Development and Intercomparison of Condensed Isoprene Oxidation Mechanisms for Global Atmospheric Modeling

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Abstract. A new condensed isoprene oxidation mechanism for global atmospheric modeling (MIM) was derived from a highly detailed master chemical mechanism (MCM). In a box model intercomparison covering a wide range of boundary layer conditions the MIM was compared with the MCM and with five other condensed mechanisms, some of which have already been used in global modeling studies of nonmethane hydrocarbon chemistry. The results of MCM and MIM were generally in good agreement, but the other tested mechanisms exhibited substantial differences relative to the MCM as well as relative to each other. Different formation yields, reactivities and degradation pathways of organic nitrates formed in the course of isoprene oxidation were identified as a major reason for the deviations. The relevance of the box model results for chemistry transport models is discussed, and the need for a validated reference mechanism and for an improved representation of isoprene chemistry in global models is pointed out.

Key words: isoprene oxidation, global atmospheric modeling, condensed chemical mechanism.

1. Introduction

Isoprene (C_5H_8) is an important nonmethane hydrocarbon in the atmosphere. Even in industrialized regions its annual emissions are comparable in magnitude to anthropogenic hydrocarbon emissions (Lamb *et al.*, 1993). Globally, isoprene is estimated to account for almost half of all biogenic nonmethane hydrocarbon emissions (about 500 out of 1150 Tg C per year (Guenther *et al.*, 1995)). The atmospheric degradation of isoprene to CO and CO_2 is initiated by reaction with OH, O_3 or NO_3 and can involve several thousand subsequent reactions and hundreds of intermediate species (Jenkin *et al.*, 1997; Poisson, 1997; Saunders *et al.*, 1997). Due to computational limitations and to a lack of chemical kinetics data on many of the involved species and reactions, strongly condensed and simplified reaction

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mechanisms are usually applied in three-dimensional global modeling studies. Thus uncertainties in quantifying the effects of isoprene chemistry on atmospheric key species like ozone arise not only from the isoprene source distribution and strength but also from its representation by simplified reaction schemes.

In this study a condensed isoprene oxidation mechanism based on a highly detailed chemical scheme is presented. In a box model intercomparison covering a wide range of boundary layer conditions, the new mechanism has been compared with the detailed mechanism and five other condensed mechanisms. Several of the condensed mechanisms involved in the intercomparison have already been used in three-dimensional studies of global atmospheric chemistry. Some of them are currently being implemented in the global 3D chemistry-transport model (CTM) MATCH-MPIC (Lawrence *et al.*, 1999). First model results using different isoprene oxidation schemes in the otherwise unchanged CTM show that the differences revealed in the box model intercomparison have significant impact on the global scale as well (von Kuhlmann *et al.*, 1999). Here we focus on the box model results and discuss the most important differences between the individual chemical mechanisms. A detailed presentation and discussion of the global modeling results will follow in a subsequent publication (von Kuhlmann *et al.*, manuscript in preparation).

2. Chemical Mechanisms

The new condensed mechanism, hereafter referred to as MIM ('Mainz Isoprene Mechanism'), is largely based on the Master Chemical Mechanism (MCM, Version 2.0, October 1998) by Jenkin *et al.* (1997) and Saunders *et al.* (1997). The MCM describes the atmospheric oxidation of a variety of volatile organic compounds in great detail and comprises about one thousand isoprene-related reactions involving hundreds of chemical species. It is highly explicit and does not involve extensive lumping of intermediates or an operator formalism, which makes it straightforward to modify and update. It is part of an ongoing effort to provide reliable atmospheric chemistry modeling tools, in which several research groups are involved. Particularly in the scientific community of EUROTRAC (European project on the transport and chemical transformation of trace constituents in the troposphere) the MCM is widely used as a reference mechanism. Only recently it was revised and updated in view of new and improved kinetic data (Version 2.0, October 1998), and it has been successfully applied to model measurements of isoprene, its oxidation products and related photooxidants in recent field studies (Biesenthal *et al.*, 1998; Carslaw *et al.*, 1999a, b; Jacobs *et al.*, 1999; Warneke *et al.*, 1999).

The MIM comprises 16 organic species and 44 chemical reactions. It involves no operator formalism and can be flexibly added to any photochemical model describing tropospheric O_3–HO_x–NO_x–CO–CH_4 background chemistry ($NO_x =$ $NO + NO_2$; $HO_x = OH + HO_2$). The involved chemical species and reactions are listed in Tables I, II and III. Most of the MIM reactions are combinations of the

Table I. MIM species

	C_5 compounds	
1	C_5H_8	isoprene
2	ISO_2	peroxy radicals from $C_5H_8 + OH$
3	ISO_2H	β-hydroxyhydroperoxides from $ISO_2 + HO_2$
4	ISON	β-hydroxyalkylnitrates from $ISO_2 + NO$ and alkylnitrates from $C_5H_8 + NO_3$
	C_4 compounds	
5	MACR	methacrolein, methylvinylketone and other C_4 carbonyls
6	$MACRO_2$	peroxy radicals from $MACR + OH$
7	$MACRO_2H$	hydroperoxides from $MACRO_2 + HO_2$
8	MPAN	peroxymethacryloylnitrate and other higher peroxyacylnitrates
	C_3 compounds	
9	HACET	hydroxyacetone and other C_3 ketones
10	MGLY	methylglyoxal and other C_3 aldehydes
	C_2 and C_1 compounds	
11	CH_3CO_3	peroxyacetyl radical
12	PAN	peroxyacetylnitrate
13	CH_3CO_3H	peroxyacetic acid
14	CH_3COOH	acetic acid
15	NALD	nitrooxyacetaldehyde
16	HCOOH	formic acid

major MCM reaction pathways, and the MIM species represent different classes of compounds as described in Table I. For example, MACR stands for methacrolein and methylvinylketone plus the sum of all other C_4 carbonyl compounds formed in the atmospheric oxidation of isoprene. The rate coefficients for the reactions of MACR with OH and O_3 are calculated as the arithmetic mean of the corresponding rate coefficients for methacrolein and methylvinylketone. $MACRO_2$ stands for the C_4 peroxy radicals formed in these reactions, and the relative abundance of the decomposition products of $MACRO_2$ reflects the relative importance of the different degradation pathways of C_4 carbonyls in the MCM. Numerous tests showed that besides the major reaction pathways and intermediates also some minor reactions and species have to be considered in the MIM to obtain a good approximation for the MCM. Early versions of the MIM, which considered only the reactions with the highest turnover at each step going from C_5H_8 via C_4, C_3 and C_2 compounds to the C_1 species of background methane chemistry, led to an unrealistically fast degradation accompanied by exceedingly high O_3 concentrations. In this context

Table II. MIM chemical reactions

	Chemical reaction	Rate coefficient	References/comments
1	$C_5H_8 + OH = ISO_2$	$k_1 = 2.54E\text{-}11 \exp(410/T)$	1
2	$C_5H_8 + O_3 = 0.65$ MACR $+0.58$ HCHO $+$ 0.1 MACRO$_2$ + 0.1 CH$_3$CO$_3$ + 0.08 CH$_3$O$_2$ + 0.28 HCOOH + 0.14 CO + 0.09 H$_2$O$_2$ + 0.25 HO$_2$ + 0.25 OH	$k_2 = 7.86E\text{-}15 \exp(-1913/T)$	1, 2, 3
3	$C_5H_8 + NO_3 = ISON$	$k_3 = 3.03E\text{-}12 \exp(-446/T)$	3, 4
4	$ISO_2 + NO = NO_2 + MACR + HCHO +$ HO$_2$	$k_4 = 0.956 \times 2.54E\text{-}12 \exp(360/T)$	3, 4, 5
5	$ISO_2 + NO = ISON$	$k_5 = 0.044 \times 2.54E\text{-}12 \exp(360/T)$	3, 4, 5
6	$ISO_2 + HO_2 = ISO_2H$	$k_6 = 2.05E\text{-}13 \exp(1300/T)$	4
7	$ISO_2 + ISO_2 = 2$ MACR $+$ HCHO $+$ HO$_2$	$k_7 = 2.0E\text{-}12$	3, 4, 6
8	$ISO_2H + OH = MACR + OH$	$k_8 = 1.0E\text{-}10$	3, 4
9	$ISON + OH = ACETOL + NALD$	$k_9 = 1.3E\text{-}11$	3, 4, 5
10	$MACR + OH = MACRO_2$	$k_{10} = 0.5 \times (4.13E\text{-}12 \exp(452/T) +$ $1.86E\text{-}11 \exp(175/T))$	1, 3
11	$MACR + O_3 = 0.9$ MGLY $+ 0.45$ HCOOH $+$ 0.32 HO$_2$ + 0.22 CO + 0.19 OH + 0.1 CH$_3$CO$_3$	$k_{11} = 0.5 \times (1.36E\text{-}15 \exp(-2112/T) +$ $+ 7.51E\text{-}16 \exp(-1521/T))$	1, 2, 3
12	$MACRO_2 + NO = NO_2 + 0.25$ HACET $+$ 0.25 CO + 0.25 CH$_3$CO$_3$ + 0.5 MGLY + 0.75 HCHO + 0.75 HO$_2$	$k_{12} = 2.54E\text{-}12 \exp(360/T)$	3,4
13	$MACRO_2 + HO_2 = MACRO_2H$	$k_{13} = 1.82E\text{-}13 \exp(1300/T)$	3, 4
14	$MACRO_2 + MACRO_2 = HACET + MGLY +$ 0.5 HCHO + 0.5 CO + HO$_2$	$k_{14} = 2E\text{-}12$	3,6
15	$MACRO_2 + NO_2 = MPAN$	$k_{15,0} = 9.7E\text{-}29 \ (T/300)^{-5.6}$ $k_{15,inf} = 9.3E\text{-}12 \ (T/300)^{-1.5}$ $F_c = 0.6$	3, 4, 8; like PAN
15	$MPAN = MACRO_2 + NO_2$	$k_{16} = k_{15}/(9.0E\text{-}29 \exp(14000/T))$	3, 4, 8; like PAN
17	$MPAN + OH = ACETOL + NO_2$	$k_{17} = 3.6E\text{-}12$	3, 4
18	$MACRO_2H + OH = MACRO_2$	$k_{18} = 3.0E\text{-}11$	3, 4
19	$HACET + OH = MGLY + HO_2$	$k_{19} = 3.0E\text{-}12$	4, 7
20	$MGLY + OH = CH_3CO_3 + CO$	$k_{20} = 1.5E\text{-}11$	4, 7
21	$MGLY + NO_3 = CH_3CO_3 + CO + HNO_3$	$k_{21} = 1.44E\text{-}12 \exp(-1862/T)$	4, 7; like CH$_3$CHO
22	$NALD + OH = HCHO + CO + NO_2$	$k_{22} = 5.6E\text{-}12 \exp(270/T)$	3, 4, 5; like CH$_3$CHO
23	$CH_3CO_3 + HO_2 = CH_3CO_3H$	$k_{23} = 4.5E\text{-}13 \exp(1000/T)/(1 +$ $1/(330 \exp(-1430/T)))$	8
24	$CH_3CO_3 + HO_2 = CH_3COOH + O_3$	$k_{24} = 4.5E\text{-}13 \exp(1000/T)/(1 +$ $330 \exp(-1430/T))$	8
25	$CH_3CO_3 + NO = CH_3O_2 + NO_2$	$k_{25} = 5.3E\text{-}12 \exp(360/T)$	8
26	$CH_3CO_3 + NO_2 = PAN$	$k_{26,0} = 9.7E\text{-}29 \ (T/300)^{-5.6}$ $k_{26,inf} = 9.3E\text{-}12 \ (T/300)^{-1.5}$ $F_c = 0.6$	8
27	$CH_3CO_3 + CH_3O_2 = HCHO + HO_2 + CH_3O_2$	$k_{27} = 1.3E\text{-}12 \exp(640/T)/(1 +$ $1/2.2E6 \exp(-3820/T))$	8
28	$CH_3CO_3 + CH_3O_2 = CH_3COOH + HCHO$	$k_{28} = 1.3E\text{-}12 \exp(640/T)/(1 +$ $2.2E6 \exp(-3820/T))$	8
29	$CH_3CO_3 + CH_3CO_3 = CH_3O_2 + CH_3O_2$	$k_{29} = 2.9E\text{-}12 \exp(500/T)$	8
30	$CH_3CO_3 + NO_3 = CH_3O_2 + NO_2$	$k_{30} = 4.0E\text{-}12$	9
31	$PAN + OH = HCHO + NO_2$	$k_{31} = 4.0E\text{-}14$	8
32	$PAN = CH_3CO_3 + NO_2$	$k_{32} = k_{26}/(9.0E\text{-}29 \exp(14000/T))$	8
33	$CH_3CO_3H + OH = CH_3CO_3$	$k_{33} = 3.7E\text{-}12$	2
34	$CH_3COOH + OH = CH_3O_2$	$k_{34} = 4.0E\text{-}13 \exp(200/T)$	8

References: 1 = Atkinson (1994); 2 = P. Neeb, private communication; 3 = this work; 4 = Jenkin *et al.* (1997), Saunders *et al.*, (1997); 5 = Chen *et al.* (1998); 6 = Jenkin *et al.* (1998); 7 = Atkinson *et al.* (1997); 8 = DeMore *et al.* (1997); 9 = Stockwell *et al.* (1997); 10 = Kuhn *et al.* (1998).

Table III. MIM photolytic reactions

	Photolytic reaction	Maximum photolysis frequency (SZA = 0)	References/comments
1	$ISO_2H = OH + MACR + HCHO + HO_2$	$j_{1,max} = 6.4E\text{-}06$	3, 4, 10; like CH_3O_2H
2	$ISON = NO_2 + MACR + HCHO + HO_2$	$j_{2,max} = 4.1E\text{-}06$	3, 4; like i-$C_3H_7NO_3$
3	$MACR = CH_3CO_3 + HCHO + CO + HO_2$	$j_{3,max} = 1.1E\text{-}05$	3, 4
4	$MPAN = MACRO_2 + NO_2$	$j_{4,max} = 2.2E\text{-}07$	4
5	$MACRO_2H = OH + 0.5\ HACET + 0.5$ $CO + 0.5\ MGLY + 0.5\ HCHO + HO_2$	$j_{5,max} = 6.4E\text{-}06$	3, 4, 10; like CH_3O_2H
6	$HACET = CH_3CO_3 + HCHO + HO_2$	$j_{6,max} = 5.8E\text{-}06$	3, 4
7	$MGLY = CH_3CO_3 + CO + HO_2$	$j_{7,max} = 1.8E\text{-}03$	4, 9
80	$NALD = HCHO + CO + NO_2 + HO_2$	$j_{8,max} = 5.4E\text{-}06$	3, 4, 5, 10; like CH_3CHO
9	$PAN = CH_3CO_3 + NO_2$	$j_{9,max} = 2.2E\text{-}07$	4
10	$CH_3CO_3H = CH_3O_2 + OH$	$j_{10,max} = 6.4E\text{-}06$	3, 4, 10; like CH_3O_2H

References: 1 = Atkinson (1994); 2 = P. Neeb, private communication; 3 = this work; 4 = Jenkin *et al.* (1997), Saunders *et al.*, (1997); 5 = Chen *et al.* (1998); 6 = Jenkin *et al.* (1998); 7 = Atkinson *et al.* (1997); 8 = DeMore *et al.* (1997); 9 = Stockwell *et al.* (1997); 10 = Kuhn *et al.* (1998).

the formation and degradation of organic nitrates were found to play a particularly important role, as will be discussed below.

Besides MIM and MCM five other chemical mechanisms describing the atmospheric oxidation of isoprene were considered in our intercomparison. The Regional Atmospheric Chemistry Mechanism (RACM) by Stockwell *et al.* (1997) is an improved and updated derivative of the widely used Regional Acid Deposition Model (RADM-2) (Stockwell *et al.*, 1990). PKM stands for a condensed chemical mechanism which has been applied in the analysis of field measurement data from the FIELDVOC campaign (Poisson *et al.*, 1999) and in a recent global modeling study of non-methane hydrocarbon (NMHC) chemistry (Poisson *et al.*, 1998). Similarly, the MOZART mechanism (Brasseur *et al.*, 1998; Hauglustaine *et al.*, 1998) has been used in a recent study on tropospheric ozone and related chemical tracers. The FPM is a modified version of the 'four-product mechanism' developed by Carter (1996) which has been adapted by Roelofs (private communication, 1999) for use in the global 3-D model ECHAM-4 and is very similar to the isoprene oxidation mechanism used in a recent study on the export of ozone and ozone precursors from the urban atmosphere to the background troposphere (Duncan and Chameides, 1998). CBM stands for a modified Carbon Bond IV mechanism which has been devised by Houweling *et al.* (1998) to investigate the influence of non-methane hydrocarbons on tropospheric photochemistry.

Table IV provides a brief characterization with respect to the number of isoprene-related chemical species and reactions considered in the different mechanisms. The numbers include all species and reactions involved in the degradation of isoprene, except for the background tropospheric O_3–HO_x–NO_x–CO–CH_4 chemistry (about 25 chemical species and 50 reactions).

Table IV. Chemical mechanisms considered in the box model intercomparison

Chemical mechanism	Isoprene-related species	Isoprene-related reactions	References
MCM	$\sim$300	$\sim$1000	Jenkin *et al.* (1997), Saunders *et al.* (1997)
RACM	$\sim$40	$\sim$120	Stockwell *et al.* (1997)
PKM	34	70	Poisson *et al.* (1998)
MOZART	19	50	Brasseur *et al.* (1998), Hauglustaine *et al.* (1998)
MIM	16	44	this study
FPM	12	44	Carter (1996), Roelofs (priv. commun., 1999)
CBM	12	30	Houweling *et al.* (1998)

All chemical mechanisms were integrated for a five day period using the solver FACSIMILE (Malleson *et al.*, 1990). The photolysis frequencies were calculated as a function of latitude, solar declination and local time, according to the parametrisation which Kuhn *et al.* (1998) used in a recent intercomparison of photochemical models. For species that are not included in this parametrisation, the one provided in the MCM was used. Moreover the MCM photolysis frequencies were used for methylglyoxal. In this case the test calculations performed with a two stream radiative transfer model (Brühl and Crutzen, 1989) showed that the MCM parametrisation was in better agreement with the current state of knowledge about absorption cross sections and quantum yields.

To suppress differences which are not directly related to the isoprene oxidation scheme, the rate coefficients of the basic reactions describing O_3–HO_x–NO_x–CO–CH_4 background chemistry were unified according to DeMore *et al.* (1997) in all schemes included in the intercomparison. In model runs which only considered background chemistry ($C_5H_8 = 0$), the results of the different schemes agreed to within a few percent. Only for CH_3O_2H, under low NO_x conditions, the background chemistry test results deviated by up to 20%, due to differences in the representation of the methylperoxy radical reactions and to a few minor reaction pathways considered in some but not in all chemical schemes (e.g., formation of CH_3OH and CH_3ONO_2). Moreover, the rate coefficients for the primary steps of isoprene oxidation ($C_5H_8 + OH$, $C_5H_8 + O_3$) and for the reactions of the peroxyacetyl radical were unified in all mechanisms according to Atkinson (1994) and DeMore *et al.* (1997), respectively.

3. Box Model Intercomparison

Out of the over fifty different scenarios which have been tested in the course of this work, eight representative cases are presented here. One set of scenarios simulates mid-latitude conditions (latitude 45°, solar declination 23°, temperature 288 K, total pressure 1013 hPa, H_2O volume mixing ratio (VMR) 1%; same parameters

as in the LAND and BIO scenarios of the recent intercomparison by Kuhn *et al.*
(1998)), the other one simulates tropical rainforest conditions (latitude 0°, solar
declination 0°, temperature 300 K, total pressure 1013 hPa, H_2O VMR 2%). Each
set comprises high NO_x and low NO_x scenarios, which were run in two different
modes. In the initialization mode no emissions were considered, and the model
runs were started at noontime with the initial concentrations listed below. In the
emission mode, source terms for isoprene and NO were included over the whole
five day integration period. The NO source was kept constant, whereas the isoprene
source strength was coupled to the cosine of the solar zenith angle and set to zero
at night; the model runs were started at midnight.

These two modes were chosen to cover two borderline cases for the influence
of isoprene chemistry on tropospheric air masses. The continuous emissions scen-
arios represent air masses in the boundary layer entering and moving slowly over
the source areas (maximum direct influence of the first steps of isoprene degrad-
ation). In contrast, the initialization mode approximates air parcels transported
away from the source areas either by convection or by advection and then evolve
without additional emissions (influence of isoprene and its oxidation products on
the background troposphere). Also a third, intermediate mode has been applied in
the course of this work: a discontinuous emission mode in which isoprene and NO
were emitted during the first day of the five day run only. The volume mixing ratios
(VMRs) calculated in this mode as well as the differences between the individual
chemical mechanisms ranged generally in between the corresponding continuous
emission and initialization scenarios. The one day emission mode results provided
additional information for the development of the MIM, but for brevity they will
not be discussed in this paper.

The initial VMRs of C_5H_8, CO, O_3, and NO_x (in the form of NO_2) and the
diurnally averaged source strengths for the scenarios discussed below are listed in
Table V. The initial VMRs of all other species were set to zero, except for H_2O_2 (2
nmol/mol), HNO_3 (0.1 nmol/mol), H_2 (500 nmol/mol), CH_4 (1700 nmol/mol) and
HCHO (1 nmol/mol), which were taken to be the same as in the LAND and BIO
scenarios of the recent intercomparison by Kuhn *et al.* (1998).

In this paper we focus on the comparison of the VMRs calculated for isoprene,
some of its most important and long lived oxidation products (CO, CH_3O_2H, PAN)
and some of the inorganic key species of atmospheric chemistry (O_3, NO_x, OH,
H_2O_2). We do not extend the intercomparison to the C_5, C_4 and C_3 intermedi-
ate products (like MACR etc.) since in each of the compared mechanisms these
intermediates represent different types of lumped surrogate species and thus are
not readily comparable. Due to the high importance of organic nitrate species also
the sum of all peroxyacylnitrates (TOTPAN) and the sum of all organic nitrates
(ORGN), including peroxyacyl- as well as alkylnitrates, will be considered. In the
remainder of this paper C_5H_8, O_3, NO_x, OH, H_2O_2, CO, CH_3O_2H, PAN, TOTPAN
and ORGN will be referred to as the 'test species'. Percentage values characterizing
VMR differences refer to the arithmetic mean of the VMRs in question.

Table V. Initial volume mixing ratios and diurnally averaged source strengths for the eight representative scenarios discussed in this paper

| Scenario	C_5H_8 (nmol/mol)	O_3 (nmol/mol)	NO_x (nmol/mol)	CO (nmol/mol)	C_5H_8 source (nmol/mol/day)	NO source (nmol/mol/day)
Mid-latitude, high NO_x, emission (**MHE**)	0	30	10	100	4.6	14
Mid-latitude, high NO_x, initialization (**MHI**)	2.0	30	10	100	0	0
Mid-latitude, low NO_x, emission (**MLE**)	0	30	0.2	100	4.6	0.7
Mid-latitude, low NO_x, initialization (**MLI**)	2.0	30	0.2	100	0	0
Tropical, high NO_x, emission (**THE**)	0	30	2.0	200	7.0	7.0
Tropical, high NO_x, initialization (**THI**)	5.0	30	2.0	200	0	0
Tropical, low NO_x, emission (**TLE**)	0	20	0.05	200	7.0	0.2
Tropical, low NO_x, initialization (**TLI**)	5.0	20	0.05	200	0	0
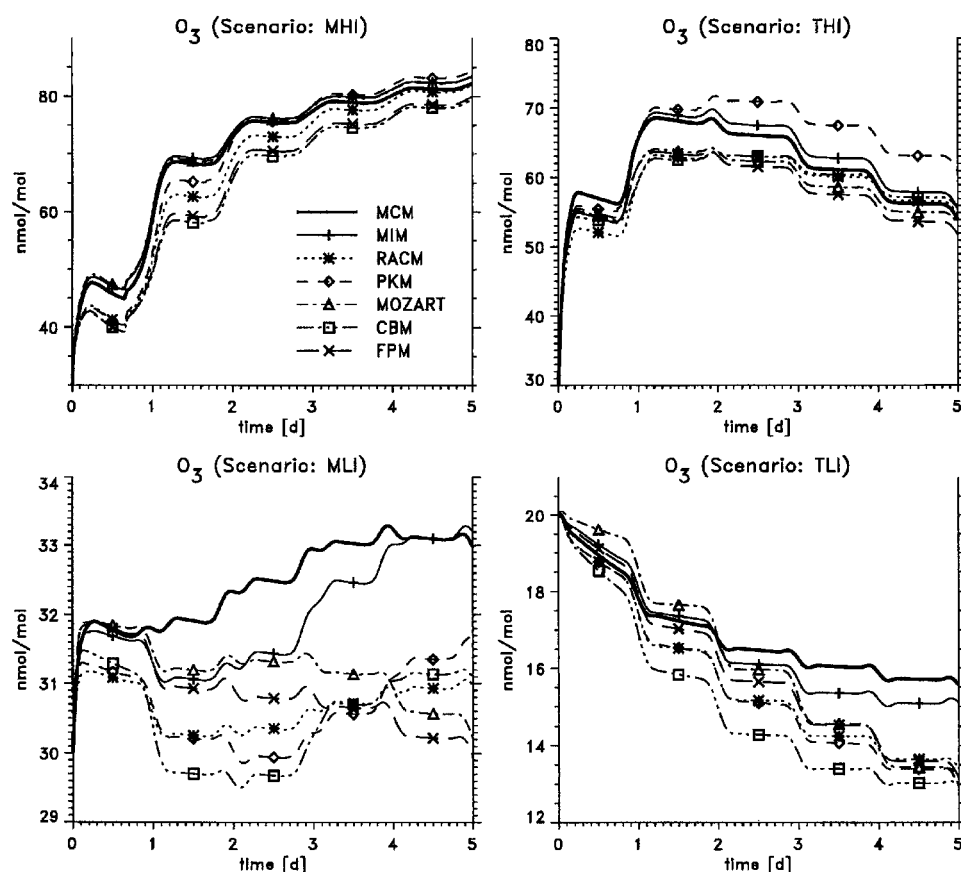
Figure 1. O_3 vs time for the initialization scenarios (MHI, MLI, THI, TLI).

In the high NO_x initialization scenarios, MHI and THI, isoprene is consumed within a few hours, at low NO_x it is consumed within 1 day (MLI) or 2 days (TLI), respectively. For O_3, CO and CH_3O_2H the VMRs calculated with the different chemical mechanisms agree to within ~20% throughout the five day model runs, although in some instances they exhibit markedly different patterns of temporal evolution. As an example the O_3 VMRs for all initialization scenarios are displayed in Figure 1. Larger deviations were calculated for the nitrogen species, of which the VMRs of NO_x and ORGN are displayed in Figures 2 and 3. Under high NO_x conditions (MHI, THI) the differences mostly fade towards the end of the 5 day simulation period, at low NO_x (MLI, TLI), however, they persist. PAN and TOTPAN exhibit similar differences as ORGN, and for conciseness their VMRs will be displayed for the emission scenarios only since the kind of deviations between individual mechanisms (over- or underestimation relative to each other) are generally the same. Also for OH and H_2O_2 deviations of up to ~50% occur
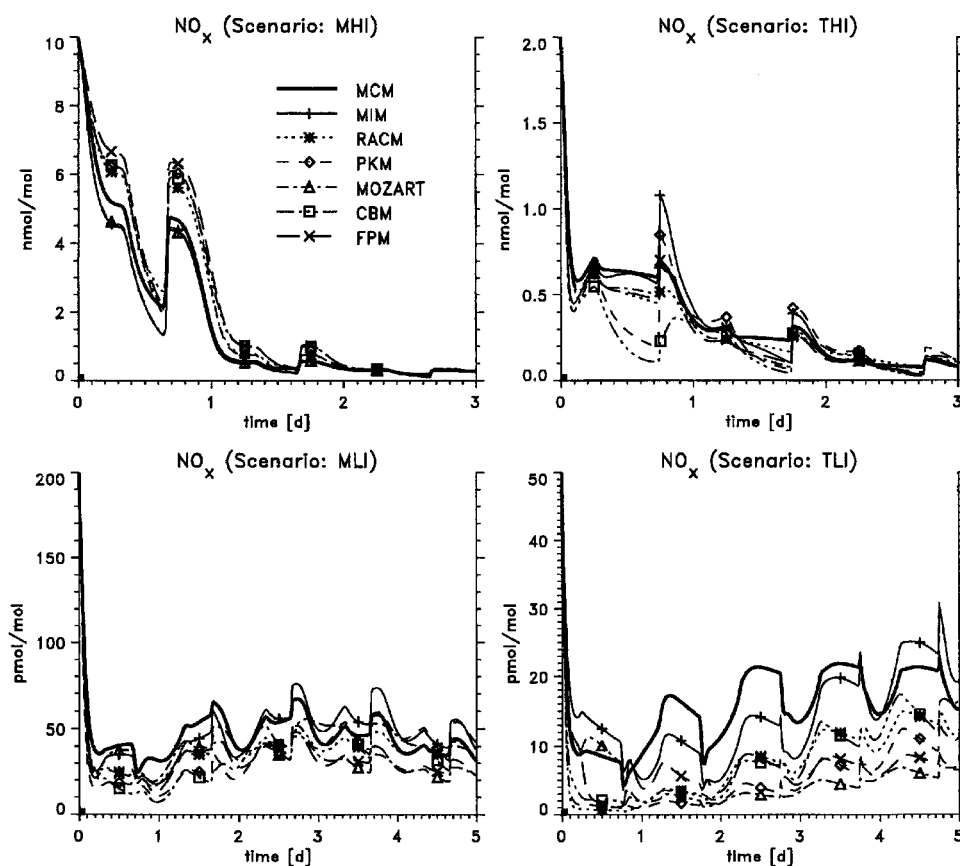
Figure 2. NO$_x$ vs time for the initialization scenarios (MHI, MLI, THI, TLI). Note that for MHI and THI only the first three days are shown, because after that the deviations are negligible.

during the first days but mostly decrease to less than ~20% on day five. In the TLI scenario, however, deviations of up to ~50% persist (Figure 4).

In the mid latitude high NO$_x$ emission scenario (MHE) all test species exhibit substantial differences (Figure 5), and the same is true for the tropical low NO$_x$ emission scenario (TLE, Figure 6). In some cases the results of different chemical mechanisms differ by a factor of five or more. The largest deviations are calculated for CH$_3$O$_2$H, PAN, TOTPAN and OH, but also for O$_3$, C$_5$H$_8$, H$_2$O$_2$ and NO$_x$ differences of more than a factor of two occur (see Figures 5 and 6).

In the mid latitude low NO$_x$ emission scenario (MLE) and the tropical high NO$_x$ scenario (THE) the deviations between the different chemical schemes are for most species smaller than in the MHE and TLE scenarios but still significant. The O$_3$ and C$_5$H$_8$ VMRs calculated for the MLE and THE scenarios mostly agree to within less than 20%. Despite temporary fluctuations of up to 50% the diurnal average NO$_x$ concentrations also agree to within ~20%, while PAN, TOTPAN and
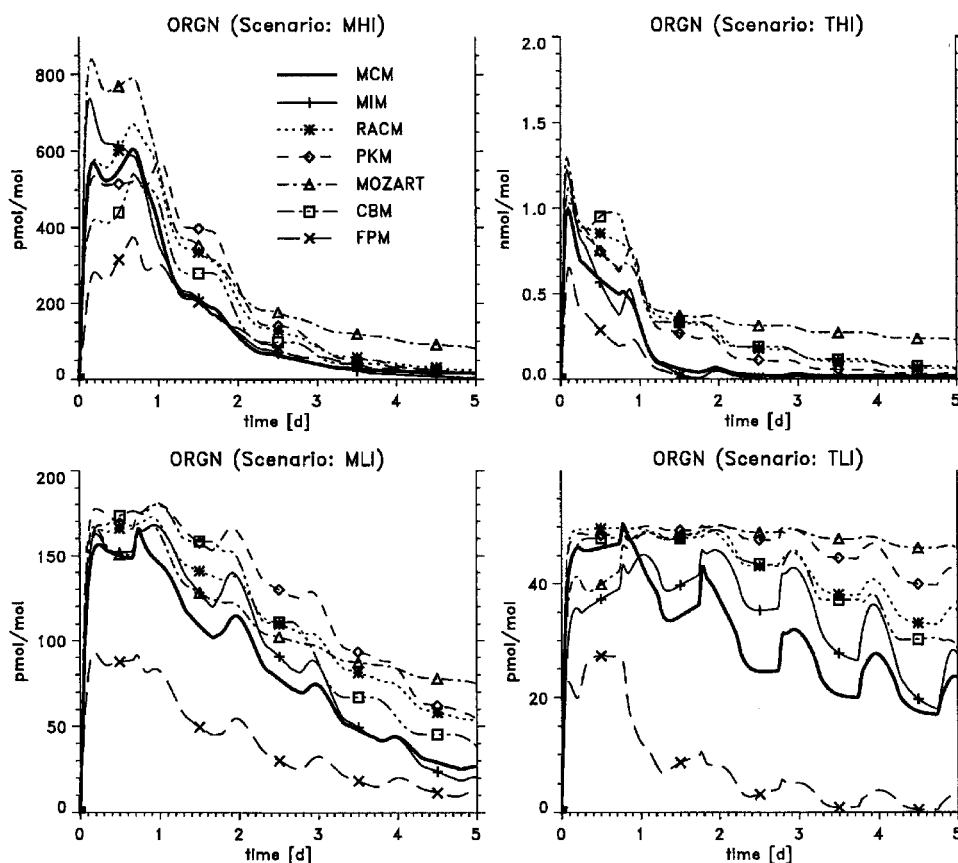
Figure 3. ORGN (total organic nitrogen) vs time for the initialization scenarios (MHI, MLI, THI, TLI).

ORGN exhibit differences by up to a factor of 2. The OH VMRs deviate by up to ~50% in the MLE scenario and up to ~20% in the THE scenario. For H_2O_2, CO and CH_3O_2H the differences in the MLE and THE scenarios (Figures 7 and 8) are not much smaller than in the MHE and TLE scenarios.

4. Discussion

The boxmodel intercomparison shows substantial differences between the invest-igated chemical mechanisms. The kind (over- or underprediction relative to each other, short fluctuations or persistent trends) and the extent of the deviations between different mechanisms vary from species to species and from scenario to scenario. Some characteristic features, however, prevailed in the scenarios presen-ted here as well as in the over forty other scenarios tested in the course of this work.
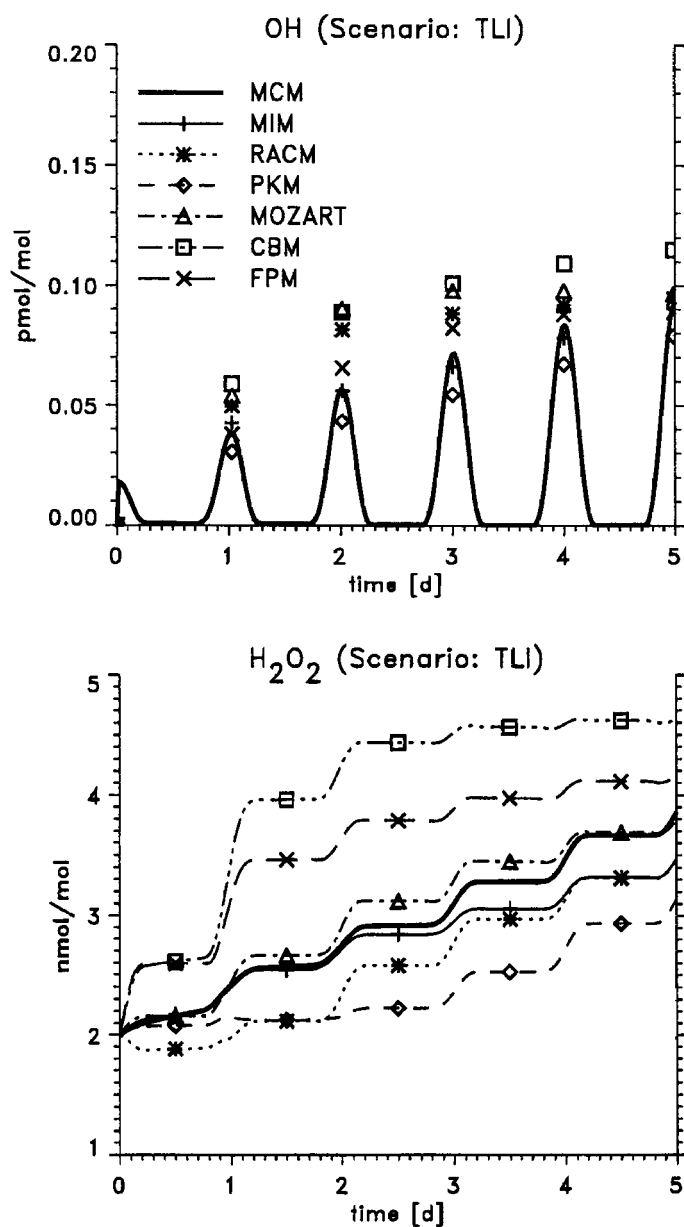
OH (Scenario: TLI)

Figure 4. OH and H_2O_2 vs time for the tropical low NO_x initialization scenario (TLI).

Besides the abundance of isoprene, the NO_x level was the most important parameter characterizing a given scenario (VOC/NO_x ratio). The scenarios presented above were chosen to cover the range of NO_x levels which are probably most relevant for global studies. The same applies to the range of additional parameters like temperature, latitude (solar irradiation and photolysis frequencies) and water vapor
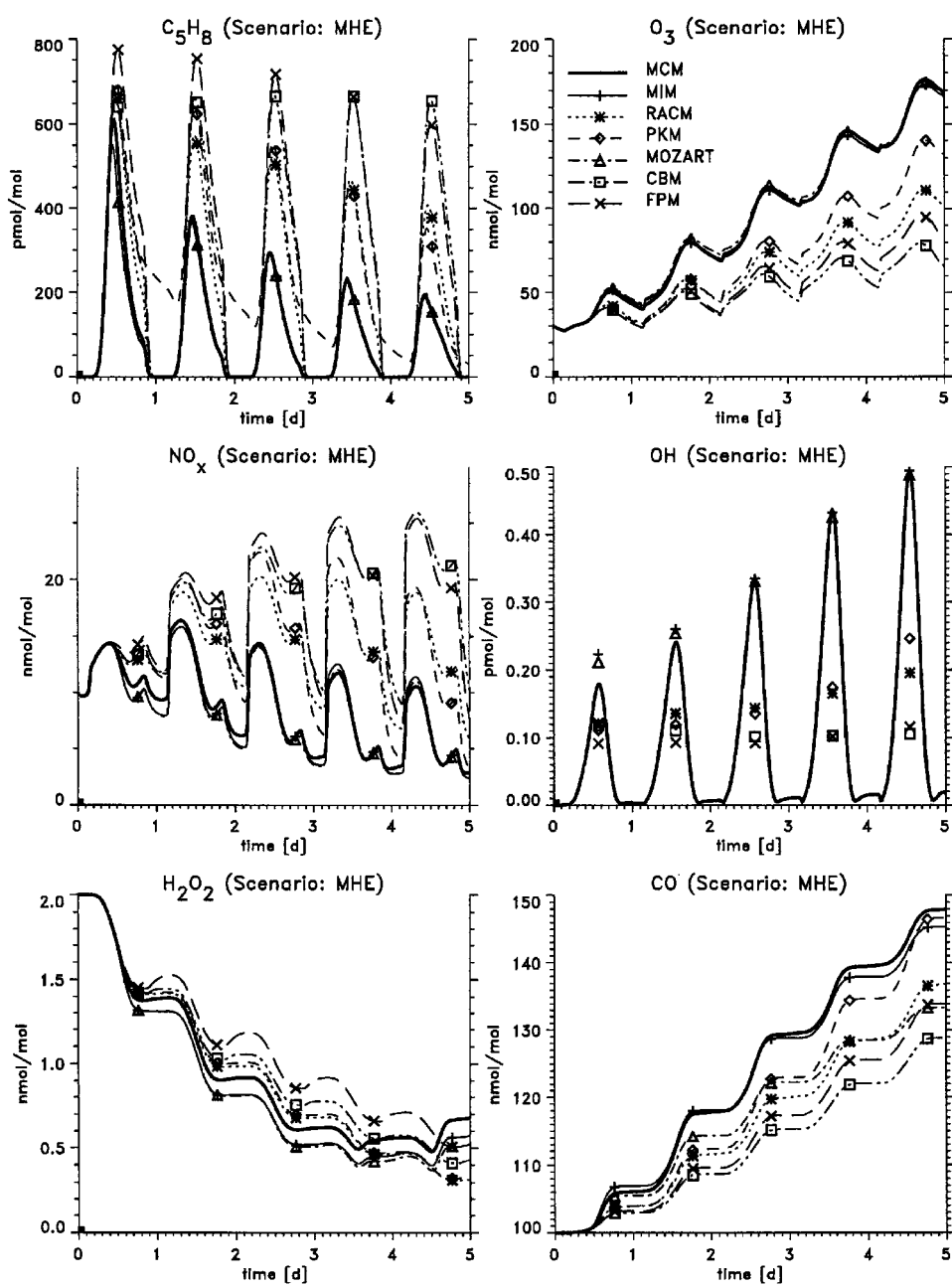
Figure 5. All test species vs time for the mid-latitude high NO_x emission scenario (MHE).
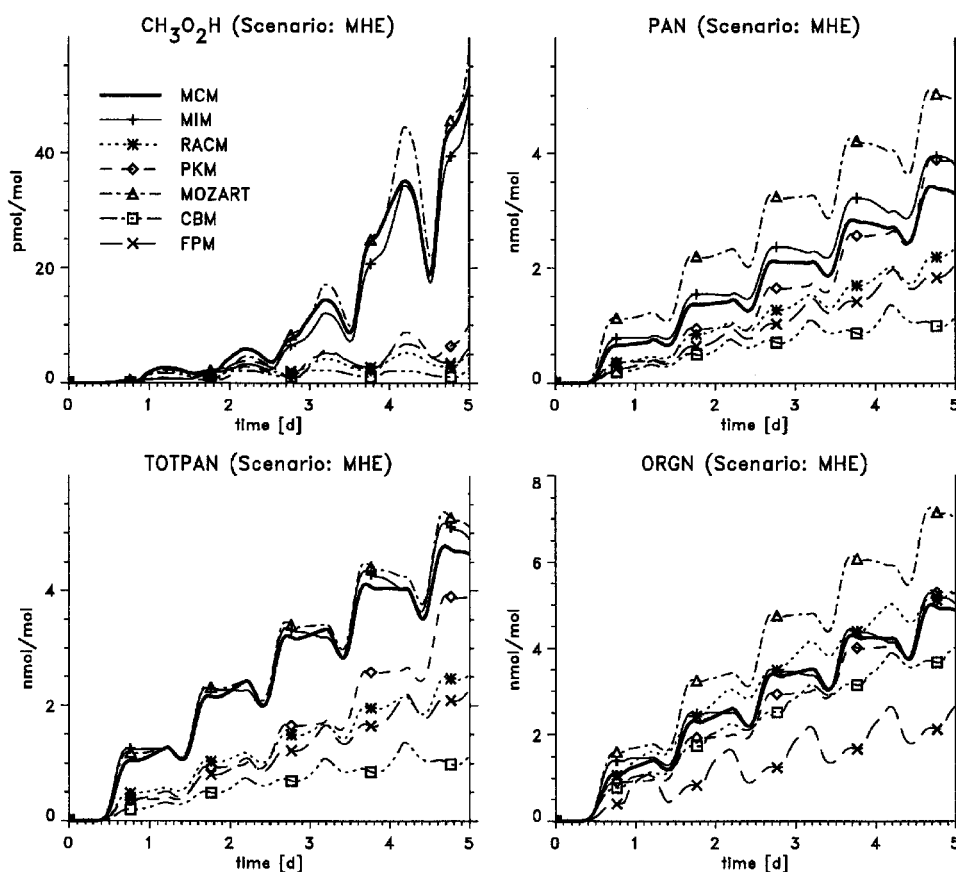
Figure 5. (Continued).

concentration. The latter parameters were, however, found to be less important for the relative deviations between different mechanisms.

Throughout the tested scenarios the MIM was in good agreement with the MCM. The differences were mostly less than 10% and hardly more than 20%. Only in a few instances nitrogen species showed larger deviations (e.g., NO_x in the initialization scenarios), which will be discussed below. For O_3, CO, CH_3O_2H, PAN and TOTPAN the MCM and MIM were mostly at the upper limit of the range of results. Only in a few cases they were exceeded by PKM and MOZART. The CBM on the other hand was mostly at the lower limit for O_3 and CH_3O_2H but at the upper limit for H_2O_2. The RACM was in the medium or lower range for most species and scenarios. The FPM showed no pronounced trends relative to the other mechanisms, except for a substantially lower sum of organic nitrates (which is largely compensated by higher HNO_3 as detailed below) and similarly high H_2O_2 values as the CBM. Note that in test scenarios with very low NO_x levels (down to $\sim$20 pmol/mol diurnally averaged) the relative deviations between the different
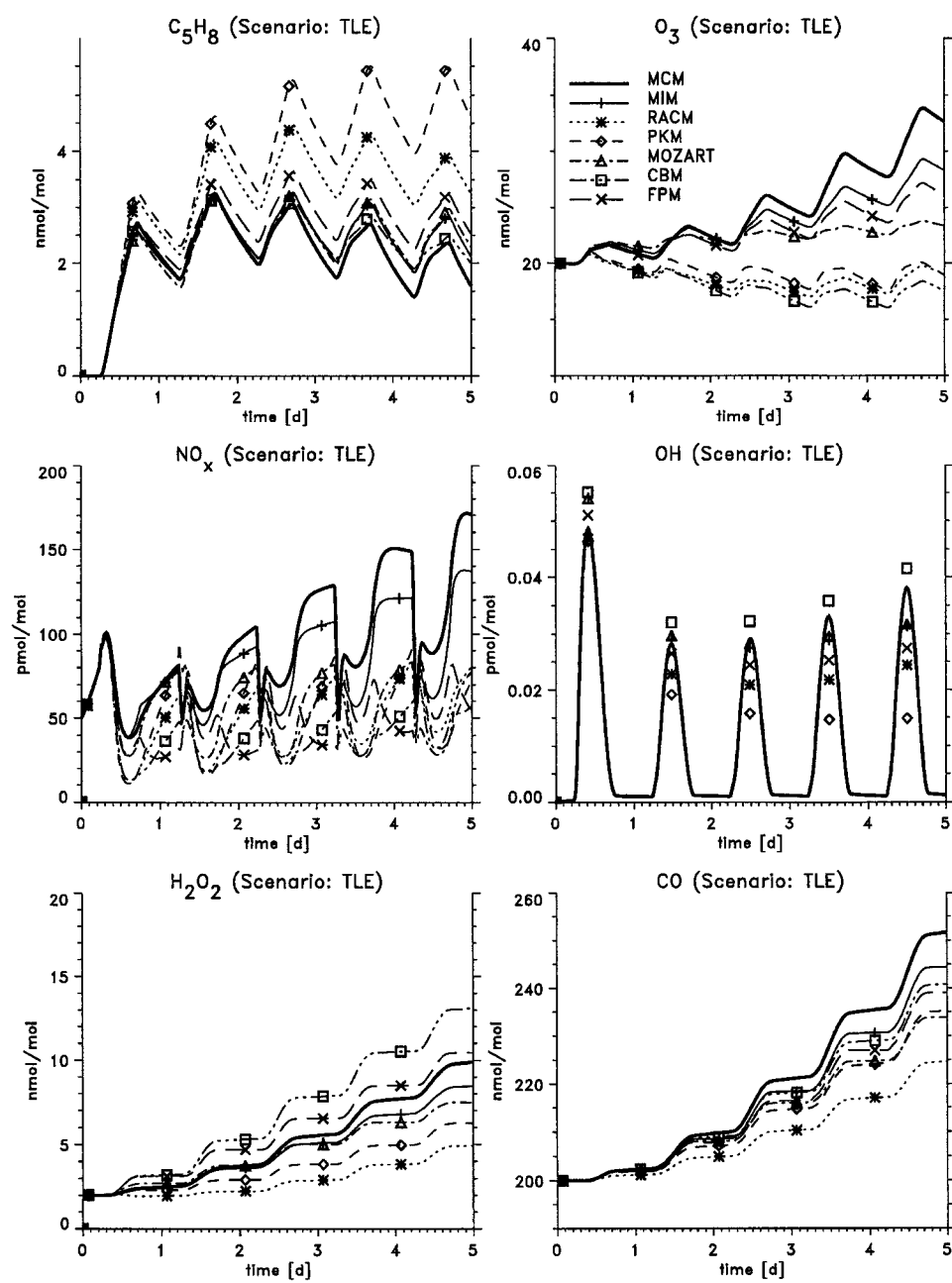
Figure 6. All test species vs time for the tropical low NO_x emission scenario (TLE).
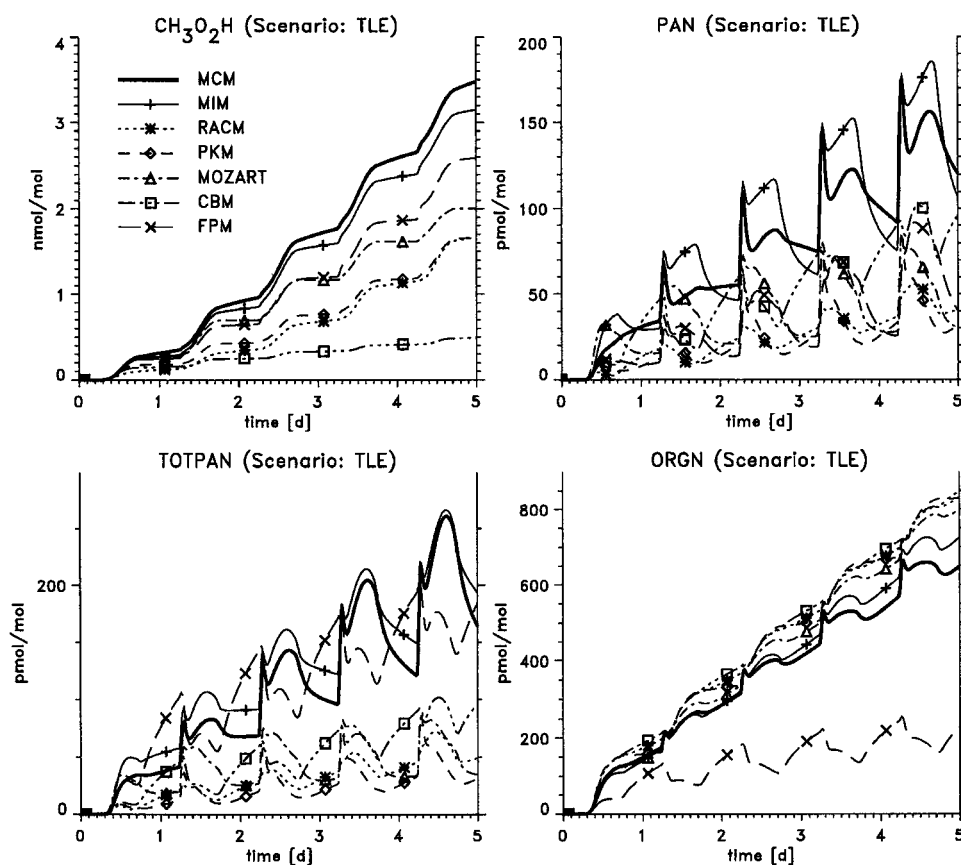
Figure 6. (Continued).

mechanisms were similar to the TLE scenario or even larger, while the MIM was still in good agreement with the MCM.

Differences in the representation of organic nitrates, alkylnitrates as well as peroxyacylnitrates, were identified as a major reason for the deviations between the chemical mechanisms. In recent studies Horowitz *et al.* (1998) and Chen *et al.* (1998) already discussed the effect of isoprene related nitrates on the atmospheric budget of reactive nitrogen, pointing out their high potential importance and the need for better information about production and loss processes. Our model results confirm and further illustrate the importance of this issue.

In the MIM the lumped species MPAN stands for peroxymethacryloylnitrate and other isoprene-related C_4 peroxyacylnitrates; the representation is based on the MCM. For the C_5-β-hydroxyalkylnitrates (ISON, see Tables I and II) formed as byproducts in the reaction of isoprene peroxy radicals (ISO_2) with NO, however, the MIM is mostly based on a recent study by Chen *et al.* (1998) rather than on the MCM. Chen *et al.* (1998) measured smaller yields and suggested lower reactivities and different degradation pathways than assumed in the MCM. Early versions of
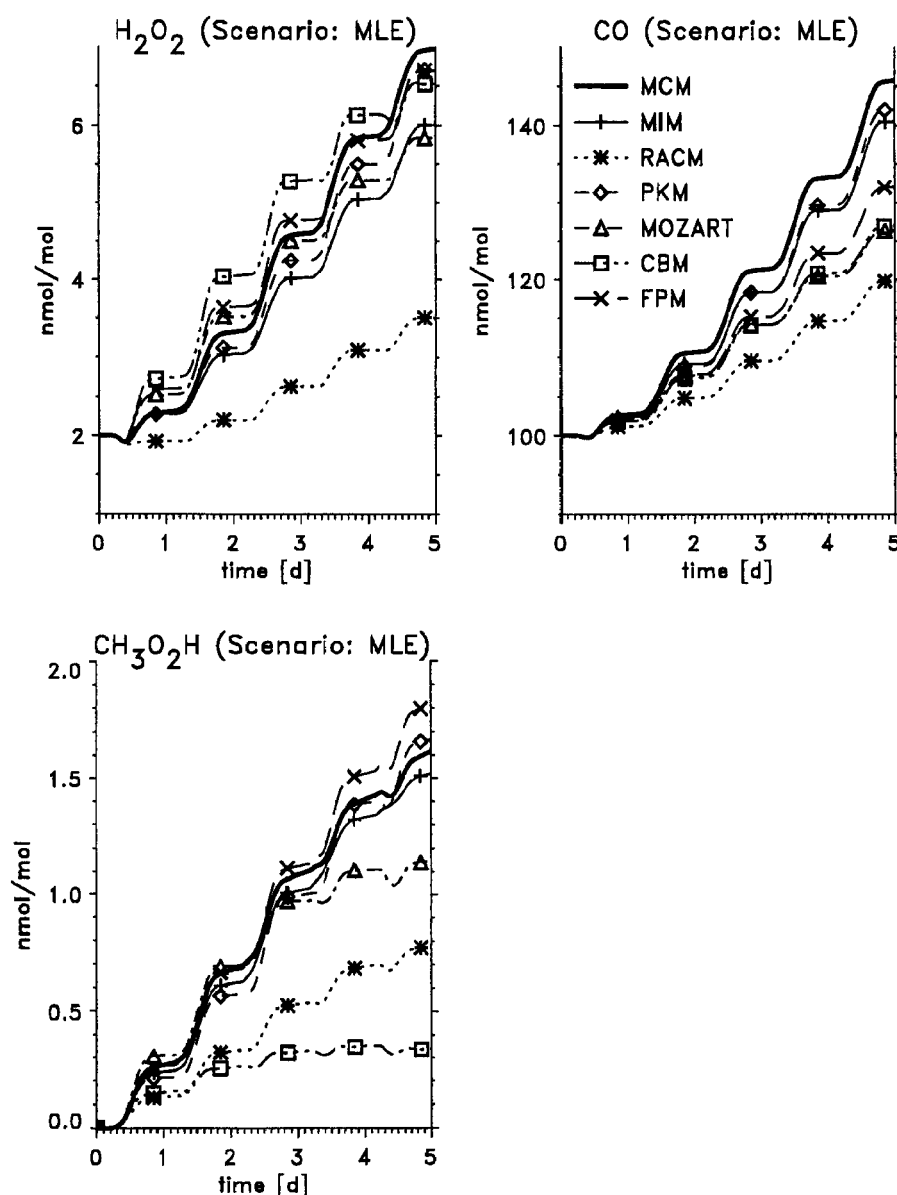
Figure 7. CO, H_2O_2 and CH_3O_2H vs time for the mid-latitude low NO_x emission scenario (MLE).

the MIM with similar C_5-β-hydroxyalkylnitrate chemistry as in the MCM (8–15% yield, OH reaction rate coefficient of $\sim 5 \times 10^{-11}$ cm^3 s^{-1} and immediate release of NO_2), were even closer to the MCM than the version presented here (particularly with respect to NO_x and PAN/TOTPAN).
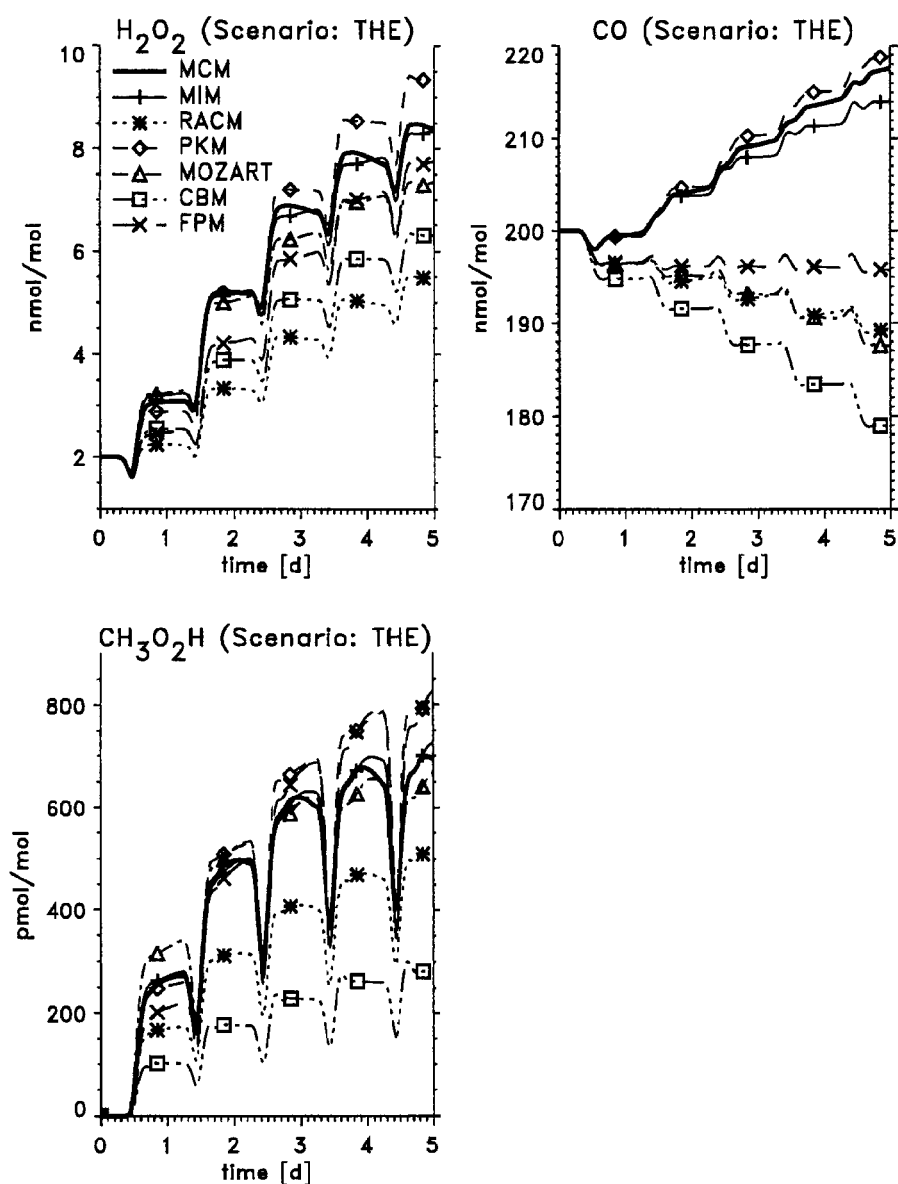
Figure 8. CO, H_2O_2 and CH_3O_2H vs time for the tropical high NO_x emission scenario (THE).

The reason why the different representations of C_5-β-hydroxyalkylnitrate chemistry in MCM and MIM do not lead to larger deviations, is the compensation of two adverse effects: higher nitrate yield versus faster decomposition. In sensitivity tests covering all scenarios listed in Table V, also the results of the MCM changed by less than 10% when the organic nitrate yield from the reaction

of isoprene peroxides with NO was reduced from 8–15% to 4.4% and the rate coefficient for the reaction of the C_5-β-hydroxyalkylnitrate products was reduced from 4–9×10^{-11} cm^3 s^{-1} to 1.3×10^{-11} cm^3 s^{-1}. On the other hand, test runs in which only one of these parameters was changed without compensation, led to substantial differences. For example, an increase of the ISON yield in the MIM from 4.4% to 10% led to a $\sim$25% decrease of NO$_x$, O$_3$, PAN and TOTPAN accompanied by a $\sim$50% increase of C$_5$H$_8$ in the TLE scenario.

MCM and MIM generally produce less alkylnitrates and more peroxyacylnitrates than the other investigated mechanisms, except for the FPM which will be discussed below. This difference appears to be the main reason, why MCM and MIM tend to calculate higher O$_3$ concentrations than the other mechanisms under low as well as under high NO$_x$ conditions. Under low NO$_x$ conditions, where ozone formation is enhanced by NO$_x$ (NO$_x$-limited O$_3$ production), only a small amount of NO$_x$ is removed by the formation of peroxyacylnitrates, since thermal decomposition equilibrates PAN and TOTPAN with NO$_2$. In contrast alkylnitrates can act as a major NO$_x$ sink under these conditions, since their stability is enhanced by the low OH concentrations resulting from low NO$_x$ and O$_3$ (positive feedback). Under high NO$_x$ conditions, where O$_3$ production decreases with increasing NO$_x$ (VOC-limitation), the same processes work the other way round. Due to the high NO$_2$ level the formation of peroxyacylnitrates efficiently reduces NO$_x$ and thus enhances O$_3$ under these conditions. On the other hand the relatively high O$_3$ and OH concentrations reduce the stability of alkylnitrates and thus diminish their efficiency as a NO$_x$ sink. In both cases the peroxyacylnitrates act as a NO$_x$ buffer, whereas the alkylnitrates represent a sink which is affected by a positive feedback.

In the FPM the representation of isoprene related alkylnitrates is conceptually different from all other condensed mechanisms. It includes a rapid direct conversion of these nitrates to HNO$_3$ upon reaction with OH and thus calculates higher HNO$_3$ values but a substantially lower sum of organic nitrates for all scenarios. In the box model intercomparison of this study, these effects largely balanced each other with respect to the NO$_x$ level and most other test species. In 3-D chemistry transport models, however, this conceptual difference might enhance the deviations between the FPM and the other mechanisms.

The importance of the representation of organic nitrate chemistry in condensed isoprene oxidation mechanisms was confirmed by numerous sensitivity tests showing that all parameters governing the formation and degradation of organic nitrates can have a strong impact on NO$_x$, O$_3$ and other atmospheric key species. For example, when the yields of alkylnitrates from the reaction of ISO$_2$ with NO were reduced from the original values (15% RACM and CBM; 13% PKM, 9% FPM) to 4.4%, the VMRs of NO$_x$, O$_3$, OH, PAN and TOTPAN calculated in the TLE scenario increased by about a factor of 2 for RACM, CBM and PKM and by $\sim$30% for FPM. In the MHE scenario the alkylnitrate yield reduction led to a decrease of NO$_x$ (–10% to –20%) and to an increase of O$_3$, OH, PAN and TOTPAN ($\sim$20%) for RACM, CBM and PKM, while the results of the FPM remained practically

unchanged. In MOZART and MIM the nitrate yields were already set close to or at 4.4%.

In the long term a more detailed representation of organic nitrate chemistry than in the MIM as well as in the other condensed mechanisms is certainly desirable, as applied by Horowitz *et al.* (1998) in a 3-D modeling study of the export of reactive nitrogen from the North American continent. However, at present such detailed representations suffer from two major drawbacks: in many cases the reaction pathways and rate coefficients are not yet well known and secondly, they require excessive computer capacities for global 3-D models.

Other than the influence of organic nitrates, no major systematic factors explaining the differences between the investigated chemical mechanisms became evident, although a large number of different sensitivity tests were performed. Rather, the deviations which could not be attributed to organic nitrate chemistry arise from the sum of a variety of differences in the choice of lumped surrogate species, rate coefficients, reaction pathways and feedbacks in each of the condensed mechanisms. A more detailed investigation of the specific differences between the chemical schemes included in the intercomparison goes beyond the scope of this study. At this point we just want to demonstrate that the newly developed MIM provides a good approximation for the detailed MCM isoprene oxidation scheme, and that most of the condensed chemical schemes which have already been used to model atmospheric isoprene oxidation on a global scale may lead to substantially different results.

The box model intercomparisons provide no direct information about the actual relevance of these differences in global 3-D modeling. Depending on meteorological conditions, source strengths and source distributions, transport and heterogeneous processes may locally and globally either weaken or enforce the deviations arising from different gas phase chemical mechanisms. For example, deposition processes and heterogeneous reactions will be of high importance for products and intermediates with polar groups (e.g., C_5-β-hydroxyalkylnitrates represented by ISON, or C_5-β-hydroxyhydroperoxides represented by ISO_2H). Thus for each mechanism the influence of heterogeneous processes will depend on the choice of lumped surrogate species and on the hydrophilic properties or deposition velocities attributed to them.

In any case the chemical mechanism which defines the chemical species and the gas phase reaction pathways will be of major importance under most circumstances. In fact, first results of an accompanying study (von Kuhlmann *et al.*, 1999) in which some of the condensed chemical mechanisms are alternatively applied in the otherwise unchanged global 3-D CTM MATCH-MPIC (Lawrence *et al.*, 1999) reveal that the differences are significant also on a global scale.

To date no conclusive validation of any of the tested chemical mechanisms under globally relevant atmospheric conditions is available. Some of the mechanisms have been evaluated against environmental chamber experiments and were found to be in good agreement with the measurement data (FPM (Carter, 1996), RACM

(M. Kuhn, private communication; Ruppert *et al.*, 1999)). However, these experiments are generally performed for NO_x and isoprene concentrations in the hundred nmol/mol to mmol/mol range which limits their comparability with globally relevant conditions. Moreover the temporal evolution of conventional environmental chamber experiments is comparable to the first day of initialization scenarios only, and under these conditions the investigated mechanisms were anyhow found to be in fair agreement for most of the test species.

For the development of the MIM the MCM has been chosen as a reference which can be expected to provide a fairly realistic representation of atmospheric isoprene oxidation, as described above. However, even though the MCM is one of the most detailed chemical schemes available and has been applied successfully before, it can still not be considered as a real validated reference mechanism. In fact, a revision of the formation and degradation of isoprene related organic nitrates in the MCM appears to be desirable in view of the study of Chen *et al.* (1998), although the sensitivity tests described above indicate that due to the compensation of lower nitrate yield and slower decomposition no major change of the MCM results has to be expected.

5. Conclusions

In this study a new condensed isoprene oxidation mechanism (MIM) has been derived from a highly detailed Master Chemical Mechanism (MCM). In a box model intercomparison the MIM is shown to provide a good approximation for the MCM; for a variety of key species including O_3, OH, CO, CH_3O_2H and PAN the two mechanisms agreed mostly to within 10%. In contrast, other condensed isoprene oxidation mechanisms, some of which have already been used in global modeling studies, exhibited substantial deviations relative to the MCM as well as relative to each other. Differences in the representation of organic nitrate chemistry were identified as a major reason for these deviations, and since chemical kinetics data on the atmospheric production and loss processes of this class of chemicals are sparse, there is clearly a need for detailed experimental investigations.

First results of an accompanying study, in which some of the investigated condensed mechanisms were alternatively applied in the same global 3-D chemistry-transport model, showed that the substantial differences found in the box model intercomparison are also significant on regional and global scales. However, to date no conclusive validation of any condensed or detailed chemical mechanism under globally relevant conditions is available. Thus there is not only a need for improvement of the representation of isoprene chemistry in global atmospheric models, but also a need for adequate experimental evaluation of the MCM and other detailed isoprene oxidation mechanisms. In the long run a reliable characterization of all relevant pathways of atmospheric isoprene degradation by individual process studies, environmental chamber studies under realistic conditions and well constrained field experiments will be required to obtain a definitive reference mechanism. In

the meantime a comparison of the MCM with other detailed isoprene oxidation mechanisms (Carter and Atkinson, 1996; Madronich and Calvert, 1989; Poisson, 1997), which is currently in preparation, should provide additional information about the most important uncertainties.

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