July 11, 1996

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Re: Isoprene Chemistry for RADM-2 Mechanism (corrected)

As you requested, I looked into the possibility of implementing the new condensed isoprene mechanism I recently developed into the RADM-2 mechanism. I was able to do this for the "one product" condensed mechanism without a significant amount of effort. The modified mechanism, given in terms of RADM species, is listed on Table 1. In addition to renaming some species which have the same meaning in both mechanisms, the modifications can be summarized as follows:

- The operators "RO2-R." and "RO2-N." were replaced by an explicit peroxy radical which reacted with NO to form either HO2 + NO2 (for RO2-R.) or ONIT (for RO2-N). Explicit peroxy radicals were added for the isoprene + OH, isoprene + NO3, and isoprene product + OH reactions.

- The reactions of the new peroxy radicals with HO2, MO2 (methyl peroxy), and ACO3 (lumped acyl peroxy) radicals were added, using the standard rate constants for the RADM-2 mechanism (Stockwell et al, 1990). The products formed in these reactions were consistent with the approached used for other species in the RADM mechanism.

- The combination "HCHO + RO2-R." was replaced by MO2, since this is in effect how methyl peroxy radicals are represented in the SAPRC mechanism.

- The RADM operator XO2 has exactly the same meaning as the SAPRC-90 operator R2O2., so the simple name substitution was made.

- The RADM-2 mechanism lumps all aldehydes into a single species ALD, and all PAN analogues into PAN, so this lumping was done in the isoprene reactions.   Thus CCHO and RCHO was represented by ALD, and CCO-O2., C2CO-O2., and HCHCO-O2. were represented by ACO3.

- Consistent with the usage in the RADM mechanism, the excited Crigee biradical species were lumped with the ozone reactions, and not represented separately. (This involves no substantial difference, since the steady state approximation is employed for these species in the SAPRC mechanism, making the treatment substantially the same.

- The SAPRC operators "RO2." and "RCO3." and the "lost carbon" counter species "-C" was removed because they are not used in the RADM mechanism.

The predictions of the RADM-2 mechanism with the new isoprene chemistry are compared with those of the Carter and Atkinson (1996) explicit mechanism, the Carter (1996) "one product" condensed mechanism, and the unmodified RADM-2 mechanism on Figures 1 and 2. These figures represent the exact same test simulations as discussed by Carter (1996). It can be seen that the agreement with the Carter and Atkinson (1996) and Carter (1996) mechanisms are not perfect in all cases, but it can be seen in most cases to be better than for standard RADM-2, especially in the initial stages of the simulations.

I hope this is useful. Let me know what additional work you need.

Sincerely,

William P. L. Carter
Research Chemist

References:

Carter, W. P. L. and R. Atkinson (1996): "Development and Evaluation of a Detailed Mechanism for the Atmospheric Reactions of Isoprene and NO_x," International Journal of Chemical Kinetics, in press.

Carter (1996): "Condensed Atmospheric Photooxidation Mechanisms for Isoprene," Atmos. Environ., in press.

Stockwell, W. R., P. Middleton, J. S. Chang, and X. Tang (1990): "The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling," J. Geophys. Res. 95, 16343-16376.

Attachment: 1 table and 2 figures.

Table 1.   Listing of the "One Product" condensed isoprene reactions for use with the RADM-2 chemical mechanism. (Corrected July 11, 1996)

Kinetic Parameters [a]			Reactions [b]
k(300)	A	Ea	
1.45E+05	3.73E+04	-0.81	ISO + HO = ISO-RO2 + 0.079 XO2
1.12E+04	6.16E+03	-0.36	ISO-RO2 + NO = 0.088 ONIT + 0.912 {NO2 + HO2 + ISOPROD} + 0.629 HCHO
8.61E+03	1.13E+02	-2.58	ISO-RO2 + HO2 = OP2
2.57E+02	1.23E+02	-0.44	ISO-RO2 + ACO3 = 0.5 {HO2 + MO2 + ORA2} + ISOPROD
1.04E+02	4.99E+01	-0.44	ISO-RO2 + MO2 = 0.5 {HCHO + HO2} + ISOPROD
1.97E-02	1.15E+01	3.80	ISO + O3 = 0.4 HCHO + 0.6 ISOPROD + 0.39 ORA1 + 0.07 {HO + HO2 + CO} + 0.2 {HO + XO2 + HCHO + ACO3} + 0.15 ALD + 0.05 ISOPROD
5.28E+04	5.28E+04	0.00	ISO + O3P = 0.75 ISOPROD + 0.25 {ACO3 + HCHO + MO2}
1.00E+03	4.45E+03	0.89	ISO + NO3 = ISON-RO2
1.12E+04	6.16E+03	-0.36	ISON-RO2 + NO = NO2 + 0.8 ALD + 0.8 ONIT + 0.8 HO2 + 0.2 ISOPROD + 0.2 NO2
8.61E+03	1.13E+02	-2.58	ISON-RO2 + HO2 = ONIT
2.57E+02	1.23E+02	-0.44	ISON-RO2 + ACO3 = 0.5 {HO2 + MO2 + ORA2} + ALD + ONIT
1.04E+02	4.99E+01	-0.44	ISON-RO2 + MO2 = 0.5 {HCHO + HO2} + ALD + ONIT
4.93E+04	4.93E+04	0.00	ISOPROD + HO = 0.5 ACO3 + 0.5 IP-RO2 + 0.2 XO2
1.12E+04	6.16E+03	-0.36	IP-RO2 + NO = NO2 + HO2 + 0.59 CO + 0.55 ALD + 0.25 HCHO + 0.08 GLY + 0.34 MGLY + 0.63 KET
8.61E+03	1.13E+02	-2.58	IP-RO2 + HO2 = OP2
2.57E+02	1.23E+02	-0.44	IP-RO2 + ACO3 = #.5 "HO2 + MO2 + ORA2" + #.5 "ALD + KET"
1.04E+02	4.99E+01	-0.44	IP-RO2 + MO2 = #.5 "HCHO + HO2" + #.5 "ALD + KET"
1.04E-02	1.04E-02	0.00	ISOPROD + O3 = 0.268 HO + 0.10 HO2 + 0.114 ACO3 + 0.054 MO2 + 0.07 XO2 + 0.155 CO + 0.146 HCHO + 0.02 ALD + 0.01 GLY + 0.85 MGLY + 0.09 KET + 0.462 ORA1
(Phot. Set = ACROLEIN) Overall q.y = 0.0036			ISOPROD + HV + 0.0036 = 0.97 ACO3 + 0.333 HO2 + 0.7 MO2 + 0.2 HCHO + 0.333 CO + 0.067 ALD + 0.033 KET
1.47E+00	1.47E+00	0.00	ISOPROD + NO3 = 0.075 {ACO3 + HNO3} + 0.643 CO + 0.282 HCHO + 0.925 ONIT + 0.282 ALD + 0.925 HO2 + 0.925 XO2

[a] Rate constants in ppm, minute units. Temperature dependence expression is given by k = A x exp(-Ea/[0.0019872 x T]) x (300/T). For the photolysis reaction, the rate is obtained by computing the photolysis rate using the acrolein absorption cross sections, then multiplying it by the overall quantum yield factor of 0.0036.
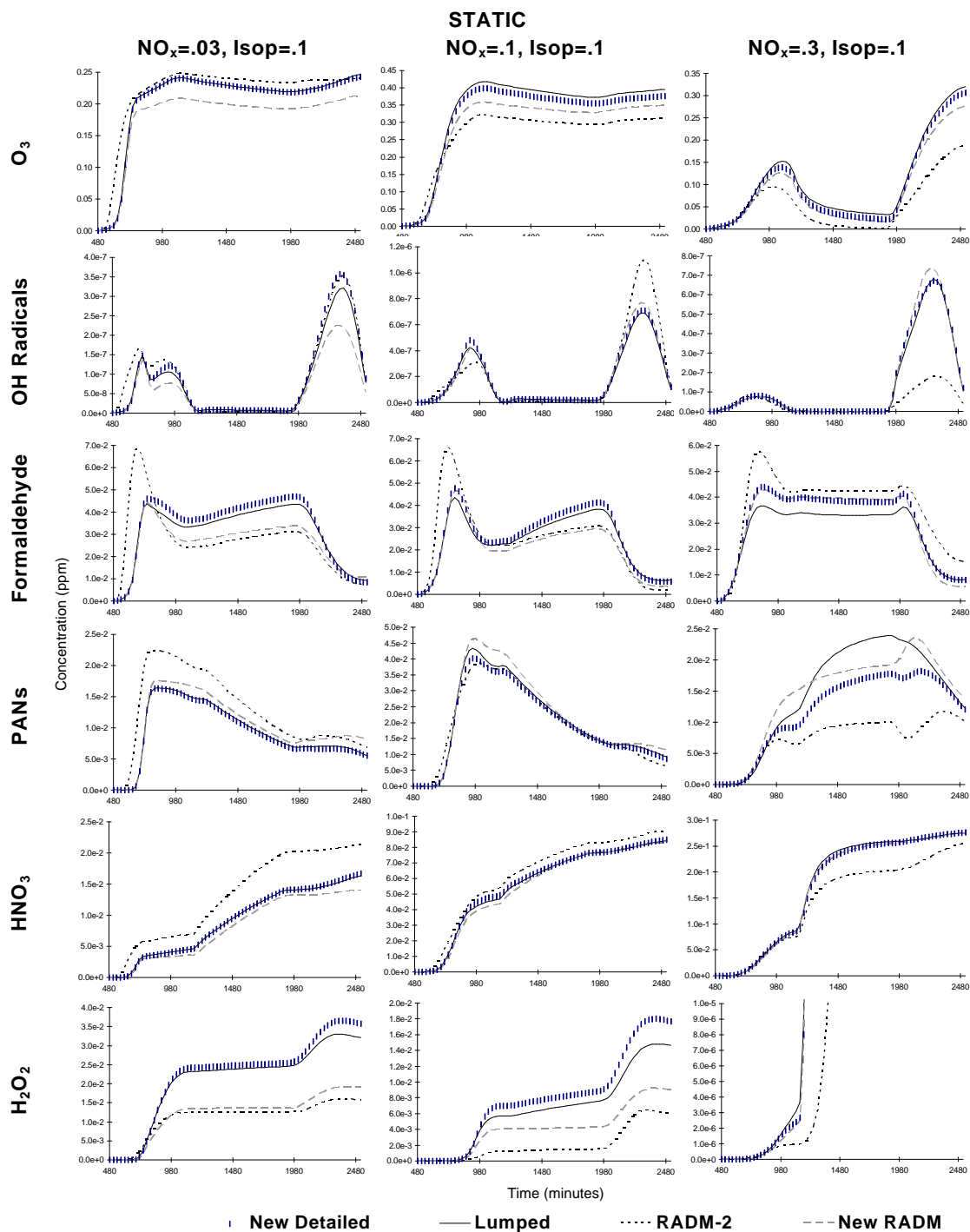[b] See Carter (1996) for format of reaction listing.

STATIC

NO$_x$=.03, Isop=.1   **NO$_x$=.1, Isop=.1**   **NO$_x$=.3, Isop=.1**

| New Detailed | Lumped | RADM-2 | New RADM |

Figure 1. Concentration-time plots of selected species calculated in representative two-day static simulations of isoprene and NOx using the detailed mechanism of Carter and Atkinson (1996), the condensed "One Product" mechanism of Carter (1996), the standard RADM-2 mechanism, and the RADM-2 mechanism with the modified isoprene chemistry. The top row gives the initial isoprene and NOx concentrations in ppm.
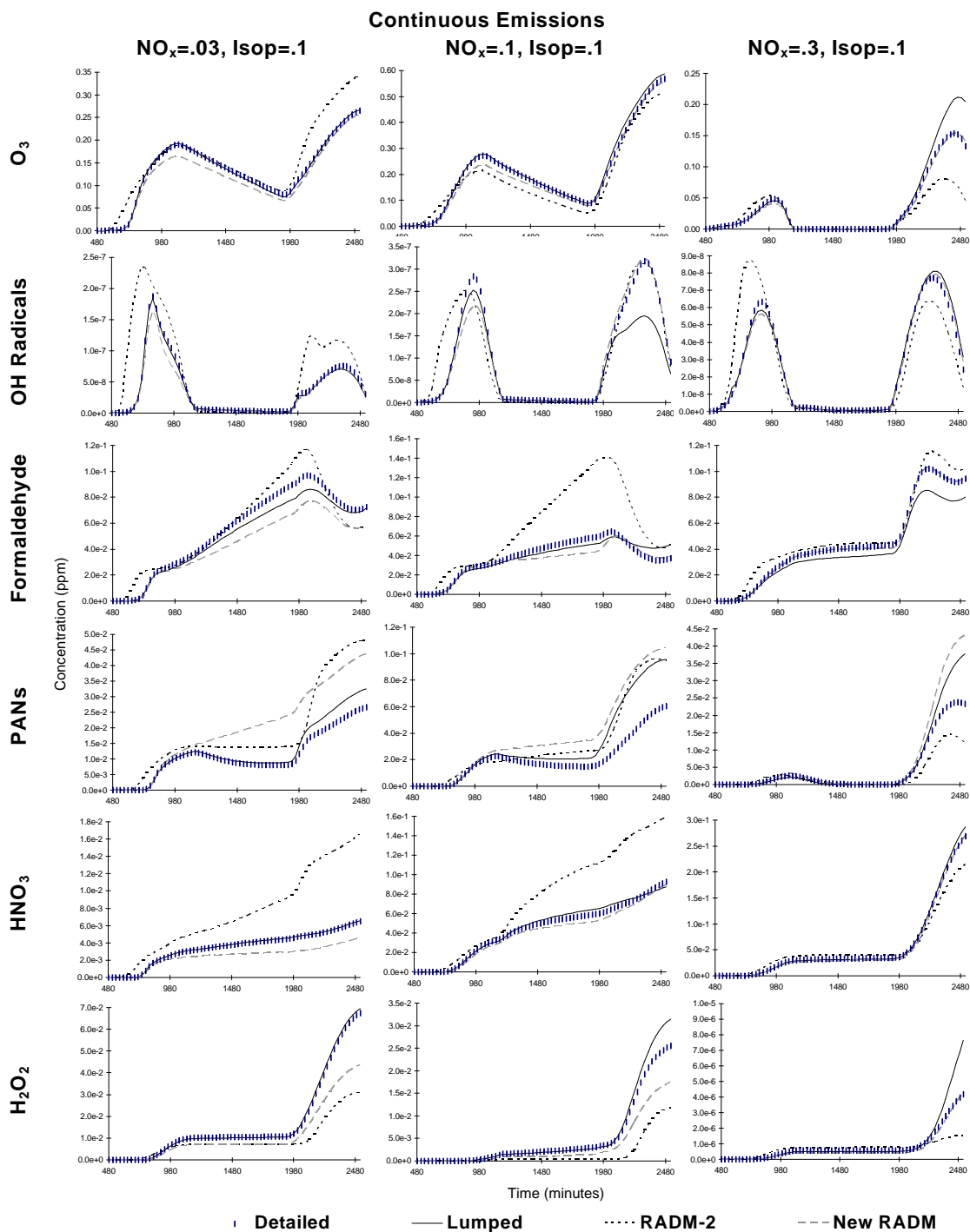
Figure 2. Concentration-time plots of selected species calculated in representative two-day continuous emissions simulations of isoprene and NOx using the detailed mechanism of Carter and Atkinson (1996), the condensed "One Product" mechanism of Carter (1996), the standard RADM-2 mechanism, and the RADM-2 mechanism with the modified isoprene chemistry. The top row gives the isoprene and NOx input rates in ppm per 12 hours.

February 27, 1997

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Re: "Four Product" Isoprene Chemistry for the RADM-2 Mechanism

As you requested, I implemented my "four product" condensed isoprene reactions into the RADM-2 mechanism. The approach used was the same as when I implemented the "one product" mechanism, as described in my letter of July 11, 1996. The modified mechanism, given in terms of RADM species, is listed on Table 1. In addition to renaming some species which have the same meaning in both mechanisms, the modifications can be summarized as follows:

- The species MACR (methacrolein), MVK (methyl vinyl ketone), ISOPROD (lumped C_5 isoprene products), MPAN (methacrolein's PAN analogue, $CH_2=C(CH_3)CO\text{-}OONO_2$), and MCO3 (the acyl peroxy radical formed from MPAN) were added to the mechanism. Note that although this is called the "four product" mechanism, you actually have to add five new species to the model. (The steady state approximation can be used for the MCO3 analogue in the SAPRC mechanism, but this cannot be done in RADM-2 because of the different method it uses for treating peroxy radical reactions.)

- The RADM-2 mechanism lumps all aldehydes into a single species ALD, so this lumping was done in the isoprene reactions.   Thus CCHO and RCHO was represented by ALD. In addition, any PAN analogues or acylperoxy radicals represented by PPN or C2CO-O2. in the mechanism were replaced by PAN and ACO3. However, as indicated above, the methacrolein PAN analogue (MA-PAN) and its acyl peroxy radical (MA-RCO3) were retained, being represented by MPAN and MCO3, respectively.

- The operators "RO2-R." and "RO2-N." were replaced by explicit peroxy radicals which reacted with NO to form either HO2 + NO2 (for RO2-R.) or ONIT (for RO2-N). Explicit peroxy radicals were added for the isoprene + OH, isoprene + NO3, and the methacrolein, MVK, and lumped C_5 isoprene product + OH reactions.

- The reactions of the new peroxy radicals with HO2, MO2 (methyl peroxy), and ACO3 (lumped acyl peroxy) radicals were added, using the standard rate constants for the RADM-2 mechanism (Stockwell et al, 1990). The products formed in these reactions were consistent with the approached used for other species in the RADM mechanism.

- The reactions of MCO3 could be implemented in one of two ways — like ACO3, which reacts with all peroxy radicals, or like TCO3, whose peroxy radical reactions are represented only by those with HO2, MO2 and ACO3. The latter approximation is appropriate if the concentration of MCO3 is always less than ACO3, and therefore was employed in this mechanism. ACO3 would certainly dominate over MCO3 in any atmosphere where there are significant levels of other VOCs besides isoprene, and it was also found that the ACO3 concentrations were always greater than MCO3 even in the isoprene condensation test calculation of Carter (1996), where isoprene was the only reactive VOC. Therefore, as with TCO3, the reactions of ACO3 with peroxy radical species other than HO2, MO2, and ACO3 were neglected. However, to handle possible cases where ACO3 may be important, the ACO3 + ACO3 reaction was also included in the mechanism.

- The combination "HCHO + RO2-R." was replaced by MO2, since this is in effect how methyl peroxy radicals are represented in the SAPRC mechanism.

- The RADM operator XO2 has exactly the same meaning as the SAPRC-90 operator R2O2., so the simple name substitution was made.

- Consistent with the usage in the RADM mechanism, the excited Crigee biradical species were lumped with the ozone reactions, and not represented separately. (This involves no substantial difference, since the steady state approximation is employed for these species in the SAPRC mechanism, making the treatment substantially the same.

- The SAPRC operators "RO2." and "RCO3." and the "lost carbon" counter species "-C" was removed because they are not used in the RADM mechanism.

The predictions of the RADM-2 mechanism with the new isoprene chemistry are compared with those of the Carter and Atkinson (1996) explicit mechanism and the unmodified RADM-2 mechanism on Figures 1 and 2. These figures represent the exact same test simulations as discussed by Carter (1996), but also show predictions of methacrolein and MVK. It can be seen that the agreement with the Carter and Atkinson (1996) mechanism are not perfect in all cases, but it can be seen to be satisfactory in most cases, and better than for standard RADM-2. The relatively large differences in H_2O_2 predictions are probably due due more to differences between the mechanisms in treatment of peroxy radicals than in the isoprene chemistry. The modified RADM mechanism tends to predict slightly more methacrolein and MVK in some cases than does the Carter and Atkinson (1996) mechanism, but the differences are probably well within any measurement or modeling uncertainties.

I hope this is useful. Let me know what additional work you need.

Sincerely,

William P. L. Carter
Research Chemist

cc: Robin Dennis, EPA

References:

Carter, W. P. L. and R. Atkinson (1996): "Development and Evaluation of a Detailed Mechanism for the Atmospheric Reactions of Isoprene and NO_x," Int. J. Chem. Kinet., 28, 497-530.

Carter, W. P. L. (1996): "Condensed Atmospheric Photooxidation Mechanisms for Isoprene," Atmos. Environ., 30, 4275-4290.

Stockwell, W. R., P. Middleton, J. S. Chang, and X. Tang (1990): "The Second Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality Modeling," J. Geophys. Res. 95, 16343- 16376.

Attachment: 1 table and 2 figures.

Table 1.   Listing of the "Four Product" isoprene reactions for the RADM-2 chemical mechanism.
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Kinetic Parameters [a]			Reactions [b]
k(300)	A	Ea	

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Reactions of Isoprene

9.88E-11	2.54E-11	-0.81	ISO + HO = ISO-RO2 + 0.079 XO2
7.66E-12	4.20E-12	-0.36	ISO-RO2 + NO = 0.088 ONIT + 0.912 "NO2 + HO2" + 0.362 ISOPROD + 0.23 MACR + 0.32 MVK + 0.629 HCHO + 0.079 XO2
5.86E-12	7.70E-14	-2.58	ISO-RO2 + HO2 = OP2
1.75E-13	8.40E-14	-0.44	ISO-RO2 + ACO3 = 0.5 "HO2 + MO2 + ORA2" + 0.362 ISOPROD + 0.23 MACR + 0.32 MVK + 0.629 HCHO
7.08E-14	3.40E-14	-0.44	ISO-RO2 + MO2 = 0.5 "HCHO + HO2" + 0.362 ISOPROD + 0.23 MACR + 0.32 MVK + 0.629 HCHO
1.34E-17	7.86E-15	3.80	ISO + O3 = 0.4 HCHO + 0.39 MACR + 0.16 MVK + 0.39 ORA1 + 0.07 "HO + HO2 + CO"+ 0.2 "HO + XO2 + HCHO + MCO3" + 0.15 ALD + 0.1 ISOPROD
3.60E-11	(No T Dep.)		ISO + O3P = 0.75 ISOPROD + 0.25 "MCO3 + HCHO + MO2"
6.81E-13	3.03E-12	0.89	ISO + NO3 = ISON-RO2
7.66E-12	4.20E-12	-0.36	ISON-RO2 + NO = NO2 + 0.8 "ALD + ONIT + HO2" + 0.2 "ISOPROD + NO2"
5.86E-12	7.70E-14	-2.58	ISON-RO2 + HO2 = ONIT
1.75E-13	8.40E-14	-0.44	ISON-RO2 + ACO3 = 0.5 "HO2 + MO2 + ORA2" + ALD + ONIT
7.08E-14	3.40E-14	-0.44	ISON-RO2 + MO2 = 0.5 "HCHO + HO2" + ALD + ONIT

Reactions of Methacrolein

3.35E-11	1.86E-11	-0.35	MACR + HO = 0.5 "MCO3 + MACR-RO2"
7.66E-12	4.20E-12	-0.36	MACR-RO2 + NO = NO2 + HO2 + 0.84 "KET + CO" + 0.15 "HCHO + MGLY"
5.86E-12	7.70E-14	-2.58	MACR-RO2 + HO2 = OP2
1.75E-13	8.40E-14	-0.44	MACR-RO2 + ACO3 = 0.5 "HO2 + MO2 + ORA2" + 0.84 "KET + CO" + 0.15 "HCHO + MGLY"
7.08E-14	3.40E-14	-0.44	MACR-RO2 + MO2 = 0.5 "HCHO + HO2" + 0.84 "KET + CO" + 0.15 "HCHO + MGLY"
1.19E-18	1.36E-15	4.20	MACR + O3 = 0.63 ORA1 + 0.21 HO + 0.11 "HO2 + CO" + 0.16 CO2 + 0.1 "HCHO + XO2 + HCHO + ACO3"
(Phot. Set = ACROLEIN)			MACR + HV + 0.0036 = 0.66 HO2 + 0.33 MCO3 + 0.67 "CO + HCHO + ACO3" + 0.34 "HO + XO2"
4.76E-15	1.50E-12	3.43	MACR + NO3 = 0.5 "MCO3 + HNO3" + 0.5 "CO + HO2 + ONIT + XO2"

Reactions of Methyl Vinyl Ketone

1.87E-11	4.14E-12	-0.90	MVK + HO = MVK-RO2
7.66E-12	4.20E-12	-0.36	MVK-RO2 + NO = NO2 + 0.7 "ALD + XO2 + ACO3" + 0.3 "HCHO + MGLY + HO2"
5.86E-12	7.70E-14	-2.58	MVK-RO2 + HO2 = OP2
1.75E-13	8.40E-14	-0.44	MVK-RO2 + ACO3 = 0.5 "HO2 + MO2 + ORA2" + 0.7 "ALD + MO2" + 0.3 "HCHO + MGLY"
7.08E-14	3.40E-14	-0.44	MVK-RO2 + MO2 = 0.5 "HCHO + HO2" + 0.7 "ALD + MO2" + 0.3 "HCHO + MGLY"
4.74E-18	7.51E-16	3.02	MVK + O3 = 0.67 ORA1 + 0.11 "HO + HO2 + CO" + 0.17 CO2 + 0.95 MGLY + 0.05 "HCHO + HO + XO2 + HCHO + ACO3"
(Phot. Set = ACROLEIN)			MVK + HV + 0.0111 = 0.7 "ISOPROD + CO" + 0.3 "MO2 + MCO3"

Table 1 (concluded)

Kinetic Parameters [a]			Reactions [b]
k(300)	A	Ea	

Reactions of Methacroein's PAN Analogue

4.79E-04	1.60E+16	26.80	MPAN = MCO3 + NO2
7.66E-12	4.20E-12	-0.36	MCO3 + NO = NO2 + CO2 + HCHO + ACO3
5.12E-12	2.80E-12	-0.36	MCO3 + NO2 = MPAN
5.86E-12	7.70E-14	-2.58	MCO3 + HO2 = PAA
2.00E-12	9.60E-13	-0.44	MCO3 + MO2 = 2.25 HCHO + 0.5 HO2 + 0.5 MO2 + 2 CO2
2.48E-12	1.19E-12	-0.44	MCO3 + ACO3 = 2 MO2 + HCHO + 3 CO2
2.48E-12	1.19E-12	-0.44	MCO3 + MCO3 = 2 MO2 + 2 HCHO + 4 CO2

Reactions of Lumped C_5 Isoprene Products

3.36E-11	(No T Dep.)		ISOPROD + HO = 0.313 ACO3 + 0.687 IP-RO2
7.66E-12	4.20E-12	-0.36	IP-RO2 + NO = NO2 + HO2 + 0.61 CO + 0.27 ALD + 0.03 HCHO + 0.18 GLY + 0.21 MGLY + 0.7 KET
5.86E-12	7.70E-14	-2.58	IP-RO2 + HO2 = OP2
1.75E-13	8.40E-14	-0.44	IP-RO2 + ACO3 = 0.5 "HO2 + MO2 + ORA2" + 0.5 "ALD + KET"
7.08E-14	3.40E-14	-0.44	IP-RO2 + MO2 = 0.5 "HCHO + HO2" + 0.5 "ALD + KET"
7.11E-18	(No T Dep.)		ISOPROD + O3 = 0.476 HO + 0.072 HO2 + 0.168 MO2 + 0.237 ACO3 + 0.1 XO2 + 0.243 CO + 0.153 CO2 + 0.218 HCHO + 0.062 ALD + 0.278 KET + 0.031 GLY + 0.653 MGLY + 0.044 ORA1
(Phot. Set = ACROLEIN)			ISOPROD + HV + 0.0036 = 1.216 CO + 0.434 ALD + 0.35 HCHO + 0.216 KET + 1.216 HO2 + 0.784 ACO3
1.00E-13	(No T Dep.)		ISOPROD + NO3 = 0.668 CO + 0.332 HCHO + 0.332 ALD + ONIT + HO2 + XO2

[a] Rate constants in cm, molecule, sec. units. Temperature dependence expression is given by k = A x exp(-Ea/[0.0019872 x T]) x (300/T). For the photolysis reaction, the rate is obtained by computing the photolysis rate using the acrolein absorption cross sections, then multiplying it by the overall quantum yield factor of 0.0036. The acrolein absorption cross sections used are given by Carter and Atkinson (1996).

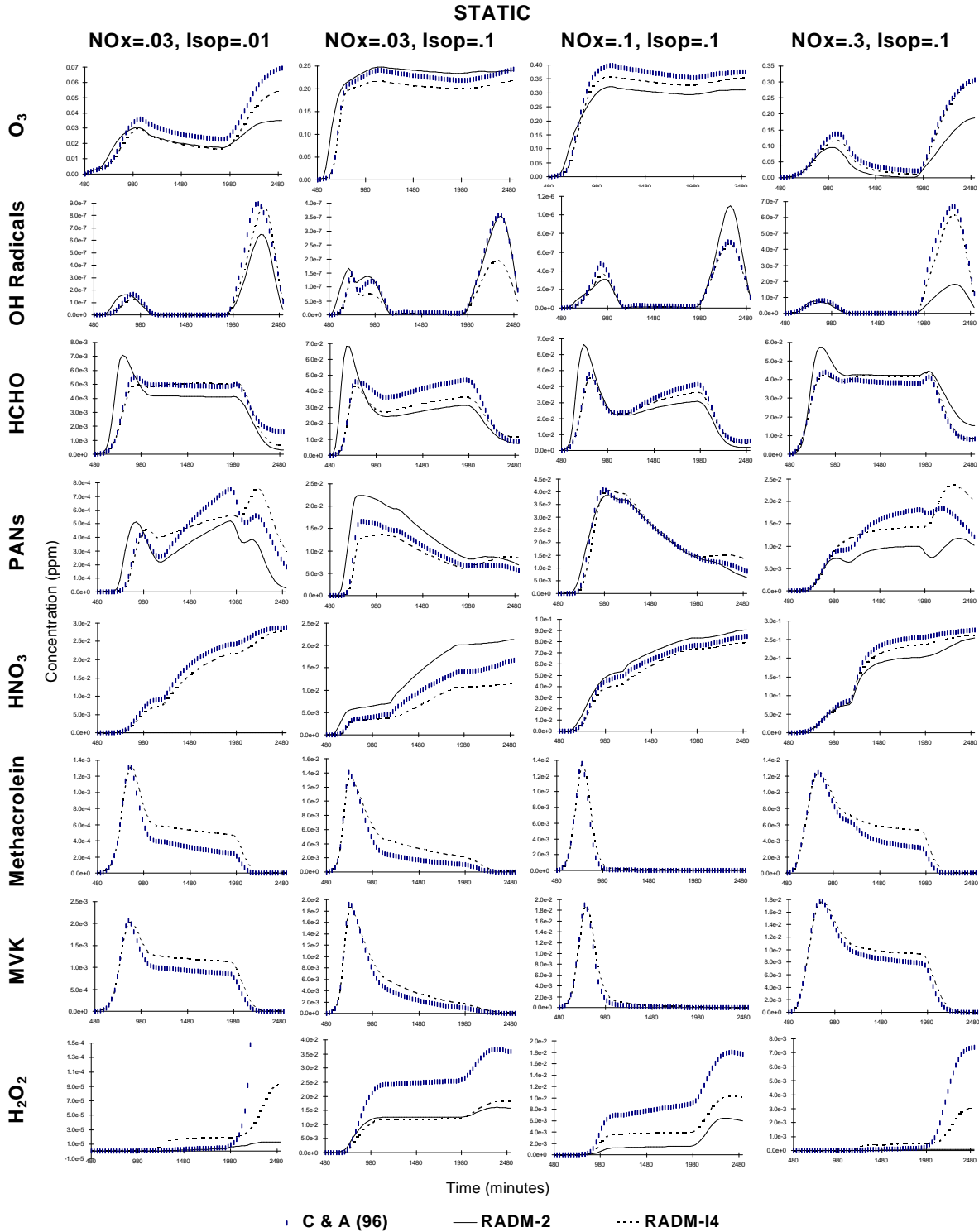[b] See Carter (1996) for format of reaction listing.

Figure 1. Concentration-time plots of selected species calculated in representative two-day static simulations of isoprene and NOx using the detailed mechanism of Carter and Atkinson (1996), the standard RADM-2 mechanism, and RADM-2 mechanism with the modified "four product" (I4) isoprene chemistry. The top row gives the initial isoprene and NOx concentrations in ppm.
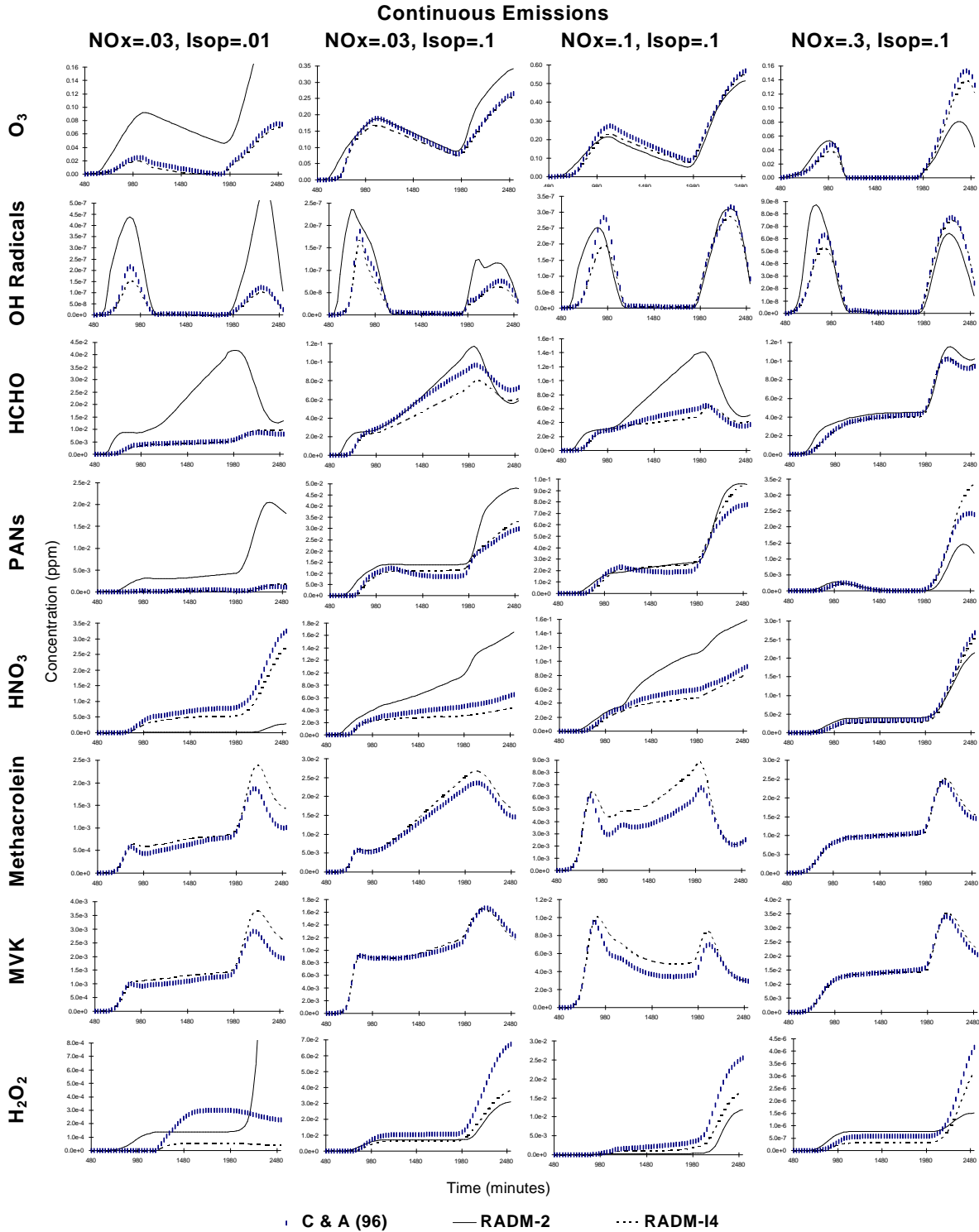
Figure 2.   Concentration-time plots of selected species calculated in representative two-day
continuous emissions simulations of isoprene and NOx using the detailed mechanism of
Carter and Atkinson (1996), the standard RADM-2 mechanism, and the RADM-2
mechanism with the modified "four product" (I4) isoprene chemistry. The top row
gives the isoprene and NOx input rates in ppm per 12 hours.