for two-day simulations, not only for ozone but also for other important species such as OH radicals, nitric acid, total PANs, H_2O_2, and formaldehyde. Some discrepancies are observed in predictions of OH radicals and other species on the second day of simulations where NO_x and isoprene are emitted together in the presence of moderate levels of ozone, which can be addressed by adding back to the condensed mechanism the model species used to represent NO_3-containing unsaturated aldehydes and their corresponding PAN analogues, but the importance of this in actual real-world model applications is unclear. Thus it is not necessary to use the full Carter and Atkinson (1996) mechanism to achieve predictive capabilities that reflect the advances in recent years in our knowledge of the atmospheric chemistry of isoprene. The available computer capability required for carrying all 19 of the species used by Carter and Atkinson (1996) to represent isoprene's products are probably better used for other purposes, particularly for simulations where isoprene is not the only reactive organic compound emitted.

The choice of which condensed mechanism to use depends on the model application. Obviously, the four product mechanism would be most appropriate if methacrolein and/or MVK predictions are desired. However, if this is not important, there do not appear to be large disadvantages in using the one product mechanism, since the simulations of almost all other major species of interest are almost exactly the same. The differences for formaldehyde and total PAN analogues are minor considering measurement uncertainties for these compounds, as well as the effects of condensations of mechanisms of most of the other VOCs that are present.

Finally, it should be recognized that although the Carter and Atkinson (1996) mechanism may represent the current state of the art, it is not without approximations and uncertainties. The detailed mechanism, and the condensed versions based on it, incorporate an approximate representation of peroxy + peroxy reactions that may reduce their accuracy under extremely low NO_x conditions. Although progress has been made in our understanding of isoprene's atmospheric reactions, important uncertainties remain which may affect model predictions (Carter and Atkinson, 1996). For example, the detailed mechanism for the NO_3 + isoprene reactions, which we have shown can have non-negligible effects under some conditions, is largely speculative. This is the major reason why we have not added NO_3 + isoprene product species to the condensed mechanisms to have them more closely represent the detailed mechanism in this regard. However, at the present time this detailed mechanism, and the condensed mechanisms

derived from it, represent our best estimate of how to represent isoprene's gas-phase reactions in the atmosphere.

ACKNOWLEDGEMENTS

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Table 1.   Summary of active species added to the general mechanism to represent reactions of isoprene's products in the detailed and condensed isoprene mechanisms.

Description	Isoprene Product Model Species [1]		
	Detailed	4 Product	1 Product
Primary Products			
Methacrolein	METHACRO	METHACRO	ISOPROD [2]
Methyl vinyl ketone	MVK	MVK	(as above)
Hydroxymethacrolein	HOMACR	ISOPROD [3]	(as above)
2-Methyl-4-hydroxy-2-butenal	IP-MHY	(as above)	(as above)
3-Methyl-4-hydroxy-2-butenal	IP-HMY	(as above)	(as above)
3-Methylfuran	MEFURAN	(as above)	(as above)
epoxy methyl butenes	ISO-OX	(as above)	(as above)
Propene (formed in O_3 reaction)	PROPENE	(as above)	(as above)
NO_3-substituted aldehydes (formed in NO_3 reaction)	RCHO-NO3	RCHO+RNO3 [4,5]	RCHO+RNO3
Secondary Products			
Hydroxyacetone	HOACET	MEK [6]	MEK
Glycolaldehyde	HOCCHO	CCHO [7]	CCHO
$H_2C=C(CH_3)-CO-OONO_2$	MA-PAN	MA-PAN	PPN [8]
$H_2C=CH-CO-OONO_2$	AC-PAN	(as above)	(as above)
$HOCH_2CH=C(CH_3)-CO-OONO_2$	MHY-PAN	(as above)	(as above)
$HOCH_2C(CH_3)=CH-CO-OONO_2$	HMY-PAN	(as above)	(as above)
$H_2C=C(CH_2OH)-CO-OONO_2$	HOMA-PAN	n/f [9]	n/f
PAN analogue from RCHO-NO3	NA-PAN	n/f	n/f
$HOCH_2-CO-OONO_2$	HO-PAN	n/f	n/f
Unknown reactive 3-methyl furan product(s)	HET-UNKN	n/f	n/f

[1] Species added to the mechanism to represent reactions of isoprene's products. Species which are already in the general mechanism, or species for which the steady state approximation can be applied, are not included, except to show when they are substituted for added product species in the detailed mechanism.

[2] Product yield parameters derived from weighed averages of those of METHACRO, MVK, HOMACR, IP-MHY, and IP-HMY. Rate constants were optimized to fit results of detailed model calculations.

[3] Product yield parameters derived from weighed averages of those of HOMACR, IP-MHY, and IP-HMY. Rate constants were optimized to fit results of detailed model calculations.

[4] RCHO (propionaldehyde) is the lumped higher aldehyde species used in the general mechanism.

[5] RNO3 (alkyl nitrates) is the lumped organic nitrate species used in the general mechanism.

[6] MEK (methyl ethyl ketone) is the lumped higher ketone and general non-aldehyde oxygenate species used in the general mechanism.

[7] CCHO (acetaldehyde) is used to represent acetaldehyde and glycolaldehyde in the general mechanism.

[8] PPN (peroxy propionyl nitrate) is used to represent lumped higher PAN analogues in the general mechanism.

[9] This species is not formed in this version of the mechanism because its precursor is represented by another species.

Table 2. Listing of the condensed mechanisms for the NO_x - air reactions of isoprene. [a]

Kinetic Parameters [b]				Notes [d]	Reactions [c]
k(300)	A	Ea	B		

Four Product Mechanism

9.88E-11	2.54E-11	-0.81	0.00		ISOP + HO. = 0.088 RO2-N. + 0.912 RO2-R. + 0.629 HCHO + 0.23 METHACRO + 0.32 MVK + 0.362 ISOPROD + 0.079 R2O2. + 1.079 RO2. + -0.079 -C
1.34E-17	7.86E-15	3.80	0.00		ISOP + O3 = 0.4 HCHO + 0.39 METHACRO + 0.16 MVK + 0.55 (HCHO2) + 0.2 (C:CC(C)O2) + 0.2 (C:C(C)CHO2) + 0.05 ISOPROD
	(fast)				(C:CC(C)O2) = HO. + R2O2. + HCHO + MA-RCO3. + RO2. + RCO3. + -1 -C
	(fast)				(C:C(C)CHO2) = 0.75 RCHO + 0.25 ISOPROD + 0.5 -C
3.60E-11	(No T Dependence)				ISOP + O = 0.75 ISOPROD + 0.25 {MA-RCO3. + RCO3. + 2 HCHO + RO2-R. + RO2. + -1 -C}
6.81E-13	3.03E-12	0.89	0.00		ISOP + NO3 = 0.8 {RCHO + RNO3 + RO2-R.} + 0.2 {ISOPROD + R2O2. + NO2} + RO2. + -2.4 -C
1.50E-19	(No T Dependence)				ISOP + NO2 = 0.8 {RCHO + RNO3 + RO2-R.} + 0.2 {ISOPROD + R2O2. + NO} + RO2. + -2.4 -C
3.35E-11	1.86E-11	-0.35	0.00		METHACRO + HO. = 0.5 {MA-RCO3. + RCO3.} + 0.42 {MEK + CO} + 0.08 {HCHO + MGLY} + 0.5 {RO2-R. + RO2.} + -0.42 -C
1.19E-18	1.36E-15	4.20	0.00		METHACRO + O3 = 0.9 {(HCHO2) + MGLY} + 0.1 {HCHO + (C2(O2)CHO)}
	(fast)				(C2(O2)CHO) = HO. + R2O2. + HCHO + HCOCO-O2. + RO2. + RCO3.
	(See Carter and Atkinson, 1996)			1	METHACRO + HV = HO2. + 0.66 HO2. + 0.33 MA-RCO3. + 0.67 {CO + HCHO + CCO-O2.} + 0.34 {HO. + R2O2. + RO2.} + RCO3.
4.76E-15	1.50E-12	3.43	0.00		METHACRO + NO3 = 0.5 {MA-RCO3. + RCO3. + HNO3} + 0.5 {CO + HO2. + RNO3 + R2O2. + RO2.} + -1 -C
1.87E-11	4.14E-12	-0.90	0.00		MVK + HO. = 0.7 {CCHO + R2O2. + CCO-O2. + RCO3.} + 0.3 {HCHO + MGLY + RO2-R.} + RO2.
4.74E-18	7.51E-16	3.02	0.00	2	MVK + O3 = 0.95 {(HCHO2) + MGLY} + 0.05 {HCHO + (C2(O2)CHO)}
	(See Carter and Atkinson, 1996)			1	MVK + HV = 0.7 {ISOPROD + CO} + 0.3 {HCHO + RO2-R. + MA-RCO3. + RCO3.} + -1.7 -C
6.19E-11	(No T Dependence)			3,4	ISOPROD + HO. = 0.418 CO + 0.125 CCHO + 0.02 HCHO + 0.124 GLY + 0.062 RCHO + 0.145 MGLY + 0.48 MEK + 0.688 RO2-R. + 0.313 MA-RCO3. + 0.688 RO2. + 0.313 RCO3. + 0.271 -C
4.18E-18	(No T Dependence)			4,5	ISOPROD + O3 = 0.062 CCHO + 0.007 HCHO + 0.031 GLY + 0.622 MGLY + 0.278 MEK + 0.063 (HCHO2) + 0.278 (HCOCHO2) + 0.559 (HOCCHO2) + 0.069 (C2(O2)CHO) + 0.031 (C2(O2)COH) + -0.208 -C
	(fast)				(HOCCHO2) = 0.6 HO. + 0.3 {CCO-O2. + RCO3.} + 0.3 {RO2-R. + HCHO + CO + RO2.} + 0.8 -C
	(fast)				(HCOCHO2) = 0.12 {HO2. + 2 CO + HO.} + 0.74 -C + 0.51 {CO2 + HCHO}
	(fast)				(C2(O2)COH) = HO. + MGLY + HO2. + R2O2. + RO2.
	(Same k as for METHACRO)			1,4	ISOPROD + HV = 1.216 CO + 0.434 CCHO + 0.35 HCHO + 0.216 MEK + 1.216 HO2. + 0.784 CCO-O2. + 0.784 RCO3. + 0.134 -C
1.00E-13	(No T Dependence)			3,6	ISOPROD + NO3 = 0.668 CO + 0.332 HCHO + 0.332 RCHO + RNO3 + HO2. + R2O2. + RO2. + -1.996 -C
	(Same k as for RCO3.)			7	MA-RCO3. + NO = NO2 + CO2 + HCHO + CCO-O2. + RCO3.
	(Same k as for RCO3.)				MA-RCO3. + NO2 = MA-PAN
	(Same k as for RCO3.)				MA-RCO3. + HO2. = -OOH + 2 {HCHO + CO2}
	(Same k as for RCO3.)				MA-RCO3. + RO2. = RO2. + 0.5 HO2. + 2 {HCHO + CO2}
	(Same k as for RCO3.)				MA-RCO3. + RCO3. = RCO3. + HO2. + 2 {HCHO + CO2}
4.79E-04	1.60E+16	26.80	0.00		MA-PAN = MA-RCO3. + NO2 + RCO3.

One Product Mechanism

9.88E-11	2.54E-11	-0.81	0.00		ISOP + HO. = 0.088 RO2-N. + 0.912 RO2-R. + 0.629 HCHO + 0.912 ISOPROD + 0.079 R2O2. + 1.079 RO2. + 0.283 -C
1.34E-17	7.86E-15	3.80	0.00		ISOP + O3 = 0.4 HCHO + 0.6 ISOPROD + 0.55 (HCHO2) + 0.2 (C:CC(C)O2) + 0.2 (C:C(C)CHO2) + 0.05 -HCHO
	(fast)				(C:CC(C)O2) = HO. + R2O2. + HCHO + C2CO-O2. + RO2. + RCO3.
	(fast)				(C:C(C)CHO2) = 0.75 RCHO + 0.25 ISOPROD + 0.5 -C
3.60E-11	(No T Dependence)				ISOP + O = 0.75 {ISOPROD + -C} + 0.25 {C2CO-O2. + RCO3. + 2 HCHO + RO2-R. + RO2.}
6.81E-13	3.03E-12	0.89	0.00		ISOP + NO3 = 0.8 {RCHO + RNO3 + RO2-R.} + 0.2 {ISOPROD + R2O2. + NO2} + RO2. + -2.2 -C
1.50E-19	(No T Dependence)				ISOP + NO2 = 0.8 {RCHO + RNO3 + RO2-R.} + 0.2 {ISOPROD + R2O2. + NO} + RO2. + -2.2 -C

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Table 2 (continued)

Kinetic Parameters [b]				Notes [d]	Reactions [c]
k(300)	A	Ea	B		
3.36E-11	(No T Dependence)			8,9	ISOPROD + HO. = 0.293 CO + 0.252 CCHO + 0.126 HCHO + 0.041 GLY + 0.021 RCHO + 0.168 MGLY + 0.314 MEK + 0.503 RO2-R. + 0.21 CCO-O2. + 0.288 C2CO-O2. + 0.21 R2O2. + 0.713 RO2. + 0.498 RCO3. + -0.112 -C
7.11E-18	(No T Dependence)			8,9	ISOPROD + O3 = 0.02 CCHO + 0.04 HCHO + 0.01 GLY + 0.84 MGLY + 0.09 MEK + 0.66 (HCHO2) + 0.09 (HCOCHO2) + 0.18 (HOCCHO2) + 0.06 (C2(O2)CHO) + 0.01 (C2(O2)COH) + -0.39 -C
	(fast)				(C2(O2)CHO) = HO. + R2O2. + HCHO + HCOCO-O2. + RO2. + RCO3.
	(fast)				(HOCCHO2) = 0.6 HO. + 0.3 {CCO-O2. + RCO3.} + 0.3 {RO2-R. + HCHO + CO + RO2.} + 0.8 -C
	(fast)				(HCOCHO2) = 0.12 {HO2. + 2 CO + HO.} + 0.74 -C + 0.51 {CO2 + HCHO}
	(fast)				(C2(O2)COH) = HO. + MGLY + HO2. + R2O2. + RO2.
(Same k as for METHACRO)				1,8	ISOPROD + HV = 0.333 CO + 0.067 CCHO + 0.9 HCHO + 0.033 MEK + 0.333 RO2-R. + 0.7 RO2-R. + 0.267 CCO-O2. + 0.7 C2CO-O2. + 0.7 RO2. + 0.967 RCO3. + -0.133 -C
1.00E-15	(No T Dependence)			8,10	ISOPROD + NO3 = 0.643 CO + 0.282 HCHO + 0.85 RNO3 + 0.357 RCHO + 0.925 HO2. + 0.075 C2CO-O2. + 0.075 R2O2. + 0.925 RO2. + 0.075 RCO3. + 0.075 HNO3 + -2.471 -C

[a] This listing is available in computer readable form on the Internet by anonymous FTP at cert.ucr.edu, directory /pub/carter/mech.

[b] Except as noted, the expression for rate constant is $k = A\ e^{Ea/RT}\ (T/300)^B$. Rate constants and A factor are in ppm, min units. Units of Ea is kcal mole^{-1}. The absorption coefficients and quantum yields for the photolysis reactions are given below. If a rate constant is given as "(fast)", then the steady state approximation can be employed on the reacting species, and any arbitrary rate constant can be used. Alternatively, the species could be replaced in reactions forming it with the set of products formed in the "fast" reaction.

[c] See Carter (1990) for a description of the species used in the general mechanism, and Table 1 for the species specific to the isoprene mechanism.

[d] Documentation notes are as follows. If no documentation notes are given, then the mechanism is the same as that given by Carter and Atkinson (1996), except with the surrogate species substitutions as indicated on Table 1, when applicable.

1. The absorption cross-sections used for the photolysis reactions METHACRO, MVK and ISOPROD are the same as used by Carter and Atkinson (1996), and are as follows (where the wavelength units are nm and the absorption cross section units are 10^{-12} cm^2 molec^{-1}, base e):

λ	σ	λ	σ	λ	σ	λ	σ	λ	σ	λ	σ	λ	σ	λ	σ
280	1.270	293	1.950	306	3.510	319	5.190	332	6.230	345	5.400	358	3.490	371	0.899
281	1.260	294	2.050	307	3.640	320	5.310	333	6.400	346	5.480	359	3.410	372	0.722
282	1.260	295	2.150	308	3.770	321	5.430	334	6.380	347	5.900	360	3.230	373	0.586
283	1.280	296	2.260	309	3.920	322	5.520	335	6.240	348	6.080	361	2.950	374	0.469
284	1.330	297	2.370	310	4.070	323	5.600	336	6.010	349	6.000	362	2.810	375	0.372
285	1.380	298	2.480	311	4.250	324	5.670	337	5.790	350	5.530	363	2.910	376	0.357
286	1.440	299	2.600	312	4.400	325	5.670	338	5.630	351	5.030	364	3.250	377	0.355
287	1.500	300	2.730	313	4.440	326	5.620	339	5.560	352	4.500	365	3.540	378	0.283
288	1.570	301	2.850	314	4.500	327	5.640	340	5.520	353	4.030	366	3.300	379	0.169
289	1.630	302	2.990	315	4.590	328	5.710	341	5.540	354	3.750	367	2.780	380	0.001
290	1.710	303	3.130	316	4.750	329	5.760	342	5.530	355	3.550	368	2.150	381	0.000
291	1.780	304	3.270	317	4.900	330	5.800	343	5.470	356	3.450	369	1.590		
292	1.860	305	3.390	318	5.050	331	5.950	344	5.410	357	3.460	370	1.192		

The quantum yields used were 0.0036 for METHACRO and ISOPROD and 0.0111 for MVK, independent of wavelength (Carter and Atkinson, 1996).

2. The mechanism of Carter and Atkinson (1996) has this reaction forming (C-CO-CHO2), which rapidly converts to (C2(O2)CHO). This is equivalent to the direct formation of the (C2(O2)CHO), as is represented here.

3. The OH radical rate constant used was the weighed average of those for HOMACR, IP-MHY, and IP-HMY in the detailed mechanism, with the weighting factor being the contributions of these to the total ISOPROD reaction in the 12-hour constant light intensity static test calculations. These contributions were ~30% for HOMACR and ~70% for IP-MHY + IP-HMY.

4. The product yields were determined by weighed averages of integrated reaction rates for OH, O₃, or photolysis reactions with HOMACR, IP-MHY, and IP-HMY in the 12-hour constant light intensity static test simulations using the detailed mechanism. The yield of a given product in an ISOPROD reaction was calculated by [(HOMACR contribution) x (yield of product in HOMACR or METHACRO reaction)] + [{1-(HOMACR contribution)} x (yield of product in IP-MHY and IP-HMY reactions)]. For example, at the end of the one day simulation where initial isoprene and NO$_x$ were both 0.1 ppm, the integrated reaction rates for the

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Table 2 (continued)

reaction of OH with HOMA, IP-MHY and IP-HMY were 6.8, 12.9 and 6.2 ppb-min, which indicates a ~25% contribution of HOMA products and a ~75% contribution of IP-MHY and IP-HMY products (which are the same) are appropriate for the OH + ISOPROD-A reaction. The average HOMACR contributions, and the contributions used to determine the product yields, are as follows:

	Average	Used		Average	Used
OH Reaction	27±2%	25%	NO$_3$ Reaction	1±2%	0%
O$_3$ Reaction	7±1%	10%	Photolysis	35±5%	35%

5. The O$_3$ rate constants were optimized to minimize the sum-of-squares differences in the concentrations, at 15 minute intervals, of O$_3$, NO, HCHO, total PANs, HNO3, and OH radicals predicted by the condensed and detailed mechanisms in the 12-hour, constant light intensity, static isoprene - NO$_x$ test simulations with initial reactant concentrations (as ppm NO$_x$, ppm isoprene) of (0.03, 0.01), (0.03, 0.1), (0.1, 0.1), (0.3, 0.1). and (0.3, 1).

6. The rate constant used is the same as that for IP-HMY and IP-MHY in the detailed mechanism because reactions with these components constitute most of the NO$_3$ + ISOPROD reaction.

7. The rate constants used in the general mechanism for other acyl peroxy radicals, given by Carter (1996) and Carter and Atkinson (1996) are employed.

8. The product yields are determined by weighed averages of integrated reaction rates for OH, O$_3$, or photolysis reactions with METHACRO, MVK, HOMACR, IP-MHY, and IP-HMY in the 12-hour constant light intensity static test simulations using the detailed mechanism. The yield of a given product was calculated from the [(METHACRO + HOMACR contribution) x (yield of product in the METHACRO reaction)] + [(MVK contribution) x (yield of product in the MVK reaction)] + {1-(METHACRO + HOMACR + MVK contributions)} x (yield of product in IP-MHY and IP-HMY reactions)]. The average METHACRO + HOMACR and MVK contributions, and the contributions used to determine the product yields, are as follows:

	METHACRO + HOMACR		MVK	
	Average	Used	Average	Used
OH Reaction	43±7%	45%	30±5%	30%
O$_3$ Reaction	12±3%	10%	61±4%	60%
NO$_3$ Reaction	17±3%	15%	no rxn.	0%
Photolysis	20±5%	20%	72±4%	70%

9. The OH and O$_3$ rate constants were simultaneously optimized to minimize least squares differences between the condensed and detailed mechanisms in predictions of O$_3$, NO, HCHO, total PANs, HNO3, and OH radicals in the same 12-hour constant light intensity static isoprene - NO$_x$ test simulations as indicated in Footnote 5.

10. The multi-day simulations indicated that a relatively low value had to be used for the rate constant for this reaction or the calculated formation rates of HO$_2$ and H$_2$O$_2$, under certain nighttime conditions when NO3 reactions important, are much greater than those calculated by the detailed mechanism. The rate constant used is arbitrarily set at 1/5 that for methacrolein, which is the highest value which can give reasonably satisfactory agreement with the detailed mechanism under these conditions. Removing this reaction from the mechanism is not reasonable because most of the species represented by ISOPROD react at significant rates.

Table 3.   Summary of results of incremental reactivity calculations for the averaged conditions scenarios for the three representative NO_x conditions.

	Max React (High NO_x)	Max O_3	Equal Benefit (Low NO_x)
Incremental Reactivity of the Base ROG [1]			
Updated SAPRC	1.13	0.41	0.225
RADM-2	0.90	0.369	0.198
Carbon Bond IV	1.02	0.39	0.198
Relative Reactivity of Isoprene [2]			
Carter and Atkinson (1996)	2.48	2.42	2.76
4 Products Condensed (this work)	2.50	2.51	2.92
1 Product Condensed (this work)	2.47	2.51	2.94
SAPRC-90 [3]	2.76	2.75	3.21
RADM-2	2.30	2.17	2.39
Carbon Bond IV	4.62	4.38	4.76

[1] The base ROG is the mixture of reactive organic gases used to represent emissions from all sources in the simulations. Incremental reactivities are in units of moles O_3 formed per mole carbon ROG emitted.

[4] Ratio of Incremental reactivities (ozone per carbon basis) if isoprene to the incremental reactivity of the base ROG mixture.

[6] This uses the same isoprene lumping approach as SAPRC-90, but with the same updated base mechanism as used with the Carter and Atkinson (1996) mechanism and the condensed mechanisms developed in this work.
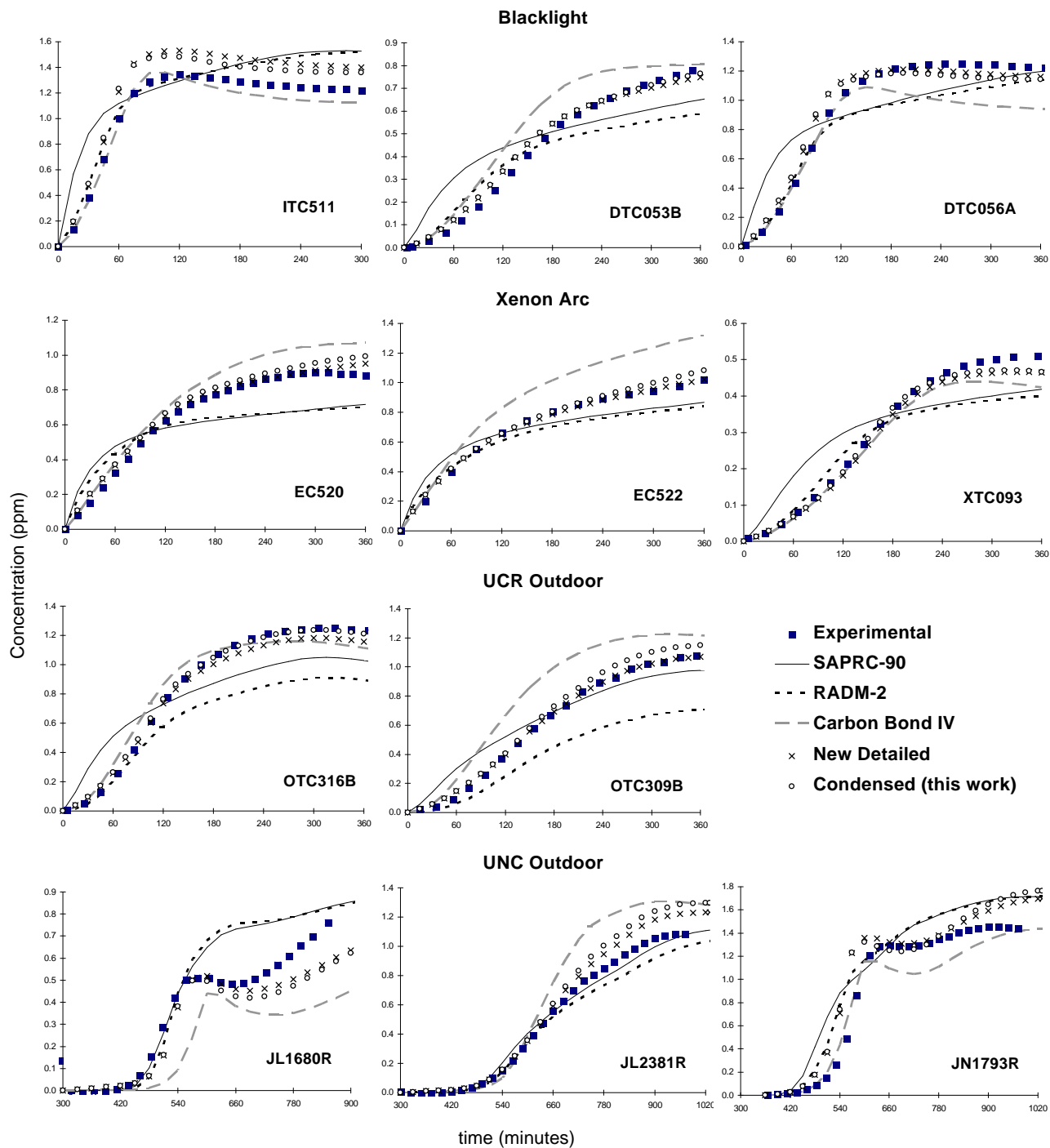
Figure 1. Plots of experimental vs calculated concentration-time profiles for d(O₃-NO) in selected isoprene - NOₓ chamber experiments. (The condensed mechanism from this work is the 1 product mechanism.)
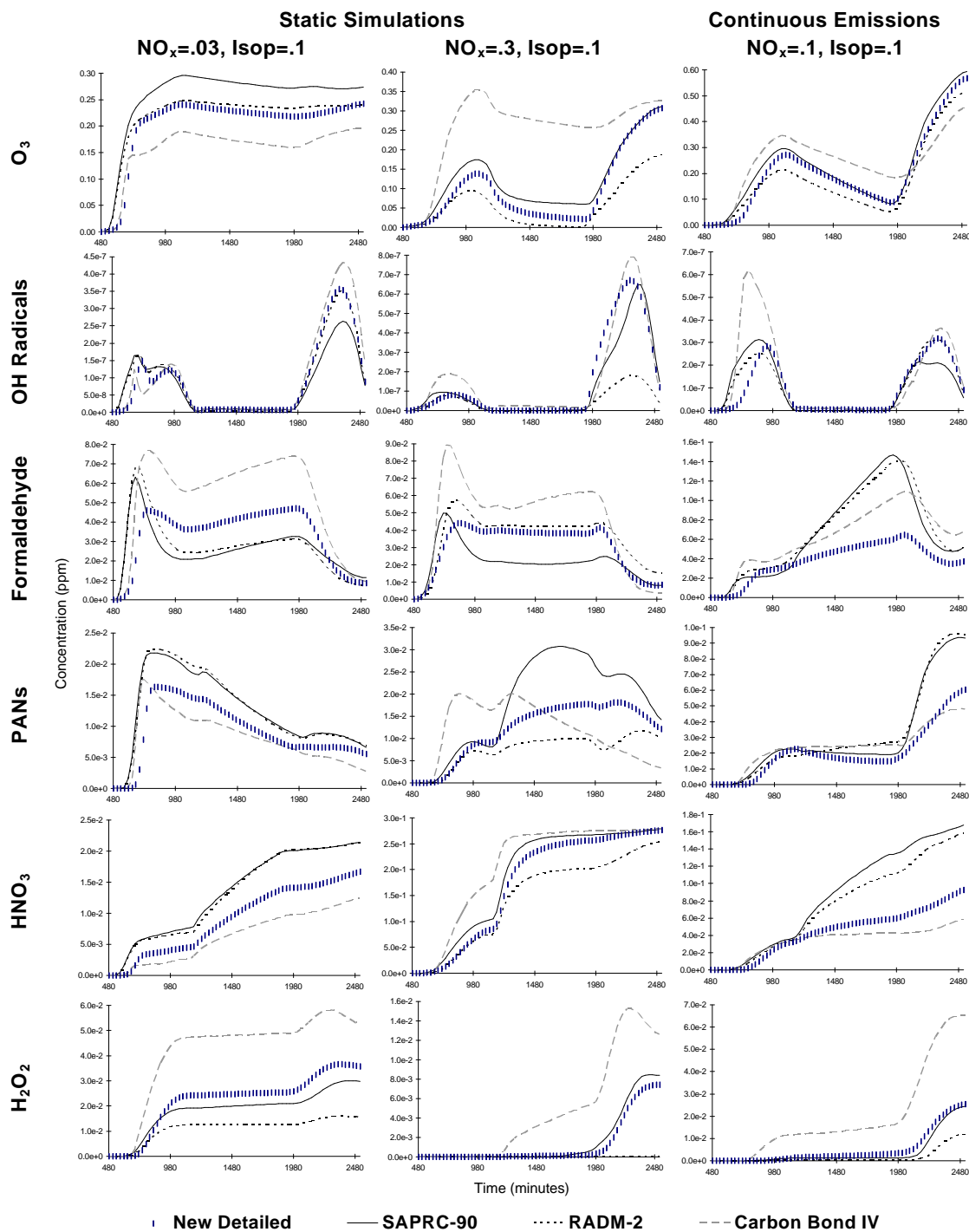
Static Simulations — **Continuous Emissions**

Figure 2. Concentration-time plots of selected species calculated in representative two-day simulations of isoprene and NOx using the new detailed mechanism and various previously published condensed mechanisms. The top rows give the type of simulation and the isoprene and NOx initial concentrations in ppm or the input rates in ppm per 12 hours.
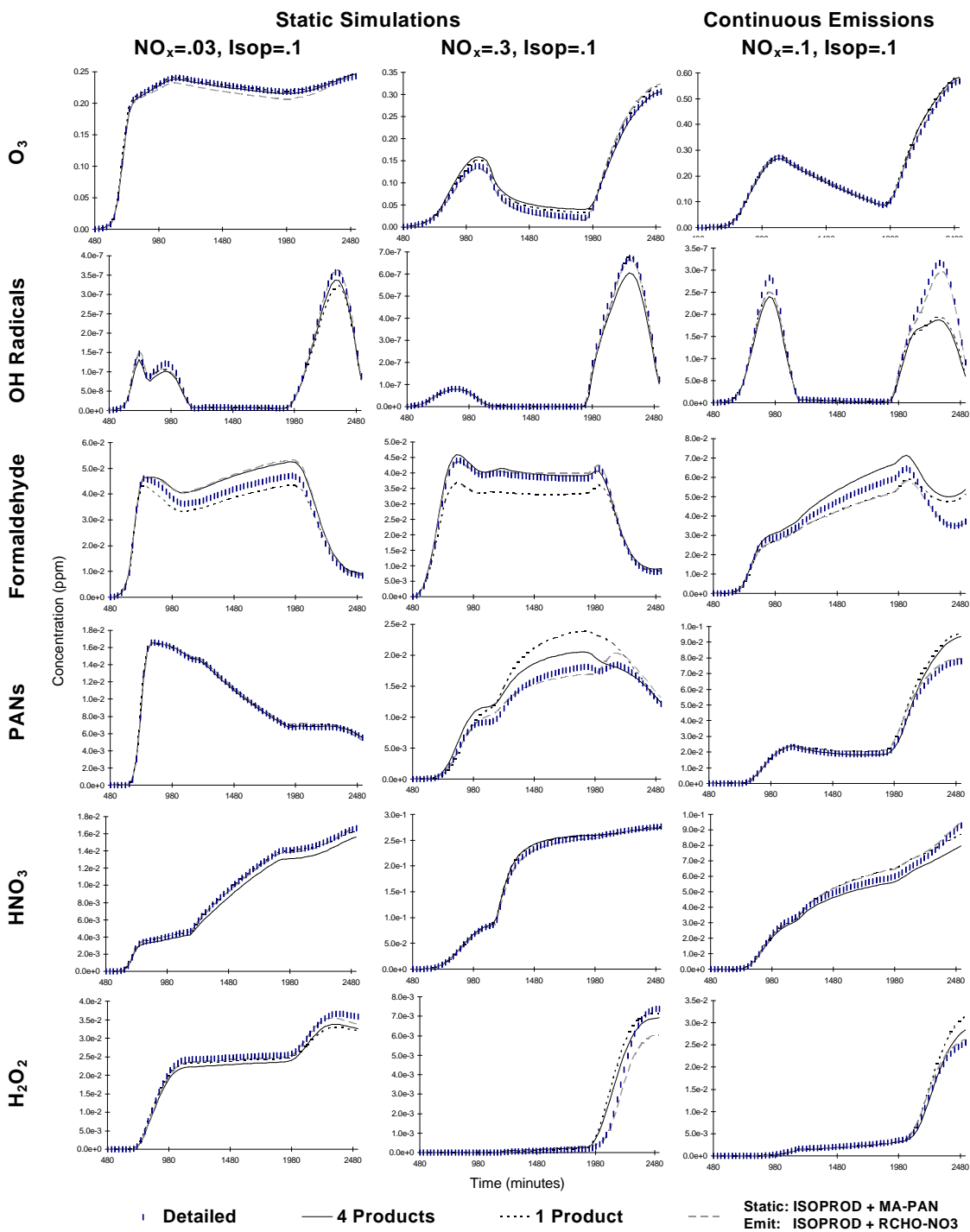
Figure 3. Concentration-time plots of selected species calculated in representative two-day
simulations of isoprene and NOx using the detailed isoprene mechanism and the
various condensed mechanisms developed in this work. The scenarios are the same
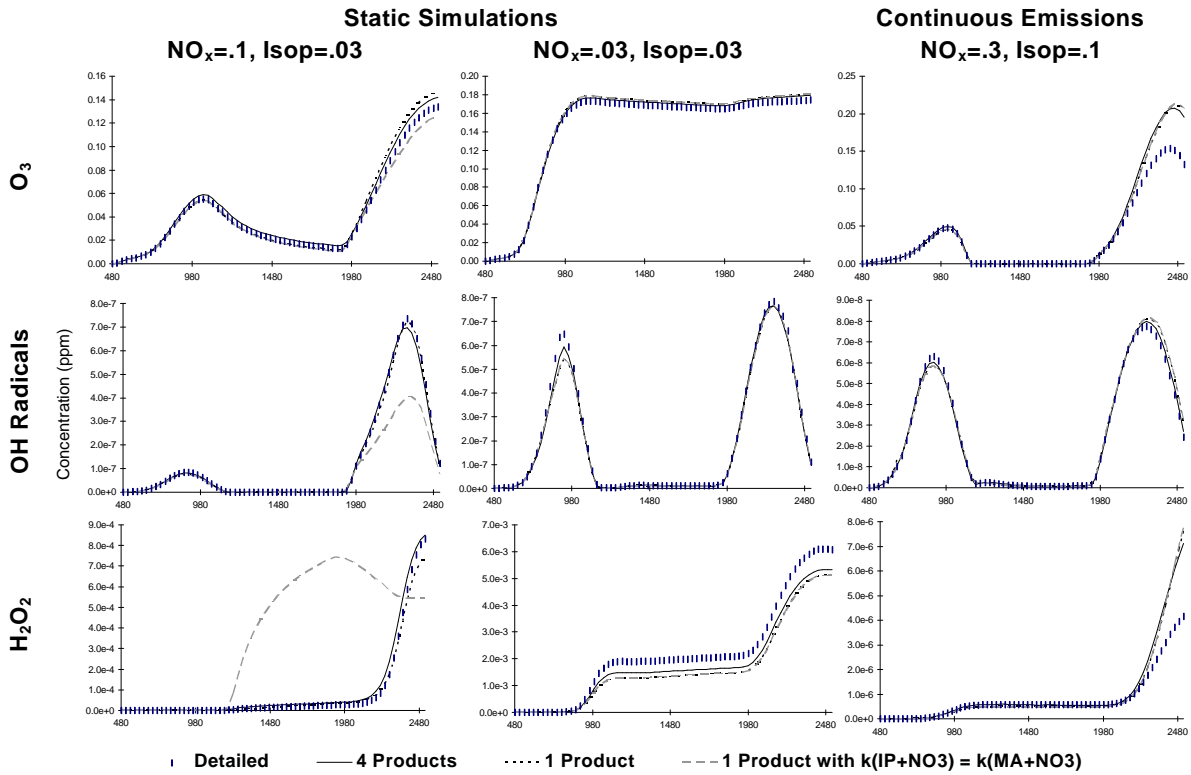as those shown on Figure 2.

Figure 4. Concentration-time plots of selected species calculated in representative two-day simulations of isoprene and NO_x using the detailed and various condensed mechanisms, showing the effect of the $ISOPROD + NO_3$ rate constant in the one product mechanism.
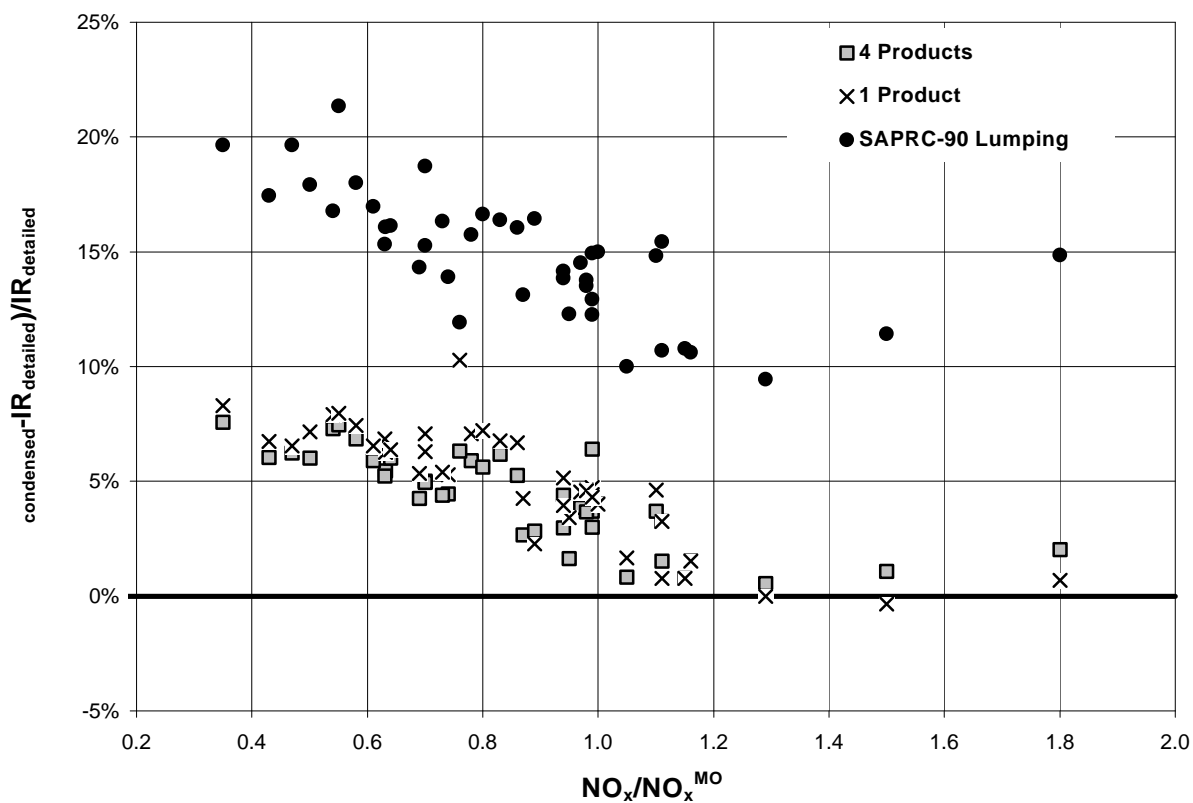
Figure 5. Plots of differences in calculated incremental reactivities in the base case and averaged conditions scenarios of isoprene calculated using various condensed mechanisms relative to those calculated using the detailed mechanism.