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Isoprene Oxidation and its Impacts on the Atmospheric Composition

by

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"An error does not become truth by reason of multiplied propagation, nor becomes truth error because nobody sees it."

Mahatma Gandhi

Abstract

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Terrestrial vegetation, especially tropical rain forest, releases vast quantities of volatile organic compounds (VOCs) to the atmosphere, which are removed by oxidation reactions and deposition of reaction products. The oxidation is mainly initiated by hydroxyl radicals (OH), primarily formed through the photodissociation of ozone. Previously it was thought that, in unpolluted air, biogenic VOCs deplete OH and reduce the atmospheric oxidation capacity. Conversely, in polluted air VOC oxidation leads to noxious oxidant build-up by the catalytic action of nitrogen oxides ($NO_x = NO + NO_2$). However, aircraft measurements of atmospheric trace gases performed over the pristine Amazon forest revealed unexpectedly high OH concentrations. Isoprene was the dominant VOC emitted in that region and its oxidation computed to be the largest OH sink. In this work the hypothesis that natural isoprene oxidation efficiently recycles OH in low-NO_x air has been investigated in great detail. A highly explicit oxidation mechanism for isoprene has been developed including recent experimental and theoretical advancements. Major OH-recycling routes have been implemented and shown to substantially enhance oxidation under low-NO_x conditions. Enhanced OH concentrations persisted under reduced light conditions typical of vegetation canopies. When compared to aircraft measurements the new oxidation mechanism shows to reproduce the OH concentrations within the uncertainty range. Furthermore, simulations showed substantial production of a dihydroxyepoxide from isoprene that may be a potentially important precursor of organic aerosols in the atmosphere. A new reduced oxidation mechanism based on traditional knowledge has been developed and tested for global atmospheric studies. The inclusion in this mechanism of the new oxidation routes will allow to study the impacts of enhanced VOC oxidation on atmospheric composition, surface-atmosphere exchanges, aerosols and climate.

Zusammenfassung

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Terrestrische Vegetation, vor allem tropischer Regenwald, emittiert grosse Mengen flüchtiger organischer Verbindungen (VOCs) in die Atmosphäre, die durch Oxidationsreaktionen und Deposition der Reaktionsprodukte wieder entfernt werden. Die Oxidation wird vor allem durch Hydroxyl-Radikale (OH) initiiert, die hauptsächlich durch Photodissoziation von Ozon gebildet werden. Zuvor ging man davon aus, dass biogene VOCs OH in unverschmutzter Luft abbauen und dadurch die atmosphärische Oxidationskapazität verringern. Umgekehrt, führt die Oxidation von VOCs in verschmutzter Luft durch die katalytische Wirkung von Stickstoffoxiden ($NO_x = NO + NO_2$) zu schädlicher Oxidationsmittelbildung. Flugzeugmessungen atmosphärischer Spurengase, die über dem unberührten Amazonas-Regenwald durchgeführt worden sind, haben jedoch unerwartet hohe OH-Konzentrationen aufgezeigt. Das VOC mit der höchsten Emission in dieser Region war Isopren, dessen Oxidation als stärkste OH-Senke berechnet wurde. In dieser Arbeit wurde die Hypothese genauestens untersucht, dass die natürliche Isopren-Oxidation in niedrig-NO_x Luft OH effizient erneuert. Es wurde ein sehr detaillierter Oxidationsmechanismus für Isopren entwickelt, in dem neueste experimentelle und theoretische Fortschritte umgesetzt worden sind. Die Haupt-OH-Rückgewinnungswege wurden angewendet wodurch gezeigt wurde, dass sie wesentlich zur Oxidation unter niedrig-NO_x Bedingungen beitragen. Verstärkte OH-Konzentrationen blieben unter verminderten Lichtverhältnissen, wie sie unter dichten Vegetationsdächern typisch sind, dauerhaft erhalten. Im Vergleich zu Flugzeugmessungen, der neue Oxidationsmechanismus reproduziert die OH-Konzentrationen innerhalb des Unsicherheitsbereiches. Darüber hinaus zeigten Simulationen eine erhebliche Produktion eines Isopren-Dihydroxyepoxids, das ein potenziell wichtiger Vorläufer organischer Aerosole in der Atmosphäre sein könnte. Es wurde einen neuen vereinfachten Oxidationsmechanismus auf Basis des traditionellen Wissenstands entwickelt und seine Anwendung für globale atmosphärische Studien getestet. Die Eingliederung der neuen Oxidationswege in diesen Mechanismus ermöglicht es folgende Auswirkungen der verstärkten VOC-Oxidation zu studieren die Zusammensetzung der Atmosphäre, den Austausch zwischen Erdoberfläche und Atmosphäre, Aerosole und Klima.

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Abbreviations

BVOC   Biogenic Volatile Organic Compound

MIM   Mainz Isoprene Mechanism

MIMvK   Mainz Isoprene Mechanism von Kuhlmann's version

MIM2   Mainz Isoprene Mechanism 2

MCM   Master Chemical Mechanism

MCMEv1   Master Chemical Mechanism Extended version 1

MCMEv2   Master Chemical Mechanism Extended version 2

SOA   Secondary Organic Aerosol

Chapter 1

Introduction

1.1 Isoprene from vegetation

The terrestrial vegetation acts as a source of biogenic volatile organic compounds (BVOCs), which are of widely recognized importance for atmospheric chemistry and climate. Isoprene (2-methyl-1,3-butadiene, C_5H_8) and monoterpenes (made up of two isoprene units) are among the most important BVOCs. Globally, isoprene dominates the emissions by far and strongly affects the composition of the troposphere. Its emissions depend strongly on temperature and light (Fehsenfeld et al. (1992)). Global emission estimates of isoprene are in the range 410–680 Tg/yr (362–601 Tg(C)/yr) (Müller et al. (2008) and Arneth et al. (2008, and references therein)). Given the magnitude of its emissions, isoprene is considered the dominant BVOC emitted into the atmosphere.

1.2 Role in the Earth system

BVOCs play numerous roles in the Earth system and provide interlinkages between its biological, chemical and physical components. Initially, the biological role of isoprene was not very well understood and thought to be basically conferring thermo-tolerance to plants by interacting with the membranes of the plant (Sharkey and Singsaas (1995), Sharkey et al. (2001), Singsaas et al. (1997)). Then its role in protecting plants from O_3 and H_2O_2 was discovered (Loreto and Velikova (2001), Loreto et al. (2001)). It was also reported that isoprene plays a role in the plant-insect interactions (Laothawornkitkul et al. (2008a,b), Loivamäki et al. (2008)). Niinemets et al. (2004) proposed that isoprene has a protective role, acting as a metabolic "safety valve". This view is also supported by the emissions of a BVOC being largely controlled by its own physicochemical properties like solubility and volatility (Penuelas and Llusià (2004)).

Isoprene oxidation by OH can, in the presence of sufficient NO_x, lead to the formation of O_3 in the troposphere allowing the oxidation of NO to NO_2 without removal of an O_3 molecule (Atkinson and Arey (2003b)). Under low-NO_x conditions a net consumption of O_3 takes place. Nitrogen-containing products like nitrates are recognized as important in the long-range transport of NO_x in the atmosphere. Nitrates from isoprene oxidation represent a large fraction of the atmospheric organic N-reservoir. Recently, alkyl nitrates from isoprene have been shown to be taken up by foliage and incorporated into the leaf amino acids (Lockwood et al. (2008)). This may be the basis for a potentially significant role of isoprene, helping nitrogen-limited forests sequestering nitrogen from the atmosphere and provide a self-fertilizing mechanism.

Isoprene not only influences gas phase atmospheric chemistry, but can also lead to the formation of Secondary Organic Aerosols (SOAs). The mechanisms by which BVOC oxidation may lead to SOAs in clean air are still not fully understood (Kulmala (2003)), but it is clear that BVOC oxidation products generally have lower vapour pressures than the primary compounds, and so may more readily condense on pre-existing molecular clusters. Recent field and laboratory evidence indicates that the oxidation of isoprene forms SOA (Carlton et al. (2009, and references therein)). Global biogenic emissions of isoprene are sufficiently large that the formation of SOA in even small yields would result in substantial production of atmospheric particulate matter. Aerosols directly affect climate by scattering solar radiation. They also indirectly alter the Earth's radiative balance by acting as cloud condensation nuclei, changing cloud albedo and the degree of cloud cover, so potentially leading to net cooling of the Earth's surface during the day. Although it is known that a substantial fraction of the aerosol particles in remote regions is organic material, and that the oxidation of BVOCs may lead to the formation of SOAs, it is not yet clear how important SOA formation is in altering the climate system. There is the possibility that SOA formation from BVOC emissions cools the Earth and so moderates temperature dependent BVOC emission from plants. On the other hand, a recent study showed how new particle formation in forests is inhibited by isoprene emissions (Kiendler-Scharr et al. (2009)). Hence, there is the potential for feedbacks between BVOC emissions, SOA and climate. Therefore, a comprehensive knowledge of isoprene chemistry is essential to understand the role of isoprene in the Earth system, since atmospheric oxidation is the link between the biological and climatic roles of isoprene.

1.3 Isoprene oxidation chemistry

1.3.1 Experimental work

The main oxidation pathways of isoprene are reactions with OH, O_3 and NO_3, with the OH-pathway being by far the most important. This is due to the high reaction rate with OH and to the coincidence of the strong light- and temperature-dependent emissions (Fehsenfeld et al. (1992), Yokouchi (1994)) with the peak in OH concentrations during the day. Many experimental studies have been conducted so far, and product yields for many species, with and without NO_x, have been determined. For instance, the OH-pathway has been investigated extensively in a number of studies (Benkelberg et al. (2000), Kwok et al. (1995), Lee et al. (2005), Miyoshi et al. (1994), Paulot et al. (2009a,b), Paulson et al. (1992a), Ruppert and Becker (2000), Sprengnether et al. (2002), Tuazon and Atkinson (1990a)). Fewer studies on the stable products from the O_3-pathway have been performed (Aschmann and Atkinson (1994), Atkinson et al. (1994), Grosjean et al. (1993), Paulson et al. (1992b), Sauer et al. (1999)), while a number of studies focused specifically on the OH-yields (Atkinson et al. (1992), Gutbrod et al. (1997), Lewin et al. (2001), Neeb and Moortgat (1999), Paulson et al. (1998), Rickard et al. (1999)). Chemical properties have been determined for only a few oxidation products (Atkinson et al. (2006)). A substantial fraction of the global isoprene production occurs in regions of the Southern Hemisphere where NO mixing ratios are below $60\,\mathrm{pmol/mol}$ (Emmons et al. (1997), Müller et al. (2008), Torres and Buchan (1988)). Under these conditions, after HCHO, the organic hydroperoxides (ROOH) are the next most abundant products, with a maximum product yield ranging between 32 and 48% (Benkelberg et al. (2000), Jenkin et al. (1997)). Their chemical properties have not been measured yet, but they are predicted to be very reactive and critical to adequately represent the isoprene chemistry in low-NO_x conditions. Other important products under all NO_x-regimes are methy vinyl ketone (MVK), methacrolein (MACR), C_5-carbonyls, glycolaldehyde, glyoxal, hydroxyacetone and methylglyoxal.

1.3.2 Oxidation mechanisms

The knowledge of isoprene chemistry is still incomplete, many uncertainties remain, and only a few detailed isoprene mechanisms exist. Three of them are described in Fan and Zhang (2004), Madronich and Calvert (1989) and Carter and Atkinson (1996), with the last one being evaluated against a chamber study (Carter (2000)). Another detailed mechanism of isoprene oxidation is included in the Master Chemical Mechanism (MCM v3.1) (Jenkin et al. (1997), Saunders et al. (2003)). It can be freely accessed at the

website: http://mcm.leeds.ac.uk/MCM. This isoprene mechanism is highly explicit, providing a description of the complete degradation of isoprene and its degradation products, initiated (where appropriate) by reaction with OH, O_3, NO_3 and photolysis. However, it already contains some level of reduction compared with the related subset mechanisms of Jenkin and Hayman (1995) and Jenkin et al. (1998), which treat the OH-initiated degradation to first generation products in greater detail. The reduction in the MCM of the more detailed chemistry consisted of neglecting the formation of two minor hydroxy peroxy radicals from the OH-addition pathway, which together represent about 10% of the reaction products.

Recently, the MCM has been evaluated against NO_x-air chamber experiments (Pinho et al. (2005)). Moreover, it has been applied in many recent field studies (Biesenthal et al. (1998), Carslaw et al. (1999a, 2001), Warneke et al. (2001), Williams et al. (2001)). However, detailed mechanisms like the MCM are not suitable for global atmospheric chemistry simulations due to computational limitations, and a reduced mechanism must be employed, although this is known to lead to loss of accuracy and information (Carslaw et al. (1999b), Whitehouse et al. (2004a,b, and references therein)). Moreover, inaccuracies in the representation of important intermediate species adds further uncertainties to 3-D atmospheric models due to the interplay between chemistry, transport and deposition. Therefore, assessments of all these uncertainties in the models must be performed. In this work we re-evaluate the Mainz Isoprene Mechanism (MIM, Pöschl et al. (2000)), which is an earlier reduction of MCM. We present and evaluate a new reduced mechanism of intermediate size for isoprene, which we call MIM2. We show that, unlike MIM, MIM2 preserves the basic features of the corresponding detailed mechanism and shows similar nonlinear behaviour. A set of reduction principles that form the basis of its development is presented in Chapter 2. A box model evaluation of MIM2 and MIM against MCM for three NO_x scenarios is presented in Chapter 3. Despite their complexity, MIM2 as well as MCM have substantially underestimated the HO_x levels during a field campaign in a pristine environment with intense vegetation (Butler et al. (2008), Kubistin et al. (2008), Lelieveld et al. (2008), Martinez et al. (2008)). In the past such underestimation has been thought to be related to the presence of unknown very reactive BVOCs that would react with O_3 and produce OH (Tan et al. (2001)). Here another approach to resolve this model-observation discrepancy is taken. In such environments isoprene is the largest sink for OH in the boundary layer. Furthermore, the current detailed isoprene oxidation mechanisms represents a rather old and limited experimental knowledge. Therefore, an alternative hypothesis is advanced. The OH sink due to isoprene has been largely overestimated, that is OH might be recycled to a substantial extent during oxidation. To examine this, a very detailed oxidation mechanism has been developed and presented in Chapter 4. Finally in Chapter 5 the new mechanism is tested

in a box model in both the free mode and constrained to field measurements. In contrast to MCM, substantial improvements for HO_x and other intermediates are shown. Implications for the atmospheric composition and biosphere-atmosphere exchanges are also discussed. Finally, the results are summarized and an outlook for future reserch is presented in Chapter 6.

Chapter 2

Mainz Isoprene Mechanism 2: Development

2.1 Background

The chemistry of terpenes (e.g. isoprene and monoterpenes) has a large range of oxidation reaction pathways and products (Atkinson and Arey (2003a,b)). To our knowledge, all VOC oxidation mechanisms employed in global atmospheric chemistry models neglect most of the products and isomers arising from terpene oxidation (Brasseur et al. (1998), Folberth et al. (2006), Geiger et al. (2003), Horowitz et al. (2007), Houweling et al. (1998), von Kuhlmann et al. (2004), Wang and Shallcross (2000), Wang et al. (1998)). Furthermore, mechanisms like MIM often include lumped species which represent many compounds, sometimes with very different chemical structures and properties. Thus, they fail to reproduce the nonlinear behaviours of its tropospheric chemistry under different conditions, e.g., differences in product yields in the absence and presence of NO_x (Jenkin et al. (1998), Ruppert and Becker (2000)). For example, MIM considers only one product for each class of C_5- and C_4-compounds: one carbonyl species instead of four isomers, two alkyl nitrates instead of eight compounds and one hydroperoxide instead of four isomers. It can only poorly reproduce the experimental results or the diurnal cycle of the total nitrates (see Sect. 3.6.1). MIM, as well as many other condensed mechanisms, has to be taken as an entity without changing individual rate constants or reaction products. For instance, while the average MCM alkyl nitrate yield is 10%, in MIM a 4.4% yield based on an experimental study by Chen et al. (1998) was adopted and the results were tuned accordingly. Afterwards, von Kuhlmann et al. (2004) increased this yield in MIM to 12% following Sprengnether et al. (2002), which we have found leads to undesirable side effects on the results of the mechanism (see Sect. 3). Changing such

yields in MIM was accepted only because of the large experimental uncertainties in the literature, with estimates ranging between 4.4 and 15% (Chen et al. (1998), Giacopelli et al. (2005), Patchen et al. (2007), Sprengnether et al. (2002)). However, we note that modifications of a highly-tuned reduced mechanism like MIM, or usage of any subset of its reactions, can lead to serious misinterpretation of either field or experimental data. Nevertheless, to date there have been several applications of such modified version of MIM. There are two global atmospheric chemistry models, MATCH-MPIC (Lawrence et al. (2003), von Kuhlmann et al. (2003)) and ECHAM5/MESSy (Jöckel et al. (2006), Pozzer et al. (2007)) in which this modified MIM was included. Moreover, 19 out of the 44 reactions of MIM were used to update the isoprene mechanism of the well-established mechanism RACM (Stockwell et al. (1997)) and were tested against a chamber study (EUPHORE) (Geiger et al. (2003)). This mechanism was then used to analyse long-term measurements of atmospheric OH concentrations (Rohrer and Berresheim (2006)). After a slight modification, the mechanism was used to perform a product and a kinetic study of isoprene chemistry with the SAPHIRE chamber (Karl et al. (2006)).

2.2 Reduction principles

Keeping in mind the background described above, the following principles for mechanism reduction have been conceived and adopted for designing MIM2:

1. **Take the MCM for isoprene as the reference (Saunders et al. (2003, and references therein)), with any errors or omissions it may contain.**

2. **Consider only C_2-C_5-species to be isoprene-related and hence belonging to the reduced mechanism.**

3. **Make the mechanism detailed enough to accurately reproduce the diurnal cycle of important intermediate species like carbonyls, hydroperoxides and alkyl and peroxy acyl nitrates.** This is expected to be of relevance in order to properly simulate the atmospheric composition with 3-D models where transport and dry and wet deposition of species play a key role. MIM was intended to perform well in reproducing the concentrations of O_3, OH, NO_x, H_2O_2, CH_3OOH, CO and isoprene. While this generally works well, it will be shown in Sect. 3 that its biases with respect to MCM are sometimes significant even for these species.

4. **Include any isoprene oxidation products which can be measured using modern instrumentation, and any other species which represent significant minor pathways but were neglected in previous mechanisms.**

Such species are glyoxal, glycolaldehyde, propene, acetaldehyde, α-nitrooxy acetone, C_5-hydroperoxides, diols, and C_5-carbonyls. Recently, measurements of oxygenated organics during field campaigns and in laboratory experiments have become widespread (Sinreich et al. (2007), Volkamer et al. (2005), Williams et al. (2001); de Gouw and Warneke (2007, and references therein)). For glyoxal, a species absent in MIM, satellite retrievals have recently become possible and are becoming more reliable (Myriokefalitakis et al. (2008), Wittrock et al. (2006)).

5. **Neglect long-lived species only if they are formed in very small amounts ($<$30 pmol/mol under all NO_x regimes studied).** This principle ensures that their elimination from the mechanism does not significantly affect species like O_3 and OH. For instance this was the case for some peroxy acyl nitrates like the MCM species GLYPAN and C4PAN6.

6. **Substitute all the species which react quickly at frequencies greater than $1\,s^{-1}$ with the respective products of the major loss pathway.** The species satisfying such principle are the Criegee biradicals (see Sect. 2.5) and alkoxy radicals with typical lifetimes being less than $1\,s$. Whitehouse et al. (2004a) successfully applied a similar principle for all species that are set to decompose at a rate of $10^6\,s^{-1}$ in MCM. This was based on the idea that the long term behaviour of a chemical mechanism can be accurately represented by assuming that the faster time-scales equilibrate with respect to the slower ones.

7. **Lump species that are always in a nearly constant ratio and have very similar reactivities.** Species that react through the same paths, in reactions with same rate coefficients, can be lumped together without any loss of accuracy to the mechanism (Whitehouse et al. (2004b)). Moreover, the loss of accuracy is small when species with very similar reactivities are lumped together. Hence, in this study, every lumped species is assumed to have reactivities and products equal to the corresponding weighted averages of the respective components. For an example see Sect. 2.4.

8. **Adopt the MCM nomenclature and give lumped species a name starting with L and being as similar as possible to the MCM names of the species it represents.**

Designing MIM2 with such principles in mind has led to a mechanism that allows further mechanism development building directly on MIM2, which is not possible with MIM or most other contemporary reduced mechanisms. It is thus straightforward to test the effects of any new laboratory kinetic developments in atmospheric chemistry models using MIM2. Moreover, the fairly large number of C_2-C_5-species included in MIM2 allows

TABLE 2.1: Number of reactions and species for each mechanism.

Mechanism	Stable species[a]	Species[a]	Reactions[b]
MCM	150	180	583(+12)
MIM	12	15	42(+2)
MIM2	53	68	195(+4)

[a] Note that only C_2-C_5 species have been taken into account.
[b] Inside the parentheses are the number of photolysis reactions of PAN-like compounds that must be included when modeling the upper troposphere.

global models like ECHAM5/MESSy (Jöckel et al. (2006)) to include rather detailed organic aqueous-phase chemistry, which appears to be potentially important by often acting as a strong sink for trace gases like glyoxal (Carlton et al. (2007), Hastings et al. (2005), Loeffler et al. (2006), Volkamer et al. (2007)) and MVK and MACR (Chen et al. (2007)), and which may also be have implications for cloud microphysics (Nenes et al. (2002)).

2.3 The whole mechanism

The size of MIM2 with respect to MCM and MIM is presented in Table 2.1.

MIM2 consists of 69 species, of which 53 are long-lived and hence need to be transported in atmospheric chemistry models (see Table A.1). These species are involved in 178 reactions (see Table A.3). When implemented in 3-D atmospheric chemistry models, photolysis reactions of the 4 peroxy acyl nitrates must be added. These photolysis reactions are not considered in MCM because it was designed to simulate the lower troposphere. However, the photolysis of peroxy acyl nitrates can become the dominant sink in the upper troposphere (Nizkorodov et al. (2005), Talukdar et al. (1995)).

2.4 The OH-pathway

Under atmospheric conditions the OH-addition pathway for isoprene oxidation is by far the most important. The MCM considers the production of only four isomers of peroxy radicals, RO_2, which is a reduction of an even more detailed mechanism (Jenkin and Hayman (1995), Jenkin et al. (1998)) that takes into account six possible isomers. In Fig. 2.1 a flow diagram illustrating the OH-pathway is shown.
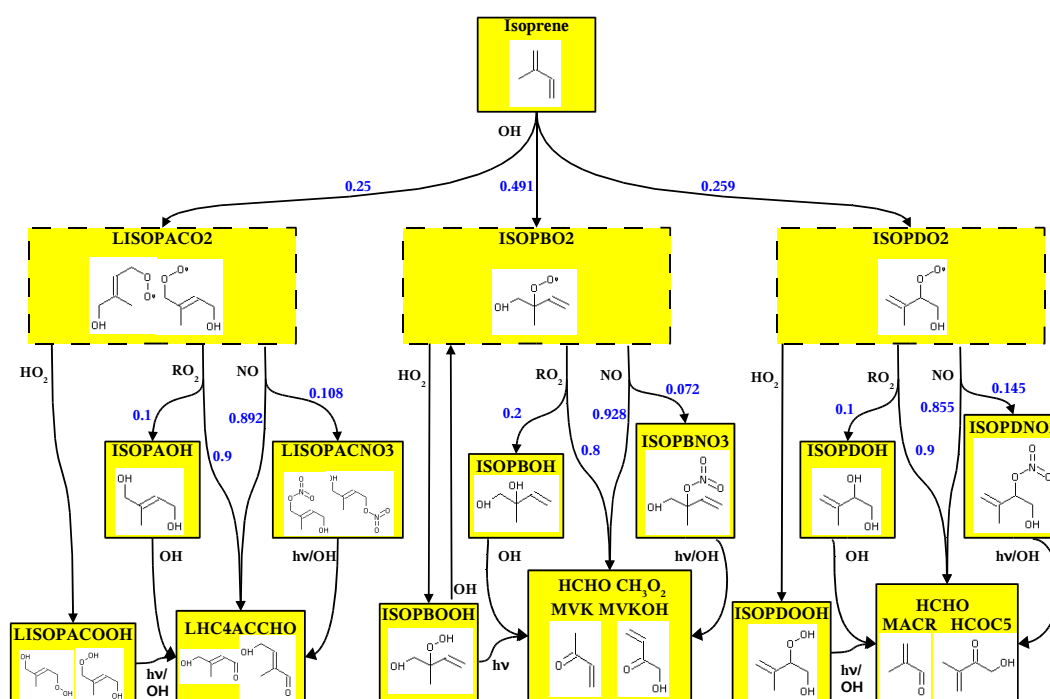
FIGURE 2.1: The OH-addition pathway in MIM2. The three short-lived peroxy radicals from isoprene are delimited by dashed lines. The branching ratios of each reaction are indicated in light blue.

MIM2, as well as MCM, implicitly assumes the OH-addition to occur only at position 1 and 4 with branching ratios being 0.655 and 0.345, respectively. The O_2-addition to the resulting alkyl radicals is assumed to be instantaneous. MIM2 considers the production of three different kinds of peroxy radicals (RO2), namely LISOPACO2, ISOPBO2 and ISOPDO2. They react with NO, NO_3, HO_2 and RO_2 according to the MCM protocol (Jenkin et al. (1997), Saunders et al. (2003)). Unlike MIM, MIM2 retains the permutation reaction formalism adopted in MCM and the production of diols from such reactions. It is a simplified parameterization in which each RO_2 reacts with a pool of $R'O_2$ at a pseudo-first-order rate (Madronich and Calvert (1990). The average alkyl nitrate yield from $RO_2 + NO$ reactions in MIM2 is 10%, as in the MCM. The yields of single isomers depend on the structure and are quite uncertain, and MIM2 enables sensitivity studies changing such yields. The species represented by LISOPACO2, namely ISOPAO2 and ISOPCO2, are not produced in equal amounts in MCM v3.1, but simulation tests showed that the corresponding products are always in a ratio of about 1:1. Since these species have identical reactivity and structurally similar products, the products have been lumped in LISOPACOOH (a lump of ISOPAOOH and ISOPCOOH), LHC4ACCHO and LISOPACNO3. They are the only first generation products that are lumped, where the term first generation denotes the first long-lived species produced in

the oxidation chain. In summary, the first generation products from the OH-pathway in MIM2 are:

- Hydroperoxides: LISOPACOOH, ISOPBOOH and ISOPDOOH

- Carbonyls: LHC4ACCHO, MVK, MVKOH, MACR and HCOC5

- Diols: ISOPAOH, ISOPBOH and ISOPDOH

- Alkyl nitrates: LISOPACNO3, ISOPBNO3 and ISOPDNO3

2.5 O_3-pathway

The ozonolysis of alkenes generates carbonyls and energetic Criegee biradicals (Atkinson and Arey (2003a)). The fate of such biradicals is described in Jenkin et al. (1997) as being a relaxation process that can yield significant amounts of OH. It consists mainly of decomposition to different products and of the production of a "thermalized" Criegee biradical. The branching ratios of such relaxation processes change according to the functional groups present and to the size of the molecule. OH is only produced in one of these decompositions, namely the hydroperoxide channel (Niki et al. (1987)). These thermalized biradicals in MCM are considered to react with H_2O, CO, NO, NO_2 and SO_2. For this, MIM2 follows the MCM protocol very closely. Since these relaxation reactions are very fast (higher than $1\,s^{-1}$) compared to the typical integration time step of 3-D models ($\approx$30 min.), MIM2 assumes that all ozonolysis reactions directly yield the corresponding final products. The thermalized Criegee biradicals are assumed to react only with H_2O since this is the predominant fate under tropospheric conditions (Jenkin et al. (1997)).

2.6   The NO_3-pathway

For the oxidation of isoprene by NO_3 MIM2 follows MCM closely until LISOPACNO3 and NC4CHO are formed. Only the reaction of the peroxy radical NISOPO2 (from $ISOP + NO3$) with NO_3 is neglected. It is worth noting that this radical was represented in MIM by the lumped species ISON (see Sect. 3.6.1), being treated as a long-lived species and not like an RO_2. Finally, the peroxy radicals from this pathway are treated similarly to the ones from the OH-pathway.

2.7 Unsaturated C_5-C_4-products

The treatment of hydroperoxides, diols and alkyl nitrates was discussed above in Sect. 2.4. Except for two species being lumped (LISOPACOOH and LISOPACNO3), their chemistry strictly follows MCM. Here we discuss the treatment of two other important C_4-C_5 groups.

2.7.1 Aldehydes

With respect to MACR (methacrolein) and its products like PAN, MIM2 follows MCM closely. The fate of the C_5-δ-hydroxy-carbonyls (LHC4ACCHO) is considered to be the average of the equally weighted reactions for HC4ACHO and HC4CCHO (MCM species). The OH-pathway for NC4CHO produces the lumped species LNISO3, consisting of equal parts of NC4CO3 (carboxylic RO_2) and C510O2 (alkyl RO_2). The subsequent reactions result from averaging both reactivities and product yields.

2.7.2 Ketones

For the chemistry of MVK (methyl vinyl ketone) MIM2 does not neglect any products. The OH-addition to it results in the production of a lumped species, LHMVKABO2, having the composition 0.3 HMVKAO2 + 0.7 HMVKBO2 (MCM species). A similar treatment is followed for MVKOH, and almost all the corresponding products are taken into account. However, a product of MVKOH photolysis, ALLYLOH (2-propen-1-ol), is neglected. The only C_5-ketone, HCOC5, is treated like in MCM.

2.8 C_3-C_2-products

The chemistry of C_3-C_2 products in MIM2 is explicit and close to MCM. Species like methylglyoxal and hydroxyacetone are not lumped together with other species as was the case in MIM. New species like propene, nitrooxy acetone, glycoladehyde, and glyoxal are present. In the case of propene the minor products of OH- and NO_3-addition, namely IPROPOLO2 and PRONO3AO2, are neglected since they behave similarly to the more abundant products. The peroxy acyl nitrate GLYPAN from glyoxal is neglected because it is found to be below 30 pmol/mol under all NO_x conditions studied.

Chapter 3

Mainz Isoprene Mechanism 2: Evaluation

3.1 Box model setup

The box model MECCA (Sander et al. (2005)) was used for this study. The model includes a kinetic preprocessor which automatically generates optimized Fortran90 code for the specific set of reactions. KPP-2.1 (Sandu and Sander (2006)), and the Rosenbrock 3rd order solver was used (Sandu et al. (1997)). From the comprehensive set of reactions, a subset of tropospheric gas-phase reactions was selected. Reactions of sulfur and halogen species were switched off in the model simulations. The box is considered to be 1 km long on each side and to be representative of the boundary layer. All the simulations start on 1st August 2000, at midnight and the latitude is set to 10° S, corresponding roughly to the Amazon forest. The relative humidity and the pressure are set to be 70% and 101 325 Pa respectively. A diurnal cycle for light and temperature was applied. The function used for the temperature cycle is a sinusoidal (Heard et al. (1998)) with values varying between 294 and 308 K and an average of 301 K:

$$T = 301 + 7 \times \sin(\frac{2\pi}{86400} \times t - 1.9635) \tag{3.1}$$

where t is the time in seconds. The photolysis rates from MCM v3.1 are used (Saunders et al. (2003)) for MCM, MIM and MIM2, while the solar zenith angle dependency used was the one included in MECCA. Only species that are not lumped in any of the mechanisms studied here were initialized with non-zero mixing ratios (see Table 3.1).

For simplicity the initialization does not change in any of the NO_x scenarios presented here. The isoprene flux was calculated using the equations given in Guenther

TABLE 3.1: Initial mixing ratios of species under the three scenarios here presented.

Species formula	initial mole fraction $(\mathrm{mol\,mol^{-1}})$
H_2O	0.01851
O_3	30×10^{-9}
H_2O_2	7×10^{-9}
NH_3	100×10^{-12}
NO_2	100×10^{-12}
NO	10×10^{-12}
$HONO$	40×10^{-14}
HNO_3	5.0×10^{-12}
CH_4	1.8×10^{-06}
$HCHO$	5.0×10^{-09}
CO	100×10^{-09}
CH_3OH	500×10^{-12}
CH_3OOH	4.0×10^{-09}
$HCOOH$	350×10^{-12}
$CH_3C(O)O_2NO_2$ (PAN)	100×10^{-12}
CH_3CO_2H	2.0×10^{-09}
CH_3CO_3H	1.5×10^{-09}
CH_3COCH_2OH	4.0×10^{-09}
CH_3COCHO	500×10^{-12}
C_5H_8 (isoprene)	2.0×10^{-09}

et al. (1995) and assuming an average photosynthetically active radiation (PAR) flux of $1000\,\mu\,\mathrm{mol\,m^{-2}\,s^{-1}}$. The maximum isoprene flux reached at noon was $7.887{\times}10^{11}$ molecule $\mathrm{cm^{-2}\,s^{-1}}$. Guenther et al. (2006) present a more sophisticated calculation of the isoprene emission depending on many more parameters compared to the one presented in Guenther et al. (1995). However, the differences in global estimates are 67 Tg/yr, well below the uncertainty range of the estimates themselves. Moreover, for a box model evaluation of mechanisms for isoprene oxidation any emission function can be used. The use of such a function serves the purpose of having a diurnal cycle for the isoprene emission that is not far off from reality. The base NO flux was constant and equal to $3.33{\times}10^9$ molecule $\mathrm{cm^{-2}\,s^{-1}}$. Three main NO_x scenarios were examined. One is the base emission scenario noted above and the other two are 10 and 100 times higher than the base emission rate, respectively. They will be referred to as, the low- , mid- and high-NO_x scenarios, respectively. Besides the isoprene and the NO_x emissions, no further emission or deposition of species was included in the simulations.

As can be seen in Figs. 3.1,3.3 and 3.5, a comparison of three reduced mechanisms versus MCM is performed. These mechanisms are:

- MIM2 (this study)

- MIM (Pöschl et al. (2000).

- MIMvK, which is MIM as implemented in Sander et al. (2005) and Jöckel et al. (2006). This version differs from the original one with the alkyl nitrate yield being increased from 4.4% to 12% as assumed by (von Kuhlmann et al. (2004)) based on (Sprengnether et al. (2002)) and with a few updates of the rate constants.

3.2 Oxidation pathways of isoprene and RO_2

The destruction of isoprene and all its peroxy radicals has been budgeted and the corresponding cumulative losses are shown in Table 3.2.

The most important oxidation pathway for isoprene is reaction with OH, ranging between $\approx$68 and 80% of the total loss depending on the NO_x mixing ratios. Reaction with O_3 is relatively more important in low-NO_x conditions ($\approx$31%). Finally, the reaction with NO_3 turns out to account for less than 1% of the total isoprene loss in unpolluted environments but it can exceed 10% in high-NO_x regimes.

The largest loss for the peroxy radicals in low-NO_x conditions is the reaction with HO_2 ($\approx$51%), while under high-NO_x conditions the reaction with NO predominates ($\approx$75%). Reactions with NO_3 are not very important under any of the conditions studied, though they can account for about 4% of the total loss under high-NO_x conditions. It is worth noting that the self- and cross-reactions ($RO_2 + R'O_2$) account for about 25% of the total loss in low-NO_x. This confirms the importance of such reactions in the oxidation of organics in the gas-phase as indicated previously by Madronich and Calvert (1990).

3.3 Low-NO_x regimes

3.3.1 MCM behaviour

In this scenario the NO emission rate was set to be 3.33×10^9 molecule $cm^{-2} s^{-1}$. In Fig. 3.1 the mixing ratios of the most important tracers are shown. The ozone mixing ratio shows that the chemical system is close to the turning point between the O_3-producing (mid-NO_x) and O_3-depleting (low-NO_x) regimes. OH and isoprene have reached an approximate photostationary state after 5 days, with maximum values of about $6.5 \cdot 10^5$ molecule cm^{-3} and 6 nmol mol^{-1}, respectively.

TABLE 3.2: Diurnal averages for the 5th day of simulation for the cumulative loss of isoprene and RO_2 (CH_3O_2 included) and the relative differences between MCM and MIM2 for selected species.

	low-[NO_x]	mid-[NO_x]	high-[NO_x]
scenario parameters			
NO emiss. ($cm^{-2} s^{-1}$)	3.33×10^9	3.33×10^{10}	3.33×10^{11}
[NO_x]max ($nmol\,mol^{-1}$)	0.128	0.765	5.066
Isoprene losses (%)			
L_{OH}	67.86	72.63	79.50
L_{O_3}	31.26	19.26	8.091
L_{NO_3}	0.8833	8.110	12.41
RO_2 losses (%)			
L_{NO}	24.46	50.34	75.22
L_{HO_2}	50.51	35.97	16.78
$L_{R'O_2}$	25.02	13.42	3.660
L_{NO_3}	<0.01	0.2678	4.338
average relative biases			
100*(MIM2-MCM)/MCM (%)			
O_3	1.115	1.095	−0.6258
OH	1.388	1.834	4.400
HO_2	−0.9017	−0.1166	4.482
H_2O_2	−0.3620	−0.3668	0.5766
NO	−0.4443	−2.771	−150.1[a]
NO_2	2.422	1.240	2.125
HNO_3	1.561	3.338	0.3348
CH3OH	2.472	1.782	1.760
CH3OOH	1.525	1.079	2.140
HCHO	0.07727	−0.8609	−0.8305
CO	−0.2780	−0.3393	−0.8868
HCOOH	−0.4829	−1.368	−1.665
CH3CHO	2.377	−4.131	−5.217
CH3CO2H	2.312	1.961	1.929
PAN	5.574	3.436	2.890
HOCH2CHO	8.901	−1.681	−2.993
GLYOX	−1.800	−0.8294	11.49
C3H6	−0.6624	−2.563	−0.8083
NOA	1.073	2.015	2.600
ACETOL	−0.4158	0.4043	3.176
MGLYOX	5.285	2.793	3.166
MPAN	1.963	0.1996	−0.1643
MVK	0.1867	−1.471	−0.5412
MACR	−0.1962	−1.506	−1.714
ISOPBOH	0.9588	−0.3463	−0.1618
ISOPBOOH	−0.7308	−1.788	−0.8294
ISOPBNO3	0.3808	−1.932	−2.417
ISOPDOH	0.2964	−0.1322	−3.129
ISOPDOOH	−1.446	−1.643	−4.978
ISOPDNO3	−0.1476	−1.885	−3.888
NC4CHO	2.569	−0.5616	−2.098
C5H8	−1.137	−4.022	62.40[a]

[a] The value has little significance as it was found to be result of very small absolute biases at night when the concentrations of the tracer are close to zero.

3.3.2 MIM2 and MIM behaviour and biases

In Fig. 3.2 the biases relative to MCM for the species presented in Fig. 3.1 are shown. MIM2, unlike MIM, is mass-conserving with respect to carbon, as can be seen from the CO and HCHO mixing ratios. For instance, in MIM there is the following non-mass
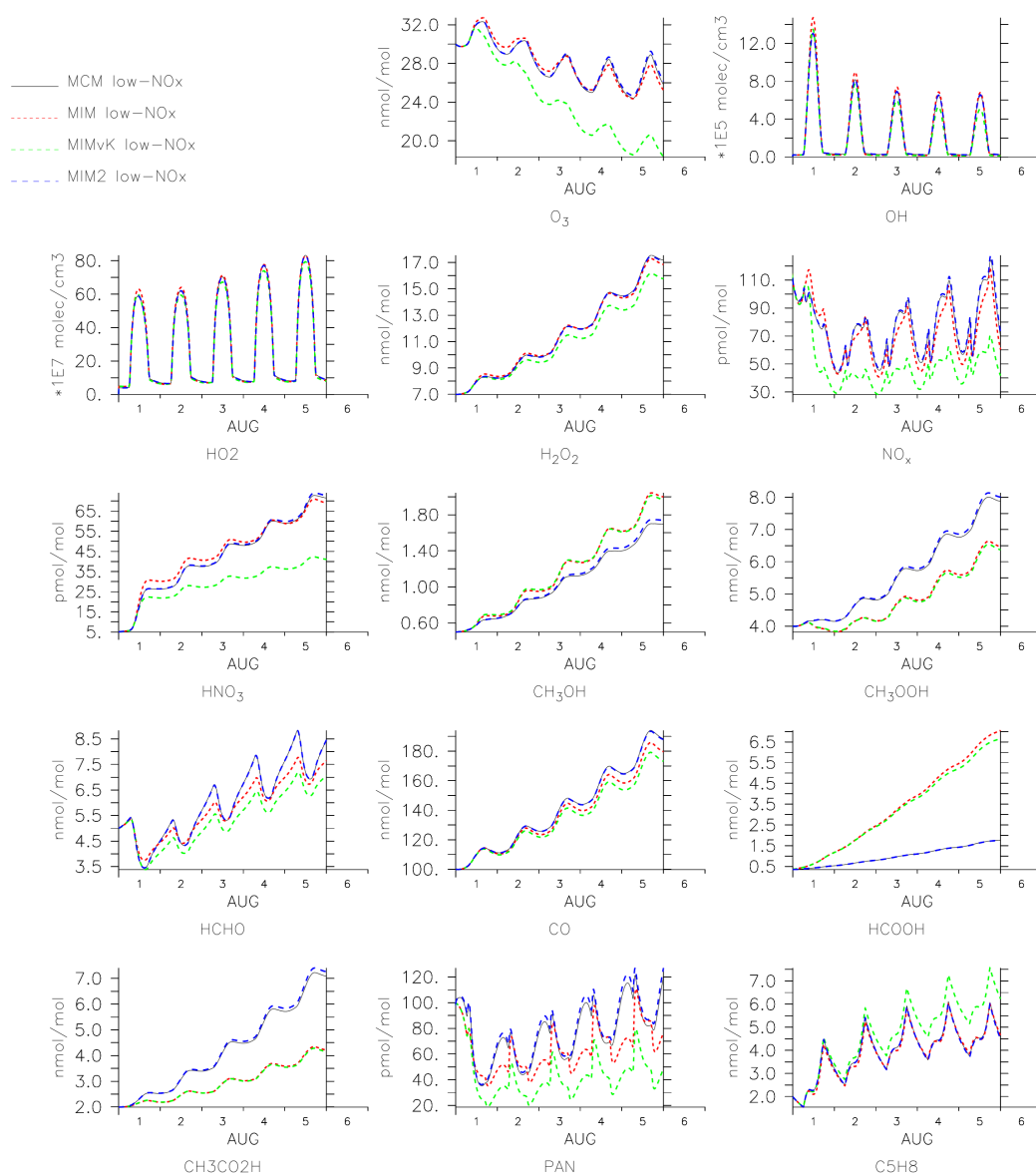
FIGURE 3.1: Low-NO$_x$ scenario: comparison of MCM, MIM, MIMvK and MIM2.

conserving reaction,

$$ISO_2H + OH \rightarrow MACR + OH \tag{R1}$$

with a rate constant $k=10^{-10} \, cm^3 \, molecule^{-1} \, s^{-1}$. In this reaction ISO$_2$H is a C$_5$-hydroperoxide and MACR reacts as a lumped C$_4$-carbonyl within the mechanism. Moreover, the ozonolysis of isoprene and MACR is not mass-conserving in MIM either. In these two reactions, product yields account for only 4.28 C atoms instead of 5, and 3.57 instead of 4, respectively. These are not the only reactions in MIM where carbon mass disappears. The contribution of isoprene oxidation to CO production in the atmosphere has been estimated by Kanakidou and Crutzen (1999) to be 330 Tg/yr, about 13.5%
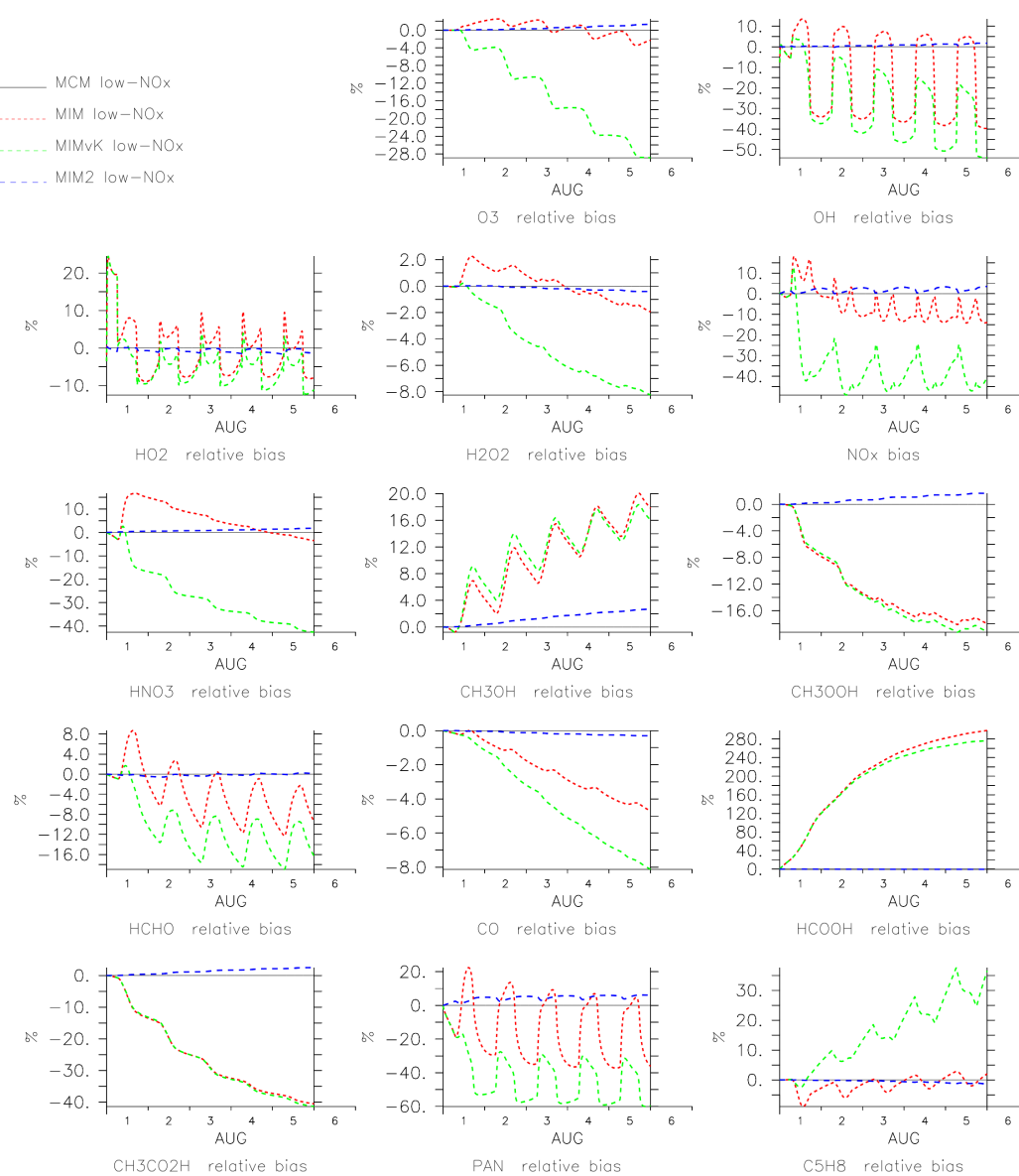
FIGURE 3.2: Low-NO$_x$ scenario: relative biases, 100*(mechanism-MCM)/MCM, of MIM, MIMvK and MIM2.

of the total estimated source. The MIM bias for CO grows steadily in absolute terms and reaches about -5% after a 5 day simulation while the MIM2 bias reaches only $\approx -0.02\%$. The CO-yield is thus higher in MIM2 compared to MIM. This might not hold in 3-D atmospheric model simulations because of dry deposition and scavenging. In fact, MIM2 differs remarkably from MIM with respect to the total alkyl nitrates and the hydroxy-peroxides from C_2 to C_5 (see Sect. 3.6). Such species are believed to be very soluble and reactive and can deposit efficiently with Henry's law coefficients in the range of $0.1 - 5 \cdot 10^5$ M atm^{-1} (Sander (1999), Shepson et al. (1996), Treves et al. (2000, and references therein)).

MIM neglects the formation of a few important species from isoprene oxidation: acetaldehyde (CH_3CHO), glycolaldehyde ($HOCH_2CHO$), glyoxal ($CHOCHO$), propene ($CH_3CH{=}CH_2$) and α-nitrooxy acetone ($CH_3C(O)CH_2OONO_2$) (see Table 3.2 and Fig. A.1,A.2 and A.3 for MIM2 comparisons with MCM results). They are not considered, neither as single species, nor as part of lumped species. MIM2 drastically reduces the bias for species like formaldehyde ($HCHO$), peroxy acetyl nitrate (PAN), carbon monoxide (CO), acetic acid ($CH_3C(O)OH$), formic acid ($HCOOH$) and methanol (CH_3OH) by the improved treatment of ozonolysis reactions, in particular the reaction $ISOP + O_3$ (see Sect. 2.5). From a simple budgeting (see Table 3.2), this latter reaction turns out to account for about 31% of the total destruction of isoprene in the low-NO_x scenario. It can be seen from Fig. 3.2 how these MIM biases for the above mentioned species increase over night. In particular, the large MIM bias for PAN (up to nearly -40%) is due to a much lower yield of CH_3CO_3 from the ozonolysis reactions. This yield from the isoprene ozonolysis is equal to 0.1 in MIM, versus 0.1575 in MIM2. These biases for MIM are all negative except for $HCOOH$ and CH_3OH. The production of methyl peroxy radical (CH_3O_2) within MIM2 is essential to adequately reproduce the mixing ratios of methanol (CH_3OH) and methyl hydroperoxide CH_3OOH. The atmospheric production of CH_3OH through the permutation reactions of CH_3O_2 was estimated recently to be about $38\,\mathrm{Tg/yr}$ (Jacob et al. (2005), Millet et al. (2008b)). This amounts to nearly 16% of the total estimated global source, and MIM2 reduces the uncertainties in this term. The overestimation of CH_3OH in MIM is due to a too high CH_3O_2 yield from the ozonolysis reactions. On the other hand the CH_3OOH underestimation is due to the complete absence of CH_3O_2 production from the reactions of the C_5-peroxy radicals and peroxides. These two reactions turn out to be important for CH_3OOH production because they take place mostly during daytime when the HO_2 concentration peaks. The production of CH_3O_2 in MCM takes place in the decomposition channel of the tertiary alkoxy radical ISOPBO that yields hydroxy-methyl vinyl ketone, MVKOH.

Unlike MIM, the MIM2 biases for the species in Fig. 3.2 are always lower than 6%. They often have constant signand grow slowly. Overall the mechanism referred to as MIMvK performs very poorly in computing O_3 and isoprene under these conditions. This is due to the representation of the alkyl nitrates (see Sect. 3.6.1). The amount of NO_x that is sequestered by the alkyl nitrates is too high, so that OH and O_3 are reduced substantially. Such differences between MIMvK and MIM are not seen when the NO emissions are increased by a factor of 10, as discussed in the next section.
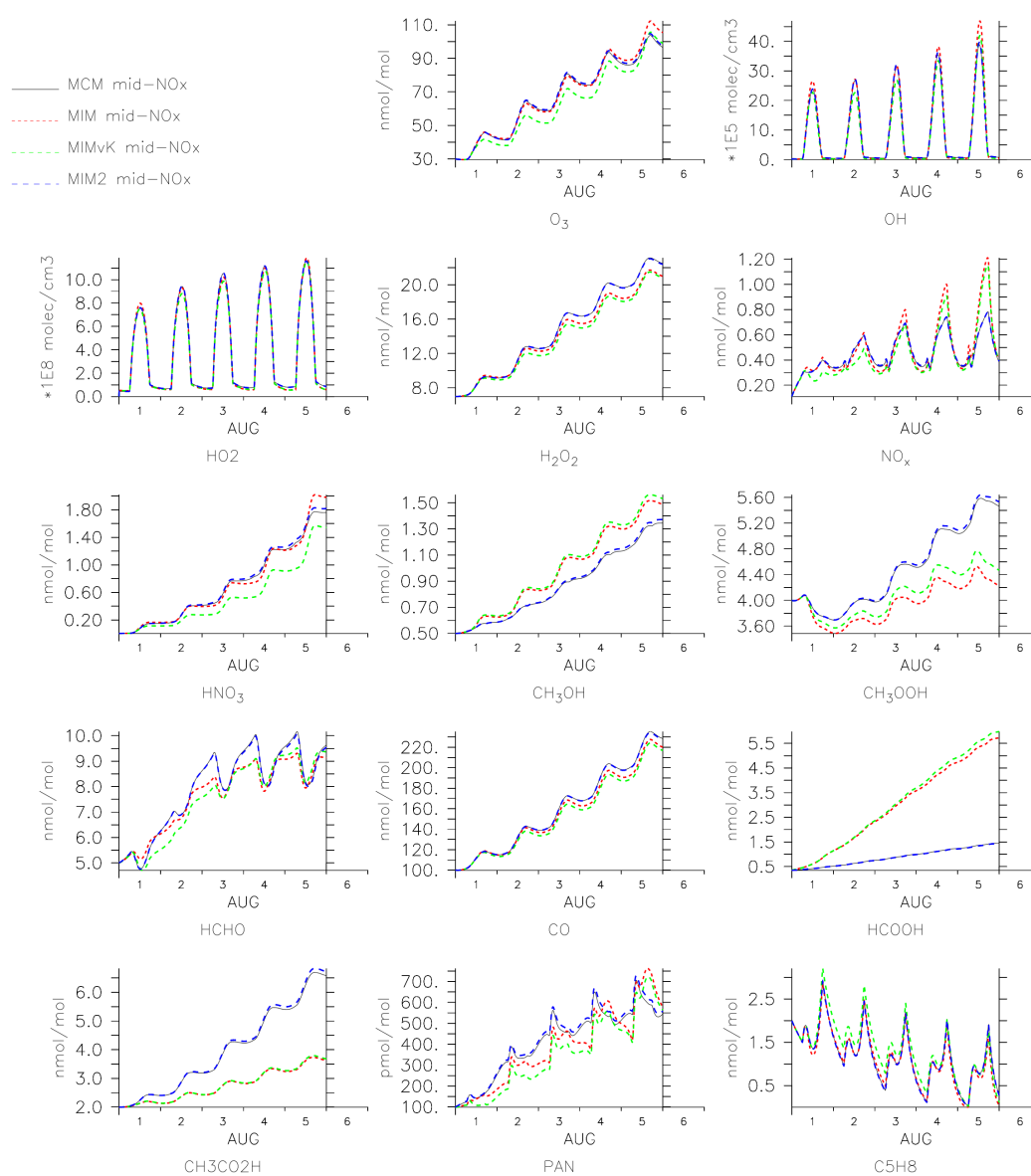
FIGURE 3.3: Mid-NO_x scenario: comparison of MCM, MIM, MIMvK and MIM2.

3.4 Mid-NO_x regimes

3.4.1 MCM behaviour

In this scenario the NO emission rate was set to be 3.33×10^{10} molecule cm^{-2} s^{-1}. In Fig. 3.3 the mixing ratios of the most important tracers are shown. The ozone and NO_x mixing ratios clearly show that the system is in the O_3-producing regime. The OH concentration keeps increasing and reaches values of about one order of magnitude higher than seen in the low-NO_x scenario (cf. Fig. 3.1). After 5 days, it peaks at about
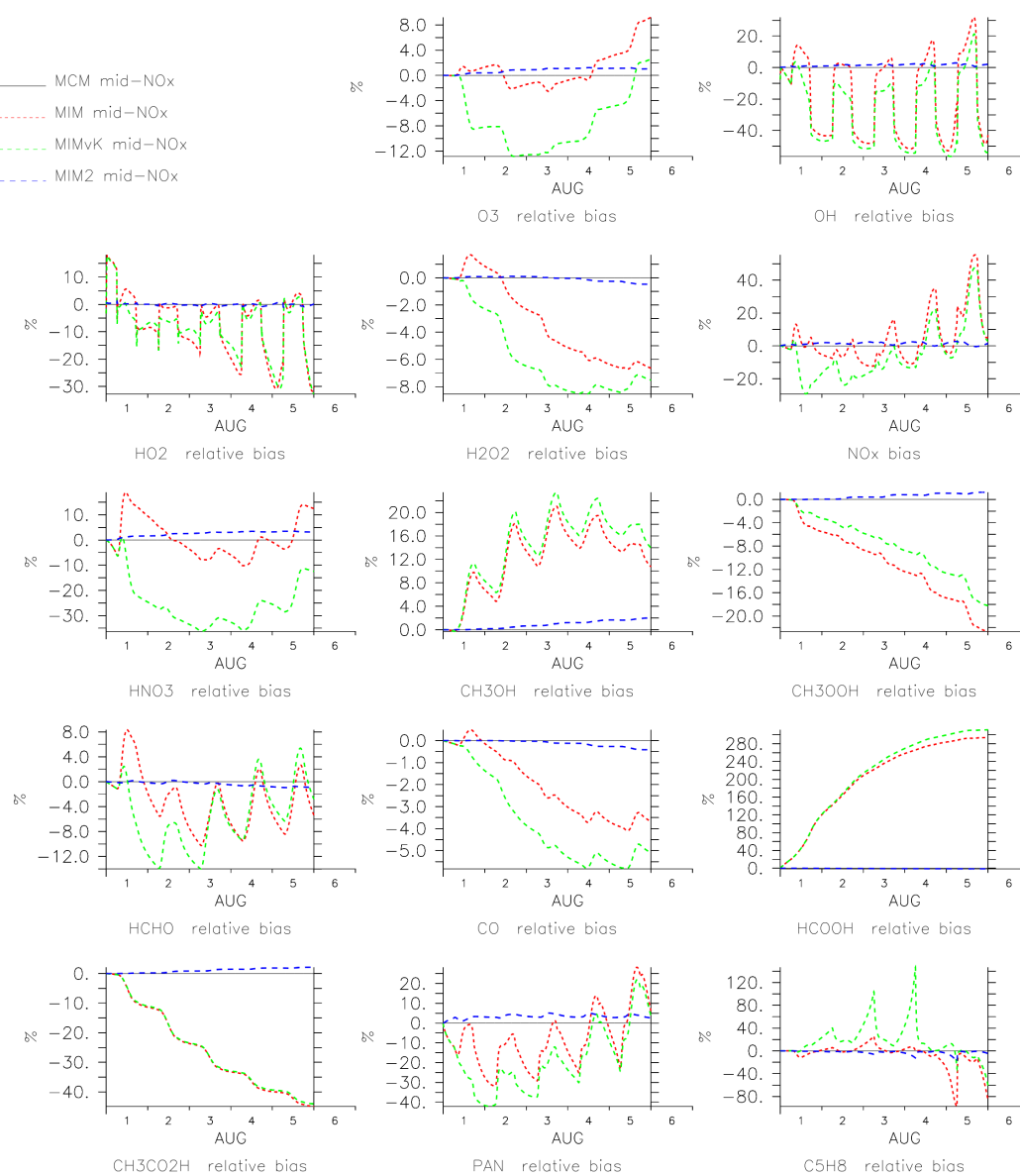
FIGURE 3.4: Mid-NO$_x$ scenario: relative biases, 100*(mechanism-MCM)/MCM, of MIM, MIMvK and MIM2.

$4 \cdot 10^6$ molecule cm^{-3}. None of the species, except isoprene and HCHO, reach photostationary state. Compared to the low-NO$_x$ scenario, both NO$_x$ and PAN have a different diurnal cycle. Their mixing ratios do not have a secondary maximum shortly after midnight and continue to peak in the late afternoon and in the morning, respectively.

3.4.2 MIM2 and MIM behaviour and biases

Between the fourth and the fifth day of simulation time isoprene in MCM is depleted to nearly zero (see Fig. 3.3). Small differences in absolute terms between the different mechanisms are expected to result in quite large relative biases. For instance, when MCM computes isoprene concentrations very close to zero (during nighttime), both MIM and MIM2 give the largest relative biases with respect to isoprene itself (see Fig. 3.4). There is no clear tendency for the MIM2 average relative biases for all species to be better or worse for this scenario compared to the low-NO_x scenario (cf. Figs. 3.2 and 3.4). Even though the sign changes for some, they remain whithin the 5% range (see Table 3.2). The other two reduced mechanisms, MIM and MIMvK, show many biases similar to the biases in the low-NO_x scenario. What is striking, however, are the large biases with respect to OH, NO_x and PAN. The explanation lies in the differences regarding the organic nitrogen reservoirs in such mechanisms (see Sect. 3.6). The MIM bias for OH reaches +30% during daytime while for NO_x it reaches more than +50%. It is worth noting that in contrast to the low-NO_x scenario, the MIM relative bias for H_2O_2 starts to be substantial, reaching $\approx -7\%$. The H_2O_2-yield from ozonolysis of isoprene is 11% in MIM2 and 9% in MIM. Moreover, the ozonolysis of C_5- and C_4-carbonyls in MIM does not produce H_2O_2.

3.5 High-NO_x regimes

3.5.1 MCM behaviour

In this scenario the NO emission rate was set to 3.33×10^{11} molecule $cm^{-2} s^{-1}$. In Fig. 3.5 the mixing ratios of the most important tracers are shown. O_3 is produced very efficiently, reaching 200 nmol mol^{-1}, and OH peaks with concentrations always higher than $1 \cdot 10^7$ molecule cm^{-3}. PAN reaches values of 1.5 nmol mol^{-1} and HCHO reaches photostationary state after 3 days simulation time. NO_x peaks in the morning at values around 5 nmol mol^{-1} and a large part of the total nitrogen is stored as HNO_3, reaching a mixing ratio of more than 45 nmol mol^{-1} at the end of the simulation. HCOOH and $CH_3C(O)OH$ mixing ratios grow much less compared to the other NO_x scenarios.

3.5.2 MIM2 and MIM behaviour and biases

Under the high-NO_x regime both MIM and MIM2 show modest relative biases for O_3 being always within 1% (see Fig. 3.6).
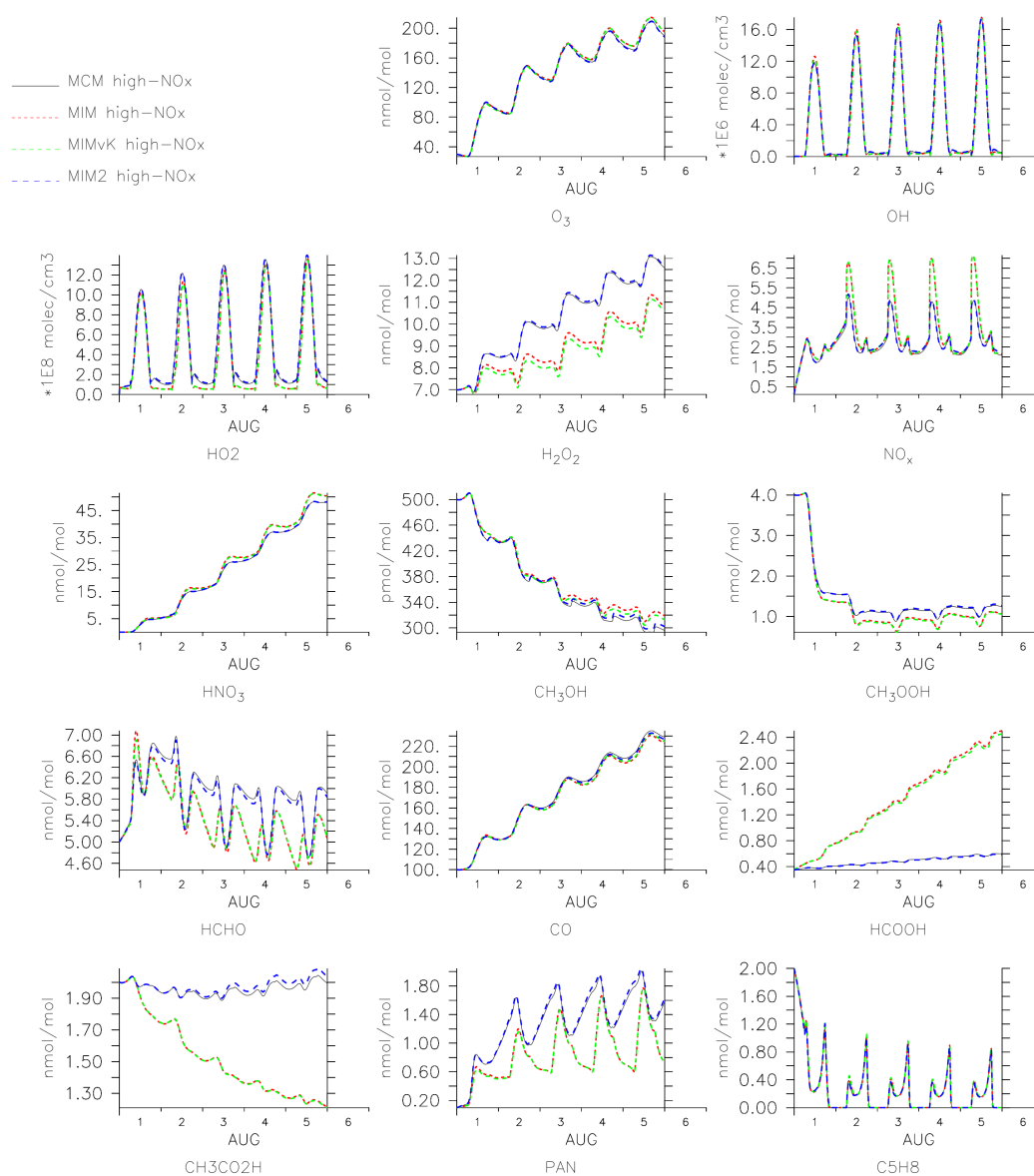
FIGURE 3.5: High-NO$_x$ scenario: comparison of MCM, MIM, MIMvK and MIM2.

As expected, MIM2 has a large average relative bias of -62.4% for isoprene and -150% for NO (see Table 3.2) that correspond, however, to small absolute biases when the mixing ratios are at night close to zero. Moreover, glyoxal shows a substantial average relative bias of about 11% mostly due to the lumping in the NO$_3$-pathway (see Table A.3). This bias grows significantly at night and becomes close to zero during the day (see Fig. A.3). In fact, the species LNISO3 is a lumped species representing two different kinds of RO$_2$, with one being alkyl and the other one acyl and having glyoxal and NOA as a reaction products, respectively. Besides isoprene, glyoxal and NO, there is no clear tendency for the MIM2 average relative biases for all other species to be better or worse for this scenario compared to the other NO$_x$ scenarios (cf. Figs. 3.2, 3.4 and
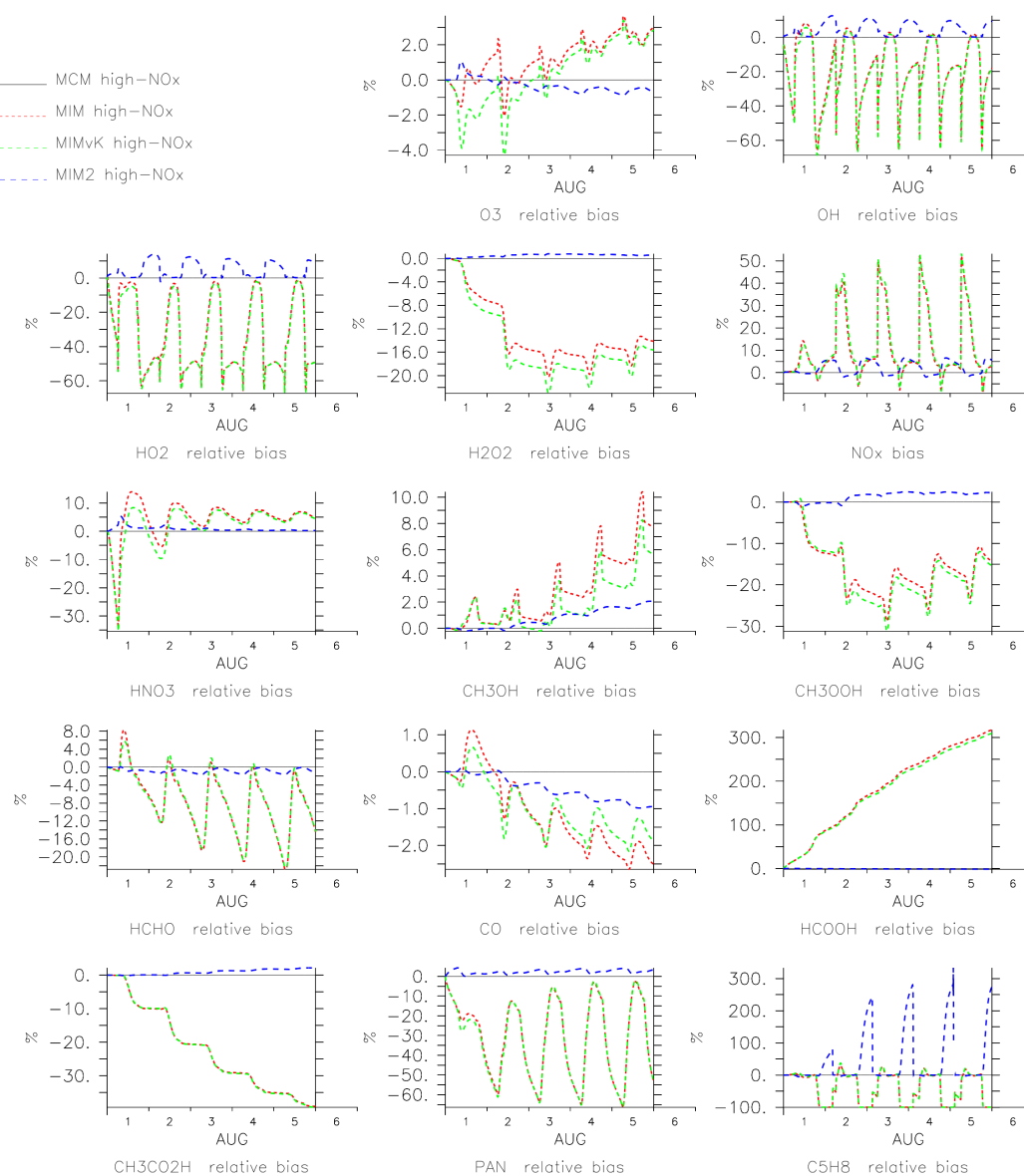
FIGURE 3.6: High-NO$_x$ scenario: relative biases, 100*(mechanism-MCM)/MCM, of MIM, MIMvK and MIM2.

3.6). The MIM relative bias for H$_2$O$_2$ becomes rather large, reaching $\approx$ -20%. Under such high-NO$_x$ regimes, isoprene ozonolysis contributes little to the production of H$_2$O$_2$ because it accounts for only $\approx$8% of the total isoprene destruction (see Table 3.2). The OH- and NO$_3$-pathways now account for $\approx$92% of the isoprene destruction, while in the mid-NO$_x$ and low-NO$_x$ scenarios they account for $\approx$81 and 69%, respectively. The total yield of the C$_5$-carbonyls in the high-NO$_x$ scenario is increased because they are not produced in the O$_3$-pathway. The ozonolysis of such species in MIM does not produce any H$_2$O$_2$.
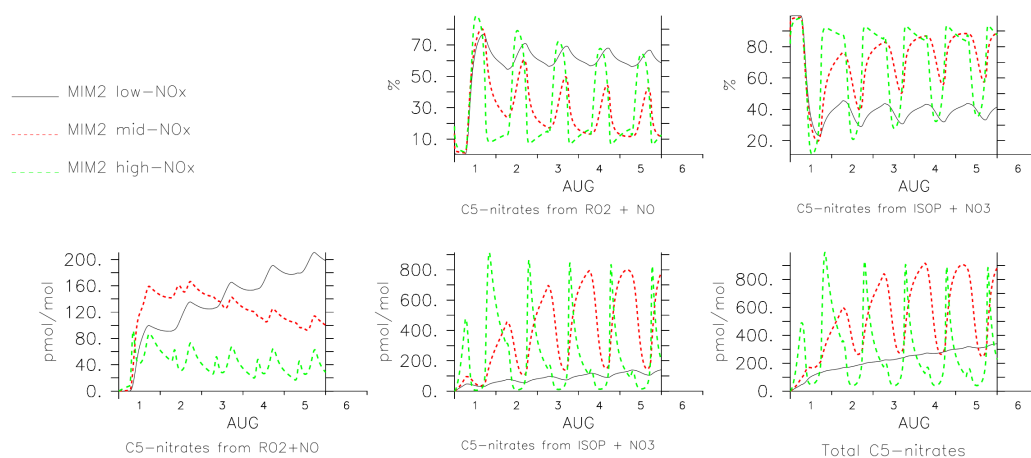
FIGURE 3.7: Alkyl nitrates in MIM2 under different NO$_x$-regimes

3.6 Organic nitrogen and peroxides

3.6.1 Alkyl nitrates

There are eight alkyl nitrates included and they can be subdivided in three groups (see Table A.1). The first group includes three C$_5$−alkyl nitrates produced by RO$_2$ + NO reactions in the OH-pathway. One has an internal double bond (LISOPACNO3) and two have an external double bond (ISOPBNO3 and ISOPDNO3). The second group includes three alkyl nitrates produced by the NO$_3$-pathway with NC4CHO and NISOPOOH having an internal double bond and LNISOOH with all carbon atoms being saturated. Finally, the third group includes two C$_3$-alkyl nitrates. One is α-nitrooxy acetone (NOA), which is produced during the oxidation of the above mentioned alkyl nitrates. The other one is PR2O2HNO3 (see Table A.3), which is produced after the NO$_3$-addition to propene. It is worth noting that one alkyl nitrate from the OH-pathway (LISOPACNO3) is produced in the permutation reaction of NISOPO2 in the NO$_3$-pathway as well (see Table reftab:reactions). The chemistry of the alkyl nitrates in MCM and MIM2 is treated in a simplified manner. However, it is easily extendable, for example including ozonolysis reactions as in two recent models (Giacopelli et al. (2005), Horowitz et al. (2007).

The mixing ratios of the MIM2 C$_5$-alkyl nitrates are shown in Fig. 3.7 in the three different NO$_x$ scenarios.

It can be seen that the relative distributions of the alkyl nitrates from the two pathways changes drastically with NO$_x$ levels. In the low-NO$_x$ scenario the C$_5$-alkyl nitrates from the OH-pathway always dominate with respect to the ones from the NO$_3$-pathway. In fact, they account for between 55–75% of the total C$_5$-alkyl nitrates. As the system

changes towards the high-NO_x regimes, the diurnal cycles of C_5-alkyl nitrates become very pronounced. Under such conditions the C_5-alkyl nitrates from the NO_3-pathway start to dominate during nighttime, accounting for about 90% of the total nitrates. In two recent studies using very reduced isoprene oxidation mechanisms, it was estimated that the total fraction of the C_5-alkyl nitrates produced at night ranges from 50% to more than 60% (Horowitz et al. (2007), von Kuhlmann et al. (2004)). When MIM2 is implemented in a global atmospheric model, the C_5-alkyl nitrates from the two pathways are produced in roughly the same amounts (see Sect. 3.8). MIM considers only one C_5-alkyl nitrate (ISON) produced by both the OH- and NO_3-pathways. The peroxy radical that should result from the addition of NO_3 to isoprene is assumed to go directly into ISON, which has the properties of a long-lived species. In fact, this lumped species in MIM reacts with OH, yielding hydroxyacetone and nitroxyacetaldehyde (called NALD in MIM). The rate constant assigned to this reaction is $k = 1.3 \cdot 10^{-11} \mathrm{cm}^3 \, \mathrm{molecule}^{-1} \, \mathrm{s}^{-1}$, being a factor between 3 and 9 lower than the actual rate constants for the single isomers that ISON represents. The rate constant for that reaction is artificial and was used by Pöschl et al. (2000) to strongly tune MIM to the MCM results. Moreover, the species NALD, and called in NO3CH2CHO in MCM, is actually a product of 1,3-butadiene and 2-methylbut-3-en-2-ol oxidation. Furthermore, we note that in such a reaction there is no release of NO_2 as for the alkyl nitrates resulting from the OH-pathway. We note that the treatment of the alkyl nitrates in MCM is also to an extent simplified. Overall this causes MIM to accumulate too much nitrogen in the alkyl nitrates (relative bias up to 900% in high-NO_x scenario), delaying considerably the release of NO_2 down the oxidation chain. Since MIM2 considers eight alkyl nitrate species, it is a very appropriate tool to constrain the chemistry of alkyl nitrates with field data and an atmospheric chemistry model like in Horowitz et al. (2007). In that study their model was found to fit the field data the best with a 4% yield of alkyl nitrates from the reaction of isoprene peroxy radicals with NO. By contrast, MCM was found to match chamber data experiments with an average yield of 10% from such reactions (Pinho et al. (2005)). The MIM2 relative biases for NOA are very small as well. By contrast, we show in Figs. 3.8–3.10 MIM computing large relative biases either for the alkyl nitrates or for NOA (compared to NALD from MIM). The chemistry and the physical properties, such as solubility, of the C_5-alkyl nitrates and NOA are rather different, with the former ones having a double bond and an hydroxy group and the latter with none of these. Hence, the interplay between the chemistry, deposition and transport is expected to be non-negligible in a 3-D atmospheric chemistry model.
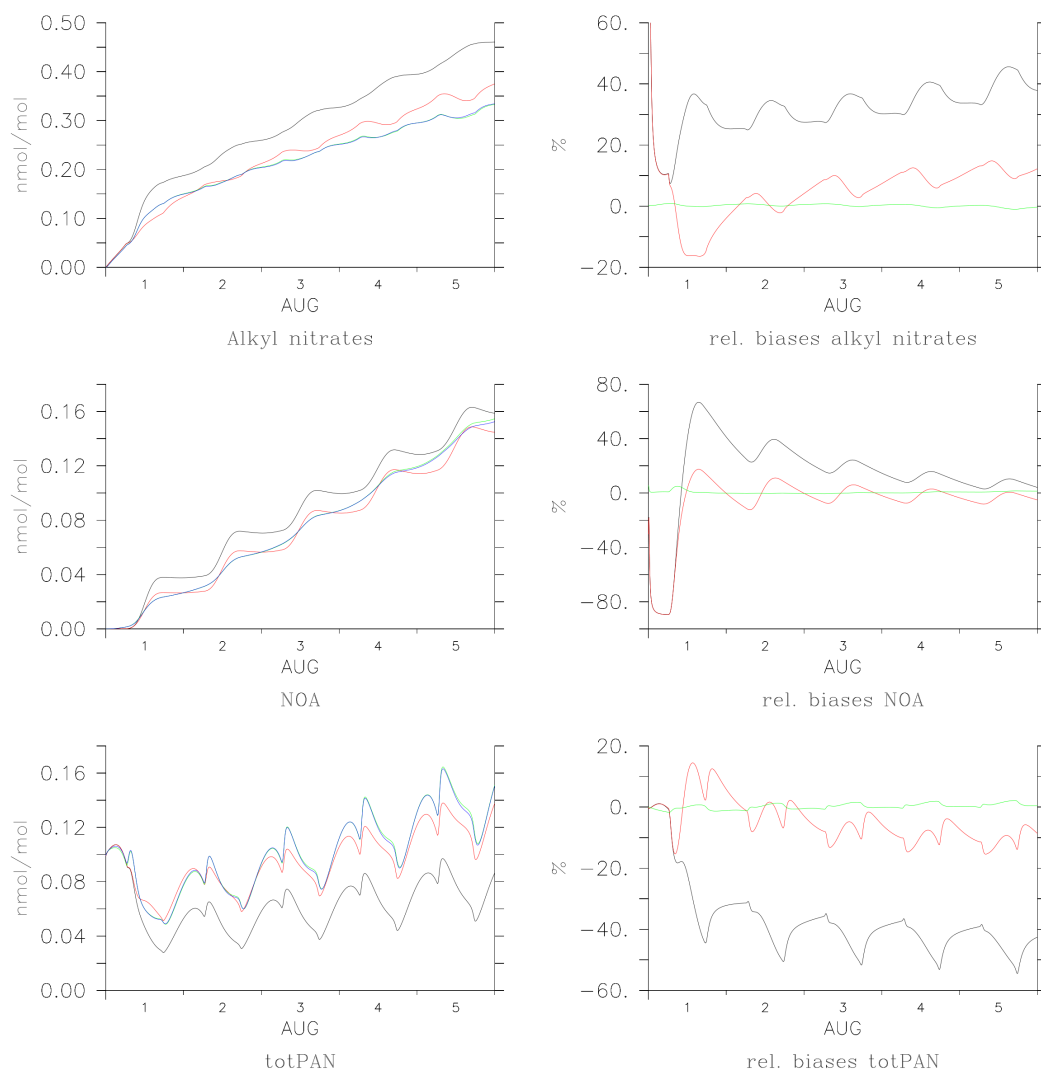
FIGURE 3.8: Nitrogen reservoirs in low-NO$_x$ scenario. In all the plots the actual mixing ratios of each species are presented with MIMvK (black line), original MIM (red line), MIM2 (blue line) and MCM (green line). The alkyl nitrates shown here are the sum of all alkyl nitrates except NOA (shown separately).

3.6.2 Peroxy acyl nitrates

PAN and its homologues have the general formula RC(O)OONO$_2$, and the isoprene mechanism in MCM considers 11 of them. MIM2 considers four peroxy acyl nitrates. In the low-NO$_x$ scenario the MIM2 relative bias for the total peroxy acyl nitrates is in the 5% range, while in the other two NO$_x$ scenarios it reaches values as low as -15% (Figs. 3.8–3.10). In all cases the largest deviations from the MCM results occur during nighttime when temperatures favour the formation of RC(O)OONO2. This indicates a lower capacity of the reduced mechanism to store nitrogen in this reservoir.
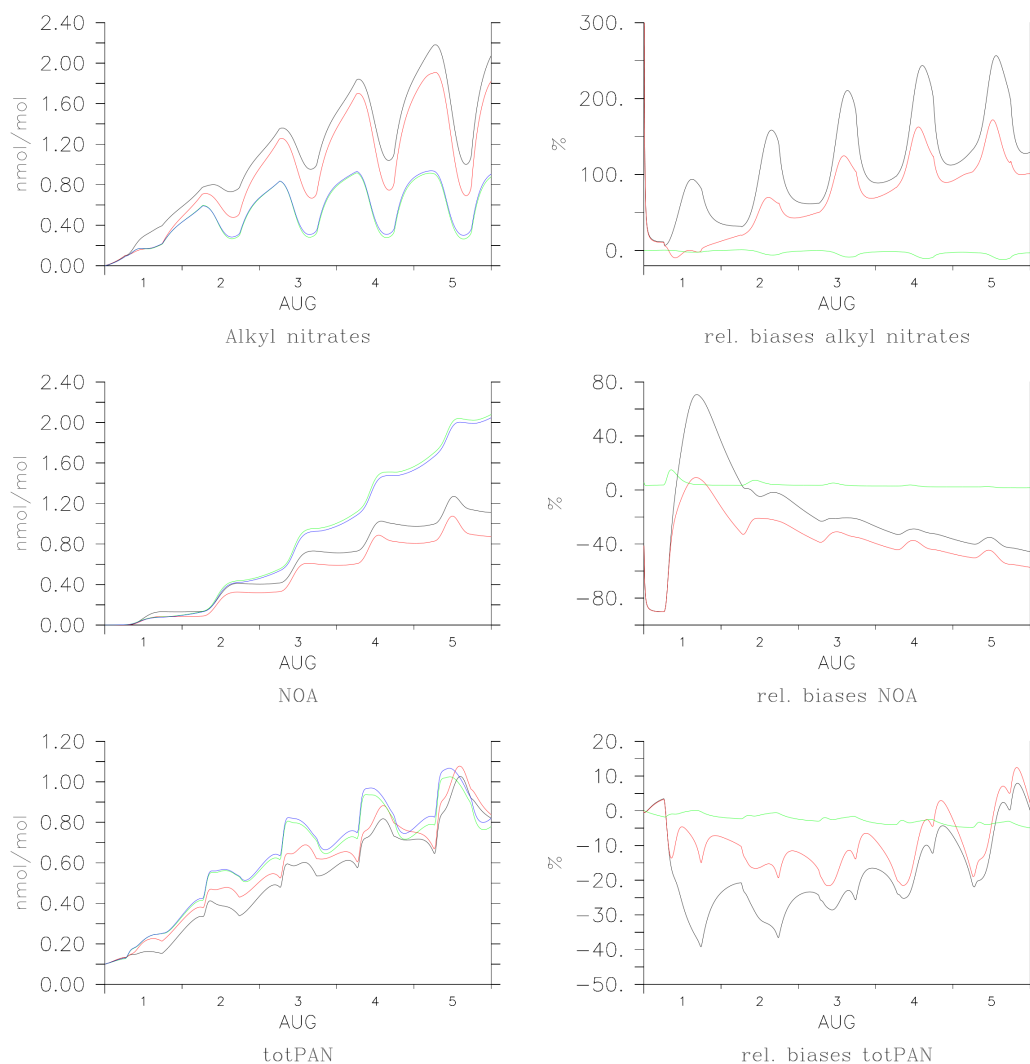
FIGURE 3.9: Nitrogen reservoirs in mid-NO_x scenario. In all the plots the actual mixing ratios of each species are presented with MIMvK (black line), original MIM (red line), MIM2 (blue line) and MCM (green line). The alkyl nitrates shown here are the sum of all alkyl nitrates except NOA (shown separately).

3.7 C_2-C_5 **peroxides**

Comparisons of the higher organic peroxides from the reduced mechanisms are shown for all NO_x scenarios considered here (see Figs. 3.11–3.13). Large MIM2 biases are computed only for the high-NO_x conditions. They originate from the nighttime chemistry that is simplified in MIM2, neglecting an important sink for the peroxy radicals, namely its reaction with NO_3 radicals (see Sect. 3.5.2). Clearly the biases grow during nighttime when NO_3 mixing ratios are non-negligible, while during daytime they decrease substantially.
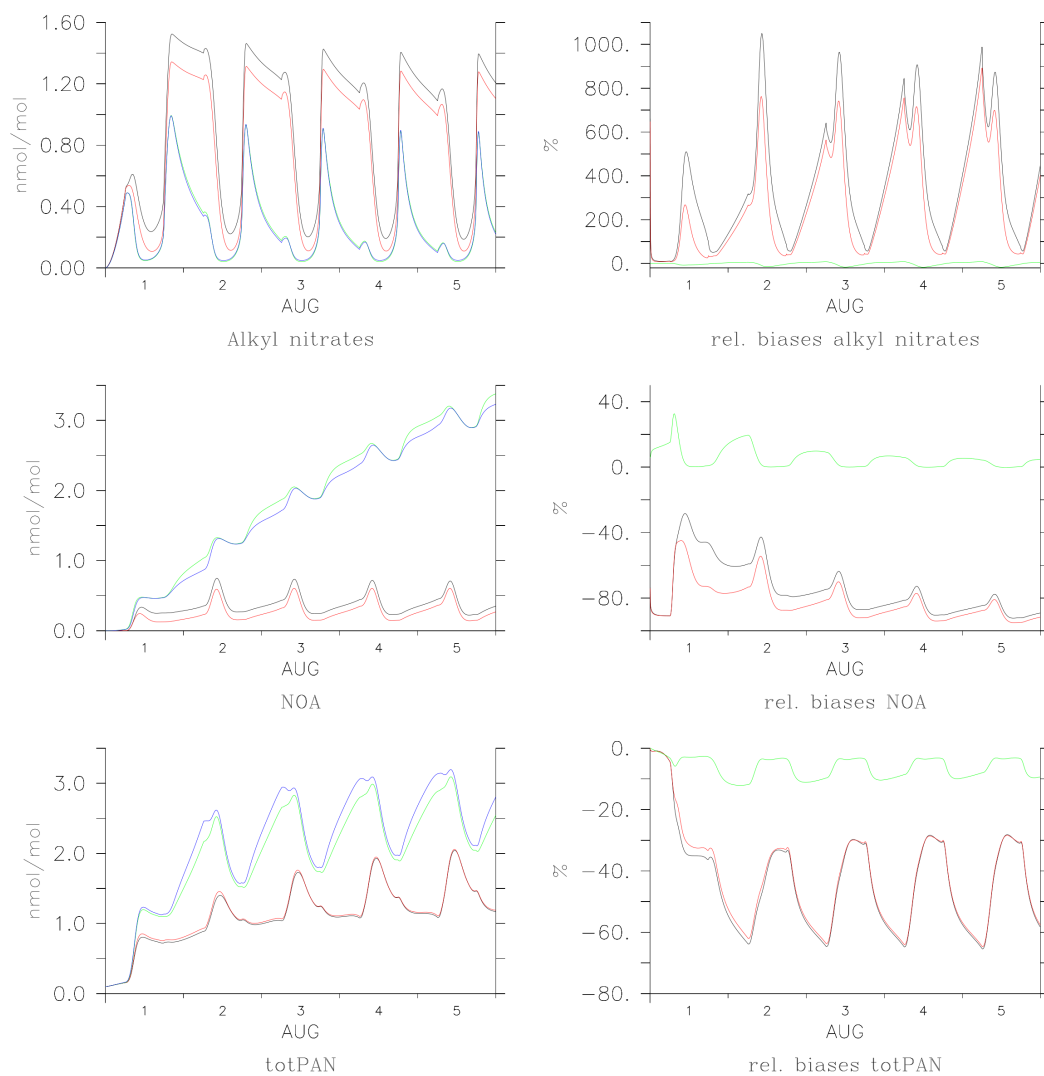
FIGURE 3.10: Nitrogen reservoirs in high-NO$_x$ scenario. In all the plots the actual mixing ratios of each species are presented with MIMvK (black line), original MIM (red line), MIM2 (blue line) and MCM (green line). The alkyl nitrates shown here are the sum of all alkyl nitrates except NOA (shown separately).

3.8 Impact on the global scale

3.9 Implementation in a global model

The focus of this section is on the differences between 3-D simulations with MIM2 and with the mechanism referred to here as MIMvK, used in a recently established global atmospheric chemistry model (Jöckel et al. (2006)). The total isoprene emission in the simulations for the year 2005 was 566.7 Tg/yr of isoprene, equivalent to 500 Tg (C)/yr. The model setup is described in more detail in Butler et al. (2008). All the tested
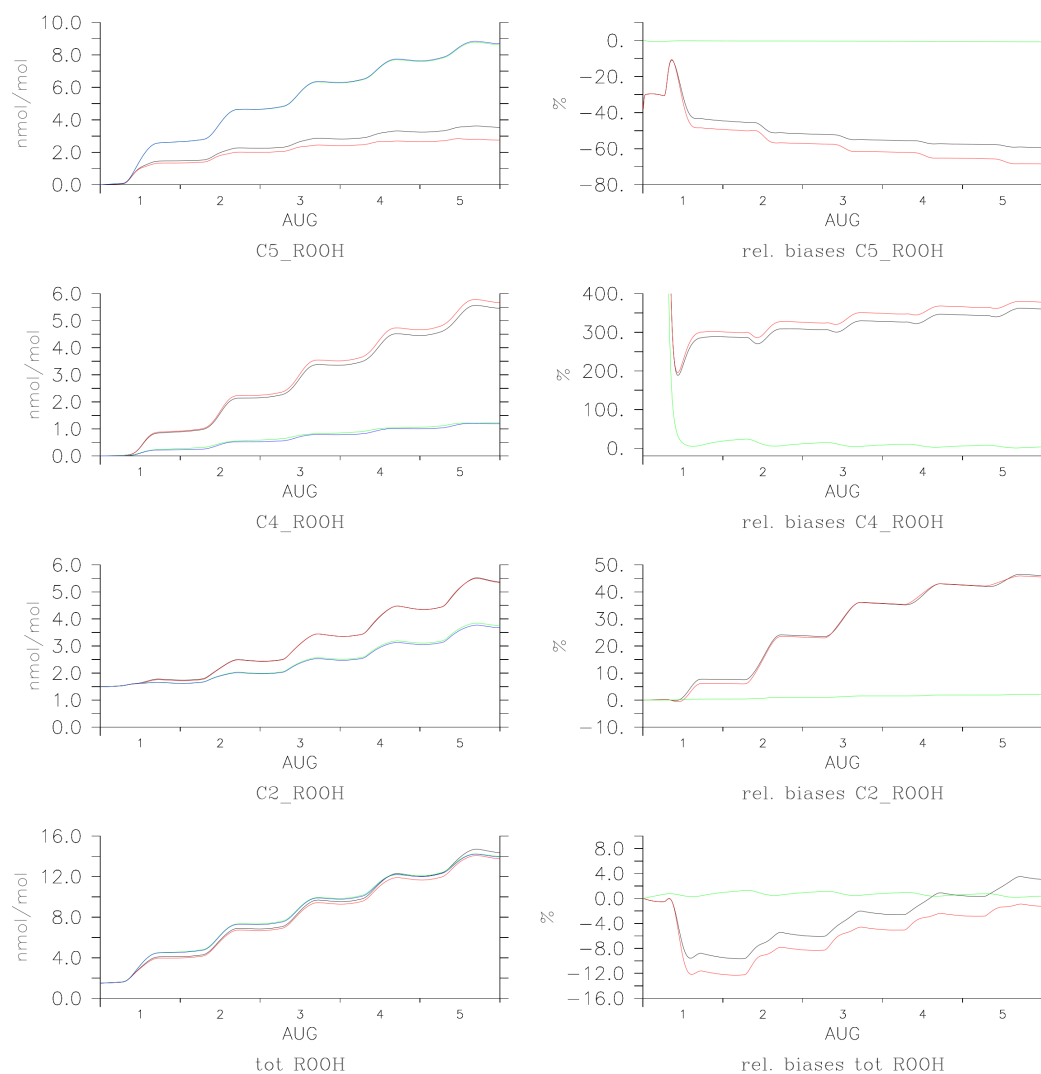
FIGURE 3.11: Organic peroxides other than CH_3OOH for all four mechanisms in this study under low-NO_x conditions. In all the plots the actual mixing ratios of each species are presented with MIMvK (black line), original MIM (red line), MIM2 (blue line) and MCM (green line). C_3-peroxides are not shown because MIM and MIMvK do not have any.

mechanisms were budgeted and the product yields per molecule of isoprene estimated. The contribution of each pathway to the isoprene oxidation was calculated to be 84% for OH, 11% for O_3 and 5% for NO_3, globally. Pfister et al. (2008) estimated similar contributions being 80% for OH, 15% for O_3 and 5% for NO_3. The product yields of isoprene in global models are subject to uncertainties due to assumptions regarding dry and wet deposition of the relative intermediates, as well as other contributing factors such as emissions and transport. Note that a few minor updates to MIM2 were made after this global run was completed, but these should be have negligible effects on the results presented here in this section.
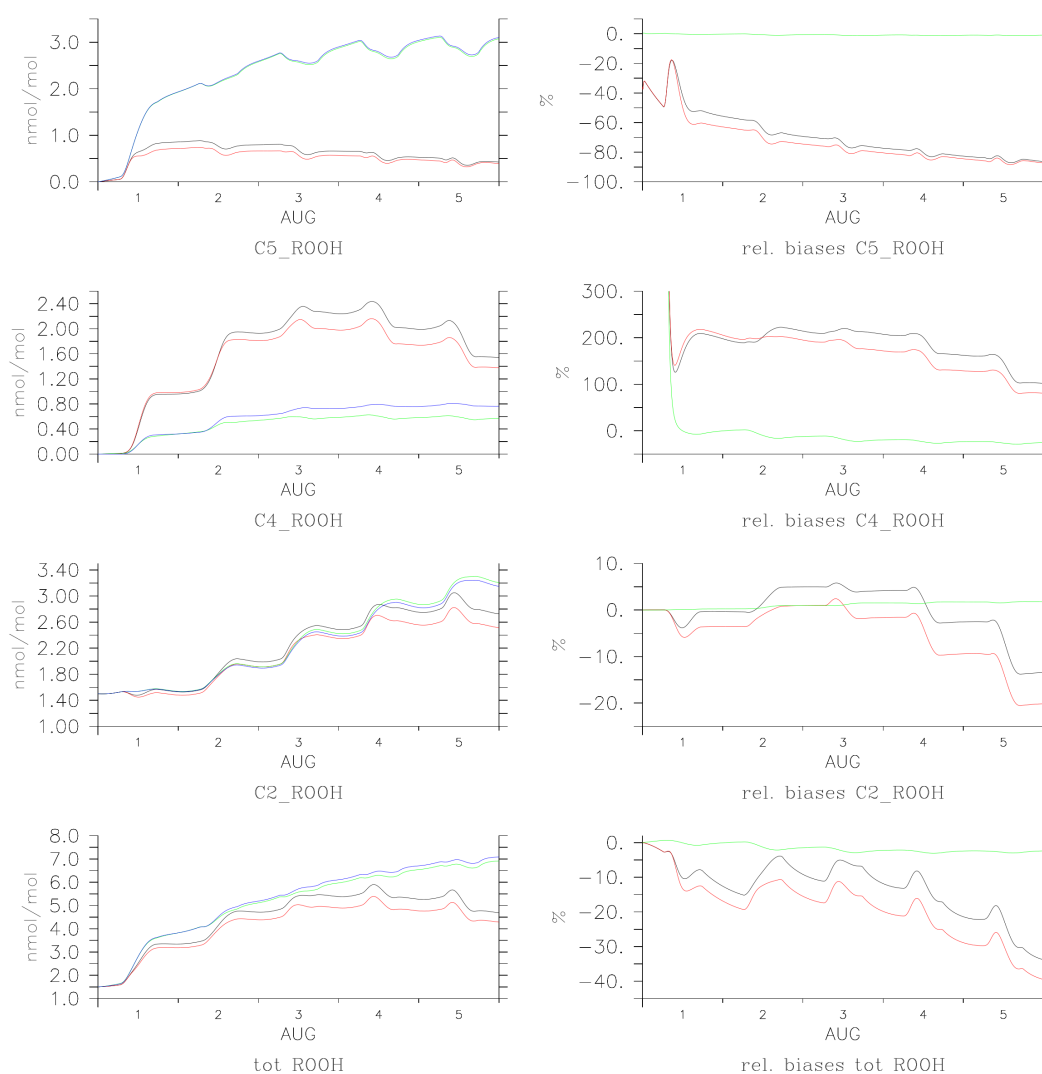
FIGURE 3.12: Organic peroxides other than CH_3OOH for all four mechanisms in this study under mid-NO_x conditions. In all the plots the actual mixing ratios of each species are presented with MIMvK (black line), original MIM (red line), MIM2 (blue line) and MCM (green line). C_3-peroxides are not shown because MIM and MIMvK do not have any.

3.10 OH and isoprene

The seasonal relative differences for OH and isoprene between the MIM2 and MIMvK isoprene mechanisms are presented in Fig. 3.14. The reduction in isoprene mixing ratios in MIM2 is expected to improve the model-measurement agreement over a region like Amazonia, in which models have traditionally overestimated isoprene mixing ratios by about a factor of 3 (von Kuhlmann et al. (2004)). For this reason such models have been implemented in the past with isoprene emission strengths in the range 215–350 Tg(C)/yr, well below the range of 424–530 Tg(C)/yr calculated by different models (Guenther et al.
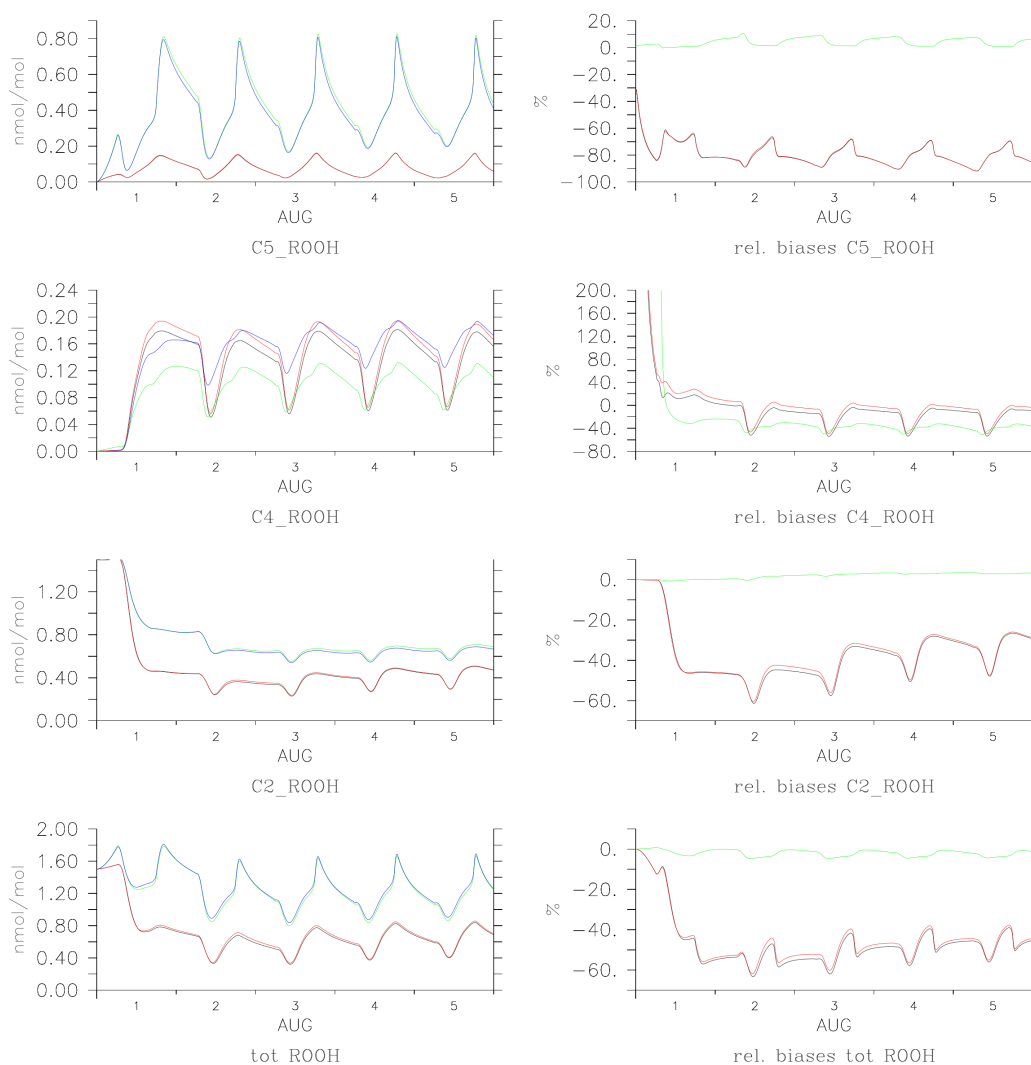
FIGURE 3.13: Organic peroxides other than CH_3OOH for all four mechanisms in this study under high-NO_x conditions. In all the plots the actual mixing ratios of each species are presented with MIMvK (black line), original MIM (red line), MIM2 (blue line) and MCM (green line). C_3-peroxides are not shown because MIM and MIMvK do not have any.

(1995, 2006), Lathière et al. (2006), Müller et al. (2008). The overall increase in OH and the decrease in isoprene mixing ratios, however, are not enough to match the observations which were made during the GABRIEL campaign (Lelieveld et al. (2008)). A more in-depth discussion of the model-measurement comparison during this campaign for OH, isoprene and many other intermediates is presented in Butler et al. (2008).
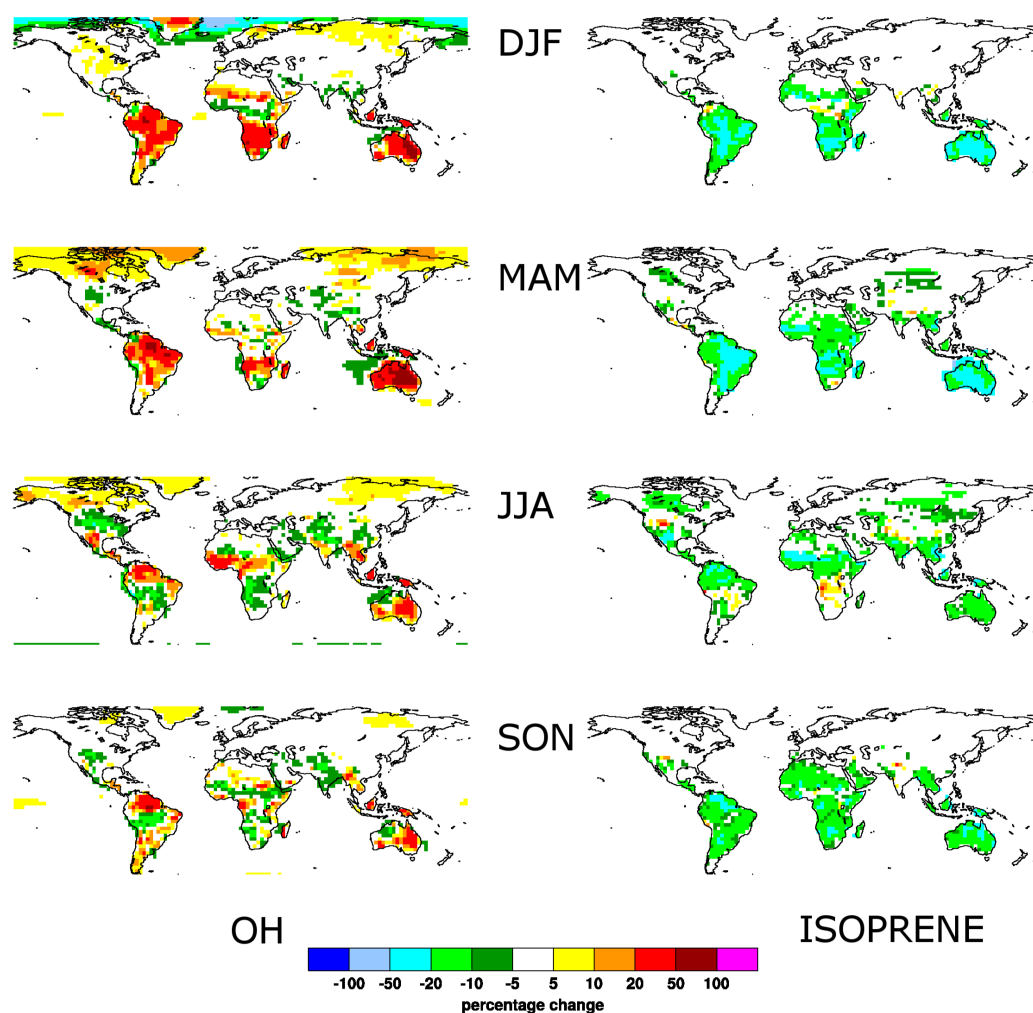
FIGURE 3.14: Seasonal relative change 100*(MIM2-MIMvK)/MIMvk for OH (left panel) and isoprene (right panel).

3.11 New species

There are many important species in MIM2 that are either new (compared to MIM) or not lumped anymore. We discuss the relevance of the chemical production of three new species with respect to their atmospheric budgets.

3.11.1 Glyoxal

The total yield of glyoxal in our 3-D simulation is estimated to be 7.0% and results in a chemical production only from isoprene oxidation of 33.83 Tg/yr. Recently, Myriokefal-itakis et al. (2008) calculated a total global production of 56 Tg/yr, of which 39.2 Tg/yr (70%) is from the oxidation of biogenic VOC. The main contributors were isoprene and

monoterpenes with global annual emissions of 501 Tg/yr and 244 Tg/yr, respectively. However, satellite retrievals show that global atmospheric chemistry models underestimate the glyoxal annual mean total column where terpene emissions are the strongest (Myriokefalitakis et al. (2008), Wittrock et al. (2006)).

3.11.2 Propene

Propene ($CH_2=CHCH_3$) is produced with yields of 12.75% from ozonolysis of isoprene and of 50% from the photolysis of MVK (Atkinson et al. (2006)). In MCM and MIM2 its yield from MVK photolysis is 60%. In a recent study by Pozzer et al. (2007) the parameterized emission from vegetation was 2.15 Tg/yr with all off-line sources amounting to 9.94 Tg/y (A. Pozzer, personal communication). The total yield of propene in the 3-D simulation is estimated to be 2.7%, resulting in a chemical production of 9.451 Tg/yr. Moreover, judging from Pozzer et al. (2007), this chemical source of propene is expected to substantially improve the representation of its diurnal cycle and its vertical distribution compared to observations.

3.11.3 Acetaldehyde

The total yield of acetaldehyde is 2% and the chemical production from isoprene oxidation amounts to 7.33 Tg/yr. It is produced in the ozonolysis of MVK and the oxidation of propene. According to our simulations isoprene oxidation can account for about 5 to 10% of the large missing global source of acetaldehyde of 80–160 Tg/yr inferred by Singh et al. (2001).

3.12 Incorporation of new experimental results

Lelieveld et al. (2008) first proposed that the current understanding of isoprene chemistry under low-NO_x conditions is not well understood yet. To date, NO_x-free experimental studies of isoprene reactions have been sparse and difficult. In fact, under these conditions the major oxidation products are the hydroperoxides that have low volatilities and are labile. The current MCM isoprene chemistry reflects the experimental knowledge that was available at the time of Jenkin et al. (1998), and has not been significantly updated since then. Therefore, we show here the impact of some recent experimental results on a simulation under the low-NO_x scenario. This highlights one of the major advancements of MIM2: unlike in MIM (and other highly lumped reduced mechanisms), the implementation of such changes in MIM2 is very straightforward.

The modifications consist of:

1) elimination of the species MVKOH (1-hydroxybut-3-en-2-one), since Benkelberg et al. (2000) found no evidence for its formation from isoprene oxidation.

2) implementation of the degradation of the methyl vinyl radical from MACR oxidation (Orlando et al. (1999)).

3) adoption of the product yields for the first peroxy radicals of isoprene as recently estimated by Paulot et al. (2009a). Two minor isomers yield MVK and MACR as products. Therefore, their yields are added to the those of ISOPBO2 and ISOPDO2. The modified yields 0.3, 0.424, 0.276 for LISOPACO2, ISOPBO2 and ISOPDO2, respectively.

4) adoption of the corresponding (see point 3) alkyl nitrate yields from the $RO_2 + NO$ reactions. For the externally and internally double bonded isomers the yields are 0.057 and 0.24, respectively.

5) inclusion of the new results on the $RO_2 + HO_2$ reactions for which OH has been found to often be a product (Dillon and Crowley (2008), Hasson et al. (2004), Jenkin et al. (2007)). For the acyl and β-keto peroxy radicals we used OH yields of 0.50 and 0.15, respectively. These yields are taken from Dillon and Crowley (2008) which is the only study in which OH was detected. The branching ratios of the radical terminating channels were then re-scaled so that the total yield was unity.

The results of the modified MIM2 are shown in Fig. 3.15.

For most species the deviations from MIM2 become significant after two days. An increase in the OH concentration of about 15% at noon appears to be the result of the non-radical terminating branches of the $RO2 + HO_2$ reactions. The isoprene mixing ratio decreases by roughly the same amount. Hydroperoxides like H_2O_2 and CH_3OOH increase by about 8%. O_3 is found to change to a mall extent (1-2%). Interestingly, the mixing ratios of the two dicarbonyls, glyoxal and methyl glyoxal, increase by more than 20%. This should significantly reduce the underestimation of glyoxal over pristine tropical forest by models (Myriokefalitakis et al. (2008)). The MVK mixing ratio increases by more the 10% while MACR decreases by about 8%. The average alkyl nitrate yield for the $RO_2 + NO$ reactions of the OH-pathway is slightly increased from 10% to about 11%. However, the total mixing ratio of the alkyl nitrates with 5 carbon atoms decreases by more than 15% already after the second day. These changes are mainly due to increases in OH mixing ratios.

Though the changes in species abundances indicated above are significant, they are are still insufficient to explain the high HO_x levels measured during the GABRIEL campaign (Lelieveld et al. (2008)). New insights in the low-NO_x chemistry of isoprene are needed.
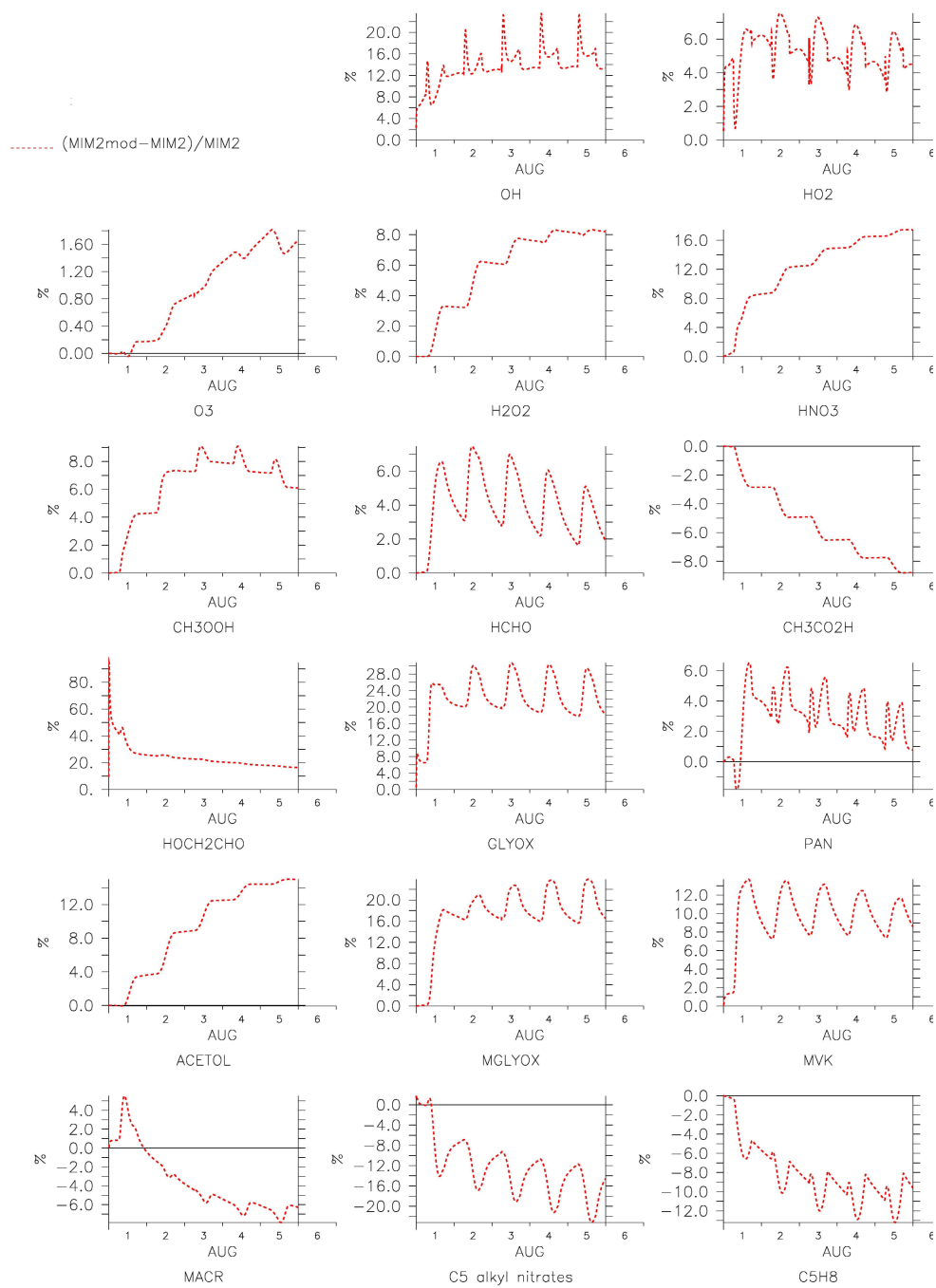
FIGURE 3.15: Relative differences of the modified MIM2 for some major species under the low-NO$_x$ scenario.

To a significant extent they involve new decomposition pathways of peroxy radicals and hydroperoxides from isoprene oxidation (see Chapters 4 and 5).

Chapter 4

Development of a new detailed isoprene oxidation mechanism

4.1   Motivation

During a field campaign in a pristine tropical environment with intense vegetation very high concentrations of HO_x were measured (Butler et al. (2008), Lelieveld et al. (2008), Martinez et al. (2008)). These results are in contrast with model results. In fact, observed OH in the boundary layer was up to 8-9 times higher than the global model output using MIM2. The discrepancy was found to be positively correlated with isoprene concentrations when a box model with the MCM constrained by measurements was used (Kubistin et al. (2008)). For isoprene mixing ratios above 1 ppb, the ratio of observed-to-modelled OH mixing ratio was in the range of 4 to 20 (see Fig. 4.1).

In these environments, isoprene is the largest sink for OH in the boundary layer and the average OH concentration was found to be $5 \cdot 10^6 \mathrm{molec\,cm^{-3}}$. The model/observation discrepancy under low-NO_x conditions for HO_x is well known (Ren et al. (2008), Tan et al. (2001)). Previously, it has been hypothesized that unknown very reactive terpenes exist that are co-emitted with isoprene and react quickly with ozone to give OH (Di Carlo (2004), Goldstein et al. (2004), Kurpius and Goldstein (2003)). Despite the potential of this hypothesis to explain the measurements in the canopy (Goldstein and Galbally (2007)), supporting evidence has not been provided. Furthermore, the emission rate and the efficiency of escaping the canopy of these hypothesized VOCs are too low to be able to explain the discrepancies for observed HO_x in the boundary layer.
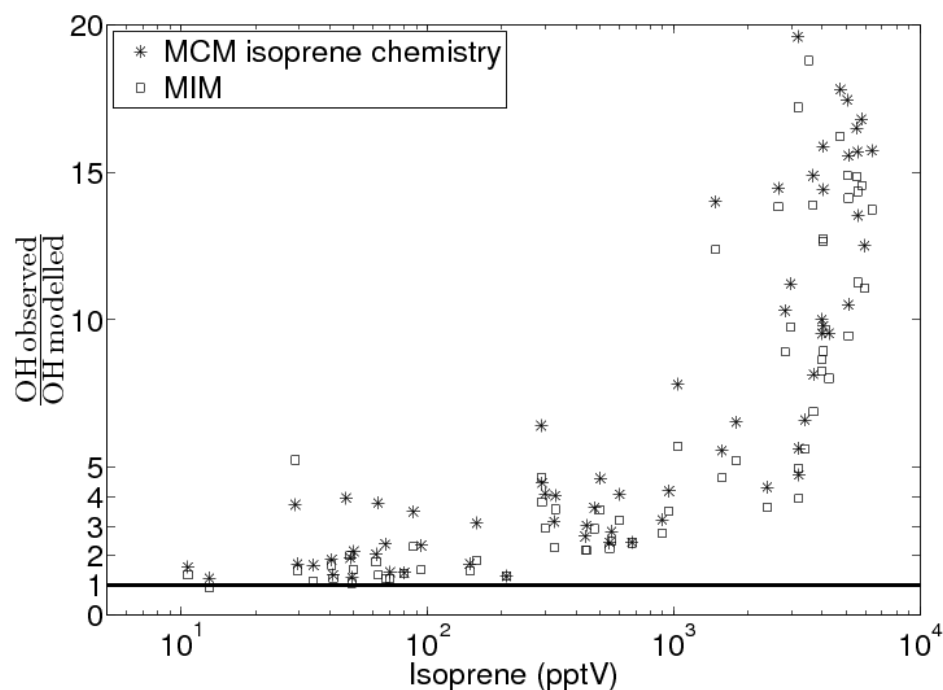
FIGURE 4.1: Ratio of observed to modelled OH mixing ratio during the GABRIEL campaign as a function of isoprene mixing ratio (Kubistin et al. (2008)).

Therefore, I approach the problem from a different angle. I question whether isoprene oxidation under low-NO_x regimes really constitutes a large OH sink, as currently assumed in models. I examine one state-of-the-art model for isoprene oxidation. In light of new experimental results, which have appeared in the literature in the last ten years, many assumptions and reactions I find to be obsolete. This chapter describes efforts to extend and update a detailed isoprene mechanism that is widely used in the atmospheric chemistry community. In Chapter 5 I evaluate this extended mechanism with a focus on the OH-recycling pathways.

4.2   Strategy

4.2.1   Starting point

The Master Chemical Mechanism v3.1 (MCM) for isoprene is taken as the starting point for the extended mechanism (Jenkin et al. (1997), Saunders et al. (2003)). The MCM has been described in Chap. 2 with respect to the MIM2 development. Its results have also been shown for box model simulations under three different NO_x scenarios (see Chap. 3). In summary, MCM implements available experimental data and makes use of

Structure Activity Relationships (SARs) for estimating the rate coefficients and reaction products.

4.2.2   Development directions

High OH levels under low-NO$_x$ regimes imply that the oxidation by OH dominates the isoprene degradation (see Sec. 4.3). However, the generation of unsaturated products is significant under these conditions and their reactions with O$_3$ are revisited (see Sec. 4.4). Hence, the mechanism development is mainly focused on the reaction of organic compounds with OH and O$_3$.

In general, new IUPAC recommendations are adopted when available (Atkinson et al. (2006)). Newer recommendations for single reactions can be accessed at the website: http://www.iupac-kinetic.ch.cam.ac.uk/. When experimental data are lacking, either new or extended Structure Activity Relationships (SARs) are used to estimate both reaction rate coefficients and branching ratios of reactions.

4.3   Reactions with OH

4.3.1   SAR formalism

Based on relatively few experimental data, R. Atkinson developed and tested a simple method to estimate the reaction rate coefficients of OH with organic compounds in the gas phase (Kwok and Atkinson (1995) and references therein). According to this formulation, the rate coefficient is the sum of the ones for H-abstraction and OH-addition to the double bonds and aromatic rings. In this case, I can:

$$k_{OH,total} = k_{OH,abs} + k_{OH,add}$$

How these terms are calculated is described in the next two sections. Even though the MCM v3.1 uses the last update of R. Atkinson to the SAR (Atkinson (2000)), I will compare my newly derived SARs to Kwok and Atkinson (1995) that, unlike the update, is publicly avalaible.

4.3.2   OH-addition to double bonds

OH radicals add to double bonds to form hydroxyalkyl radicals. The reaction coefficient is determined by the functional groups that are bound to the carbon atoms participating in that double bond. Because of the nature of these reactions, the OH radical has two
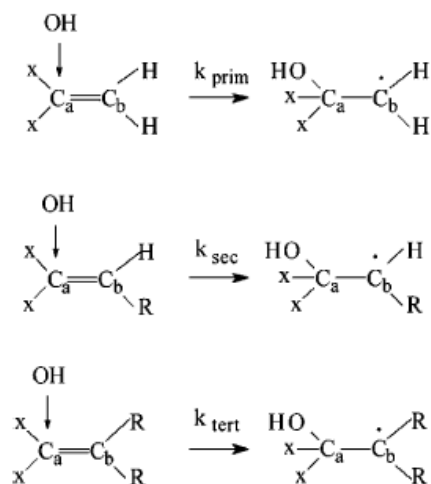
FIGURE 4.2: Site specific addition of OH to different double bonds. The reactions are ordered according to the increasing stability of the resulting organic radicals, from primary to tertiary (Peeters et al. (2007)).

possible sites to add. If the unsaturated molecule being considered is asymmetric with respect to the double bond, OH addition to one of the two carbon atoms is expected to be preferred. Experimental data on both rate coefficients and branching ratios for major compounds like isoprene (see Sec.4.3.9.2) and methacrolein (see Sec.4.3.9.1) are available. However, many products of isoprene oxidation have not been studied yet and a SAR is needed to estimate their reactivity.

Peeters et al. (2007) recently developed a site-specific SAR for polyalkenes at 298 K. It was established that $k_{OH,add}$ can be approximated well by the sum of individual rate constants that depend solely on the stability of the alkyl radicals being formed (see Fig. 4.2). In fact, from quantum mechanical calculations it is known that the OH first forms a π complex with the alkene through a barrierless association reaction. The electron density of the pre-reactive π complex is affected by the substituents. These substituents affect the energy of the (late) transition states that bring to the radicals. The substituents that affect the energy of one transition state do not affect significantly the energy of the second possible one. For each double bond there are two transition states and their relative energies (stabilities) affect the branching ratios of radical production from OH-addition.

This means that the following simple formula for non-conjugated polyalkenes [1] can be used:

$$k_{OH,add} = p\ k_{prim} + s\ k_{sec} + t\ k_{tert}$$

where p, s and t are the number of possible primary , secondary and tertiary radicals that can be formed from OH addition and k_{prim}, k_{sec} and k_{tert} from Peeters et al. (2007) are listed in Tab. 4.1.

The present SAR shows that the OH addition that forms the most stable alkyl radical is also the fastest. Hence, one does not need to make any additional assumptions about the branching ratios. This SAR is only for alkenes that do not include functional groups. However, many oxygenated unsaturated compounds arise from isoprene oxidation. In fact, functional groups like $> C{=}O$ and $-CH_2OH$ that are next to double bonds affect the rate of OH addition. Therefore, I extend the SAR by Peeters et al. (2007) following the approach of Atkinson (1987) that make use of "group substituents factors". I assume that each substituent does not affect the branching ratios of the addition and calculate these factors as ratios of the well known rate constants of the compound bearing the "substituent" and of its associated parent alkene (Atkinson and Arey (2003a)). For instance, the substituent factor for the group $CH_3C({=}O)$ is calculated taking the rate constants of methyl vinyl ketone and propene. Substitutent factors are needed only for groups other than H or alkyl groups. For an alkene of formula XCH=CYZ the SAR is:

$$k_{OH,add} = F_a(X)F_a(Y)F_a(Z)(k_{sec} + k_{tert})$$

where the F_a are the substituents factors for the group X, Y and Z.

All parameters used for predicting OH addition are shown in Tab. 4.1. Because of the lack of data I assume that all substituents bearing the hydroperoxidic group (–OOH) have the same factors as the corresponding ones bearing the hydroxy group (–OH). This extended SAR has not been fully evaluated yet and future modifications are not excluded.

4.3.3   H-abstraction by OH

OH radicals can also abstract H atoms from organic molecules to form H_2O and $R^\bullet$ alkyl radicals. Making use of the latest IUPAC recommendations I built a SAR very similar to the one by Kwok and Atkinson (1995). For a compound with the general formula XCH_2CHYCH_2Z the total abstraction reaction rate is estimated in the following manner:

---

[1]An alkene that does not bear two or more alternating double bonds.

TABLE 4.1: Site-specific rate constants and group substituent factors of the extended SAR for OH addition to double bonds and comparison with Kwok and Atkinson (1995) (KA95). k are for 298 K and 1 bar and expressed in $cm^3\,molec^{-1}\,s^{-1}$ and F_a is unitless.

Parameters	KA95	this study	source[a]
k_{prim}	–	0.45×10^{-11}	$0.5\ k_{ethene}$
k_{sec}	–	3.00×10^{-11}	$0.5\ k_{2-butene}$
k_{tert}	–	5.50×10^{-11}	$0.5\ k_{2,3-dimethyl-2-butene}$
$k_{prim} + k_{sec}$	2.63×10^{-11}	3.45×10^{-11}	
$k_{prim} + k_{tert}$	5.14×10^{-11}	6.05×10^{-11}	
$k_{sec} + k_{tert}$	8.69×10^{-11}	8.50×10^{-11}	
$F_a(-C(O)CH_3)$	0.90	0.76	$k_{MVK}/k_{propene}$
$F_a(-CHO)$	0.34	0.31	$\dfrac{k^{add}_{methacrolein}}{k_{2-methylpropene}}$
$F_a(-C(O)OONO_2)$	–	0.56	$k_{MPAN}/k_{2-methylpropene}$
$F_a(-CH_2OH)$	1.6	1.7	$k_{2-propene-1-ol}/k_{propene}$
$F_a(>CHOH)$	1.6	2.2	$k_{1-pentene-3-ol}/k_{1-pentene}$
$F_a(>C(OH)-)$	1.6	2.2	$\dfrac{k_{3-methylbut-1-en-3-ol}}{k_{3,3-dimetyl-1-butene}}$
$F_a(-CH_2ONO_2)$	0.47	0.64[b]	$\dfrac{k_{O_2NOCH_2C(CH_3)=CHCH_2OH}}{F_a(-CH_2OH)\ k_{2-methyl-2-butene}}$

[a] k_{prim}, k_{sec} and k_{tert} are taken from Peeters et al. (2007), the k for the oxygenated alkenes are taken from the IUPAC recommendations and the k for the simple alkenes are taken from Atkinson and Arey (2003a)
[b] Taken from Paulot et al. (2009a)

$$k_{OH,abst} = k_{OH,C^1} + k_{OH,C^2} + k_{OH,C^3}$$

where C^1, C^2 and C^3 are the carbon atoms from left to right in the formula and each term of the previous equation is expressed as:

$$k_{OH,C^1} = F(-X)\ F(-CHYR)\ k_s$$
$$k_{OH,C^2} = F(-CH_2X)\ F(-CH_2Z)\ F(-Y)\ k_t$$
$$k_{OH,C^3} = F(-CHYR)\ F(-Z)\ k_s$$

where k_s and k_t are the rate coefficients specific for secondary and tertiary H atoms, respectively. The substituent factors (F) are analogues to the ones in the SAR for OH addition. It is assumed that $F(-CH_3)$ is 1 and the substituent factors for all other groups are calculated relative to it. The details of the SAR and its comparison to Kwok and Atkinson (1995) are shown in Tab. 4.2.

The abstraction of H atoms from the hydroxy group is assumed to have the rate coefficient of the following reaction as recommended by IUPAC.

$$CH_3CH_2OH + OH \rightarrow CH_3CH_2O + H_2O \qquad k = 1.6\,10^{-13}\ cm^3 molecule^{-1}s^{-1}$$
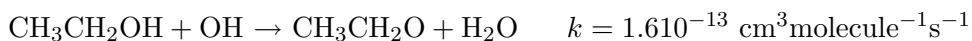
TABLE 4.2: Parameters of the new SAR for H abstraction by OH and comparison with the one by Kwok and Atkinson (1995) (KA95). k_p, k_s and k_t are the rate constants for the $-CH_3, -CH_2-$ and $> CH-$ groups. They are given for 298 K and 1 bar and expressed in $cm^3\, molec^{-1}\, s^{-1}$ and F is unitless.

Parameters	KA95	this study	source[a]
k_p	1.36×10^{-13}	1.24×10^{-13}	$1/2 k_{ethane}$
k_s	9.34×10^{-13}	8.42×10^{-13}	$k_{propane} - k_{ethane}$
k_t	1.94×10^{-12}	1.75×10^{-12}	$k_{2-methylpropane} - 3/2 k_{ethane}$
$F(-CH_3)$	1.00	1.00[b]	
$F(-CH_2-)$	1.23	1.23[b]	
$F(> CH-)$	1.23	1.23[b]	
$F(> C <)$	1.23	1.23[b]	
$F(= O)$	8.70	8.15	$\frac{k_{CH_3CHO+OH\to CH_3CO}}{k_t}$
$F(-C(= O)R)$	0.75	0.73	$\frac{k_{CH_3COCH_3}}{k_{ethane}}$
$F^{sec}(-OH)$	3.50	3.44	$\frac{k_{CH_3CH_2OH+OH\to CH_3CHOH}}{k_s}$
$F^{tert}(-OH)$	3.50	2.68	$\frac{k_{2-propanol} - 2k_p - k_{ROH+OH\to RO}}{k_{2-methylpropane}-3k_p}$
$F^{sec}(-OOH)$	–	18.13	$\frac{F^{sec}(-OH)\ k_{CH_3OOH+OH\to CH_2OOH}}{k_{CH_3OH+OH\to CH_2OH}}$
$F^{tert}(-OOH)$	–	14.12	$\frac{F^{tert}(-OH)\ F^{sec}(-OOH)}{F^{sec}(-OH)}$
$F(-CH_2OH)$	1.23	1.29	$\frac{k_{CH_3CH_2OH+OH\to CH_2CH_2OH}}{k_p}$
$F^t(-CH_2OH)$[c]	–	0.53	$\frac{k_{HOCH_2CHO+OH\to HOCH_2CO}}{k_t\ F(=O)}$
$F(-CHO)$	0.75	0.55	$\frac{k_{HOCH_2CHO+OH\to HOCHCHO}}{k_p\ F_s(OH)}$
$F(-COOH)$	0.74	1.67	$\frac{k_{CH_3COOH+OH\to CH_2COOH}}{k_p}$
$F(-ONO_2)$	0.04	0.04[b]	
$F(-CH_2ONO_2)$	0.20	0.20[b]	
$F^{sec}(allyl)$	1	3.6[d]	

[a] the k for the simple alkanes are taken from Atkinson and Arey (2003a) and k for the oxygenated saturated compounds are taken from the IUPAC recommendations
[b] not updated and taken from Kwok and Atkinson (1995)
[c] in cases the group $-CH_2OH$ is attached to aldehydic carbons
[d] calculated using the results by Vereecken and Peeters (2001)

Finally, the H abstraction from methyl groups $(-CH_3)$ and vinyl groups $(-CH=CH_2)$ is usually neglected because the rate constants are very low. For a methyl group attached to a general alkyl my SAR estimates a group rate constant of $1.5\ 10^{-13}$ $cm^3 molecule^{-1}s^{-1}$. In the mechanism H abstraction from methyl groups is considered only for the reactions of OH with CH_3OH and CH_3OOH, for which the experimental values recommended by IUPAC are used.

TABLE 4.3: Comparison of predicted (this study and Kwok and Atkinson (1995)) with experimental rate constants (k_{OH}) for selected organic compounds at 298 K and 1 bar. k_{OH} is expressed in $cm^3molecule^{-1}s^{-1}$.

Compound	$k_{OH}^{exp.}$	err.(%) KA95	err.(%) new SAR
$HOCH_2CHO$	8.0×10^{-12} [a]	166	16.4
$HCOCHO$	9.7×10^{-12} [a]	161	62
$CH_3CH_2CH_2OH$	5.8×10^{-12} [a]	−6	−12
$CH_3C(=O)CH=CH_2$ (MVK)	2.0×10^{-11} [a]	19	31.5
$CH_3CH_2CH_2CHO$	2.4×10^{-11} [a]	−4.6	−20
$(CH_3)_2COHCH=CH_2$	6.3×10^{-11} [a]	−32	21
$HOCH_2CH=C(CH_3)CH_2ONO_2$	9.5×10^{-11} [b]	−27	8
$HOCH_2CH=C(CH_3)CHO$	1.1×10^{-10} [b]	−38	19

[a] recommended by IUPAC
[b] from isoprene whose k_{OH} was experimentally estimated by Paulot et al. (2009a)

4.3.4 Reaction with OH: measurements vs. predictions

A comparison of the SAR's predictions with the experimental rate constants for selected compounds is shown in Tab. 4.3. A clear improvement is seen for C_5 unsaturated multi functional compounds from isoprene. Contrary to the old SAR, there is a tendency for the new one to overestimate the k_{OH} of these species. Overall the new SAR performs better mainly for two reasons. The first one is obviously the fact that it has been built with the most recent data available. The second is the reliance on a recent SAR for OH addition that makes use of both recent experimental and quantum chemistry data.

H-abstraction for isoprene is predicted to be negligible (Atkinson et al. (1989)). Isoprene undergoes almost entirely OH-addition because of its two conjugated double bonds. I have not shown the SARs parameters for structures having conjugated double bonds since isoprene is the only compound in the mechanism of such kind. Furthermore, its reaction with OH has been well studied and the IUPAC recommends a rate constant of 1.0×10^{-10} $cm^3molecule^{-1}s^{-1}$. Both my new SAR and the one by Kwok and Atkinson (1995) fit well the IUPAC value, estimating similar values of 1.05 and 0.955×10^{-10} $cm^3molecule^{-1}s^{-1}$. The temperature-dependent expression for its rate constant recommended by IUPAC is used in this mechanism.

4.3.5 Alkyl radicals

Both abstraction and addition by OH produce alkyl radicals ($R^\bullet$). They generally react with O_2 with high pseudo-unimolecular rate constants of ($k \cdot [O_2] > 1 \times 10^7 s^{-1}$). α-hydroxy radicals [2] undergo the following general reaction:

$$RC^\bullet HOH + O_2 \rightarrow RCHO + HO_2$$
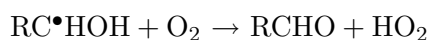
The most common fate of alkyl radicals is the exothermic O_2-addition to form excited peroxy radicals (RO_2^*). Their fate is discussed in Sec. 4.3.6. In some cases, even if thermalized, RO_2 is unstable enough to undergo fast decomposition before other reactions can take place. One case is the thermal decomposition of α-hydroperoxy radicals promptly giving OH back as predicted by Vereecken et al. (2004):

$$R_1R_2C^\bullet OOH \rightarrow R_1R_2C{=}O + OH$$
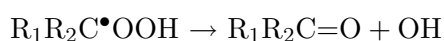
The other case involves the acyl radicals ($R_1R_2R_3CCO$). When they are produced by H abstraction they have excess energy because of the exothermicity of such reactions. According to Baeza-Romero et al. (2007) the CH_3COCO^* radical, resulting from reaction of methyl glyoxal with OH, has an excess energy of about 30 kcalmol^{-1}. This energy is sufficient for the radical to lose CO fragments in the following way:

$$
\begin{array}{lll}
CH_3COCO^* & \rightarrow CH_3CO^* + CO & \\
CH_3CO^* & \rightarrow CH_3 + CO & 40\% \\
CH_3CO^* + M & \rightarrow CH_3CO + M & 60\%
\end{array}
$$
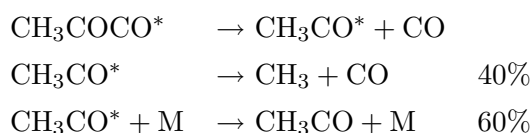
The energized α-dicarbonyl radical ($HCOCO^*$) from the reaction of glyoxal with OH has also been shown to decompose promptly to CO and HCO (Niki et al. (1983), Orlando and Tyndall (2001)). In these studies it is stated that unimolecular decomposition competes with the reaction with O_2. However, in light of the study by Baeza-Romero et al. (2007), it is more likely that decomposition competes with collisional stabilization instead. Therefore, I assume that at 298 K and 933 mbar

$$
\begin{array}{lll}
HCOCO^* & \rightarrow HCO + CO & 40\% \\
HCOCO^* + M & \rightarrow HCOCO + M & 60\%
\end{array}
$$
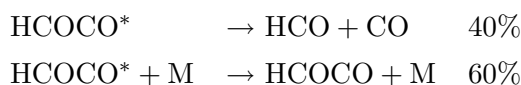
Then the HCO and HCOCO radicals reacts with O_2 to give $HO_2 + CO$ and $HCOCO_3^*$ (Sec. 4.3.6.4), respectively.

---

[2]Greek letters are used to specify the relative position of a functional respect to another. Denoting with α the carbon atom bearing the reference functional group, the other carbon atoms next to it are denoted as β, γ, δ etc., progressively.

Reaction of glycoaldehyde with OH and decomposition of alkoxy radicals from isoprene produce the acyl radical $HOCH_2CO^*$. It has been predicted to have a too slow decomposition under atmospheric conditions (Mereau et al. (2001)). Butkovskaya et al. (2006a) confirmed this arguing that the slow HCHO formation was incompatible with decomposition. After collisional stabilization, reaction with O_2 takes places yielding significant amounts of HO_2. Butkovskaya et al. (2006a) also determined the fate of the second alkyl radical HOCHCHO from glycolaldehyde oxidation. These two alkyl radicals undergo H-abstraction and addition by O_2 with following branching ratios:

$$
\begin{aligned}
HOCH_2CO + O_2 \quad &\rightarrow HO_2 + OCH_2CO \quad &58\% \\
&\rightarrow HOCH_2CO_3^* \quad &42\% \\
HOCHCHO + O_2 \quad &\rightarrow HO_2 + HCOCHO \quad &81\% \\
&\rightarrow HOCH(O_2)CHO^* \quad &19\%
\end{aligned}
$$
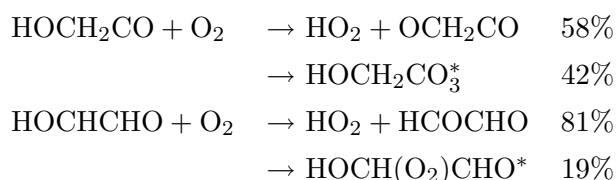
The product OCH_2CO of the first reaction decomposes to HCHO and CO. The excited peroxy radicals $HOCH_2CO_3^*$ and $HOCH(O_2)CHO^*$ undergo decomposition as described in Sec. 4.3.6.5 and 4.3.6.6, respectively. Similar mechanistic insights have also been determined in the reaction of hydroxyacetone with OH (Butkovskaya et al. (2006b)).

Another important excited radical is $HOOCH_2CO^*$. It is produced during the oxidation of acetaldehyde and the decomposition of the Criegee intermediate $CH_3CH{=}O^+{-}O^-$ (see Sec. 4.4). The same radical with similar excess energy is also produced by H abstraction of $HOOCH_2CHO$, a species that is not considered by the MCM. Kuwata et al. (2003, 2005) calculated that $HOOCH_2CO^*$ undergoes unimolecular decomposition quantitatively producing $HCHO + CO + OH$. The effect of hydroxy and hydroperoxy groups has also been studied for acyl radicals. Mereau et al. (2001) studied the radical $(CH_3)_2C(OH)CO$ and predicted a loss of CO with a 78% yield. Kuwata et al. (2005) studied the fate of $HOOCH(CH_3)CO^*$ originating from vinoxy radicals $+ O_2$. Even in this case the quantitative unimolecular decomposition yielding OH was predicted. Compared to $HOOCH_2CO^*$, the presence of the methyl group lowered the decomposition energy barrier by $1.7\,kcal\,mol^{-1}$. The acyl radical from the hydroperoxide of methacrolein bears two alkyl groups and one HOO-group and therefore decomposition is likely to take place:

$$
\begin{aligned}
HOCH_2C(CH_3)(OOH)CO \quad &\rightarrow HOCH_2C^\bullet(CH_3)OOH + CO \\
HOCH_2C^\bullet(CH_3)OOH \quad &\rightarrow HOCH_2C(CH_3)O + OH
\end{aligned}
$$
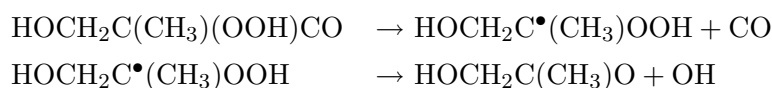
Hence, I assume that both $R_1R_2C(OH)CO$ and $R_1R_2C(OOH)CO$ radicals decompose by losing a CO, with the latter ones producing α-hydroperoxy radicals that in turn decompose yielding OH and a ketone.

4.3.6 Excited RO_2 radicals

4.3.6.1 General atmospheric fate

Under atmospheric conditions most of the $R^\bullet$ radicals react quantitatively with O_2 in the following manner:

$$R^\bullet + O_2 \rightarrow RO_2^*$$
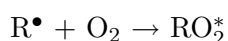
where RO_2^* is the excited peroxy radical.

The reaction is highly exothermic and it leads to the formation of excited peroxy radicals. The excess energy is in the range of 33-37 $kcal\,mol^{-1}$ (Clifford et al. (1998)). This energy must be dissipated in one way or another. In fact, they can either undergo collisional stabilization or decomposition.

$$
\begin{aligned}
RO_2^* + M \quad &\rightarrow RO_2 + M &\quad \text{collisional stabilization} \\
RO_2^* \quad\quad &\rightarrow CO + CO_2 + OH + prod. &\quad \text{decomposition}
\end{aligned}
$$
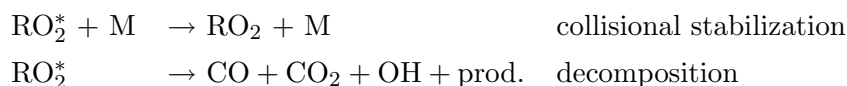
The competition between the two processes is obviously a function of density and less of temperature. At constant temperature, as pressure decreases the branching ratio of the decomposition becomes more important for RO_2^* that forms during the oxidation of acetaldehyde (see Sec. 4.3.6.2). In the oxidation of glycolaldehyde, a decrease in temperature results in an increase of the fraction of excited radicals undergoing decomposition (see Sec. 4.3.6.6 and 4.3.6.5).

In the past years some experimental studies have shown how decomposition is an important pathway for RO_2 having 2 or 3 carbon atoms. Often this decomposition produces OH radicals. Peroxy radicals with 4 and 5 C atoms are unlikely to undergo decomposition. In the case of isoprene + OH, their formation is significantly less exothermic, 19-24 $kcal\,mol^{-1}$, than regular alkyl + O_2 reactions (Lei et al. (2001)). The low exothermicity of the reaction and the bigger size of such radicals make collisional stabilization the fastest process under tropospheric conditions. In the next section the relatively new chemistry of some major C_2-C_3 products of isoprene oxidation is discussed.

4.3.6.2 $CH_3CO_3^*$ radical

Oxidation of acetaldehyde with OH and decomposition of major alkoxy radicals from isoprene produce the acetyl radical, CH_3CO. In the atmosphere this radical undergoes the following reaction:

$$CH_3CO + O_2 \rightarrow CH_3CO_3^*$$
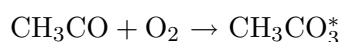
The atmospheric fate of the resulting excited intermediate has been determined in a few experimental studies (Blitz et al. (2002), Butkovskaya et al. (2004), Carr et al. (2008), Tyndall et al. (1997)). Carr et al. (2008) studied these reactions as function of pressure measuring OH directly with He as bath gas. At 300 K they determined the following branching ratios:

		933 mbar	267 mbar
$CH_3CO_3^* + M$	$\rightarrow CH_3CO_3 + M$	97%	91%
$CH_3CO_3^*$	$\rightarrow OH + HCHO + CO$	3%	9%
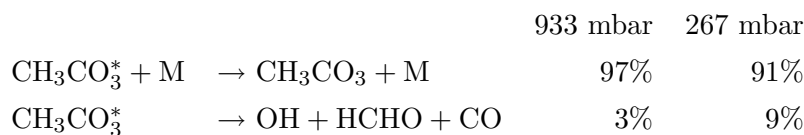
For the present purposes I adopt the branching ratios at 933 mbar pressure as a good approximation for the ones at 1 bar.

4.3.6.3 $HCOCH_2O_2^*$ radical

This excited peroxy radical is produced by the reaction between O_2 and vinoxy radicals:

$HCOCH_2 + O_2 \rightarrow HCOCH_2O_2^*$
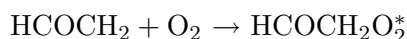
Vinoxy radical is in turn produced in the reaction of acetaldehyde with O and in the decomposition of a Criegee intermediate (see Sec.4.4). Based on previous experimental studies by Gutman and Nelson (1983) and Zhu and G.Johnston (1995), Butkovskaya et al. (2004) implemented the fate of this radical in a mechanism for the oxidation of acetaldehyde at 267 mbar. This included two channels for the decomposition with a combined yield of 38%. However, Kuwata et al. (2003) give theoretically a decomposition yield of 58% and 25% at 200 and 1 bar, respectively. Even though at 267 mbar the yields from the two studies differ significantly, it seems reasonable to use the yield of Butkovskaya et al. (2004) scaled by the reduction from 267 to 1000 mbar calculated by Kuwata et al. (2003). Therefore, I implemented the following branching at 1 bar pressure:

$HCOCH_2O_2^* + M$	$\rightarrow HCOCH_2O_2 + M$	$\sim$84%
$HCOCH_2O_2^*$	$\rightarrow HCOCHO + OH$	$\sim$6%
$HCOCH_2O_2^*$	$\rightarrow HOOCH_2CO^*$	$\sim$10%
$HOOCH_2CO^*$	$\rightarrow HCHO + CO + OH$	
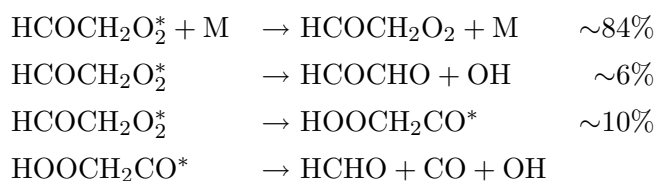
The excited radical $HOOCH_2CO^*$ decomposes to give $HCHO + CO + OH$ (see Sec. 4.3.5).

4.3.6.4   HCOCO$_3^*$ radical

This radical is formed from the reaction of O$_2$ with the thermalized HCOCO radical. The latter can be formed in two ways. The first is by decomposition of multifunctional alkoxy radicals from isoprene oxidation. The second and most important way is by the reaction of HCOCHO with OH. This reaction produces an energetic HCOCO* radical that to a large extent is collisionally stabilized (see Sec. 4.3.5). At 298 K and 933 mbar, Niki et al. (1983) and Orlando and Tyndall (2001) determined its fate to be:

$$
\begin{aligned}
\text{HCOCO}_3^* \quad &\rightarrow 2\text{CO} + \text{HO}_2 \quad 50\% \\
&\rightarrow \text{HCOCO}_3 \qquad 50\%
\end{aligned}
$$
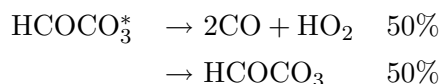
In that study no PAN-like compound from the reaction HCOCO$_3$ + NO$_2$ could be detected and the following reactions were assumed:

$$
\begin{aligned}
\text{HCOCO}_3 + \text{NO}_2 \quad &\rightarrow \text{HCOCO}_2 + \text{NO}_3 \\
\text{HCOCO}_2 \qquad &\rightarrow \text{HCO} + \text{CO}_2
\end{aligned}
$$
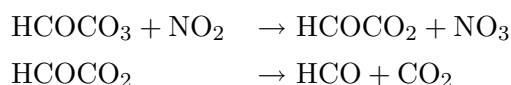
Unlike Orlando and Tyndall (2001), Feierabend et al. (2008) studied the reaction of glyoxal with OH monitoring the latter by direct detection. They could determine a 30% maximum OH-reformation varying pressure (max. 267 mbar) and 21% O$_2$). This number is very similar to the branching ratio of the CO$_2$-forming channel (Orlando and Tyndall (2001)). Therefore, I consider it very likely that OH is produced together with CO$_2$. I assume that under atmospheric conditions the HCOCO$_3^*$ radical is not collisionally stabilized and undergoes a complete decomposition following the mechanism:

$$
\begin{aligned}
\text{HCOCO}_3^* \quad &\rightarrow 2\text{CO} + \text{HO}_2 \qquad 50\% \\
&\rightarrow \text{CO}_2 + \text{CO} + \text{OH} \quad 50\%
\end{aligned}
$$
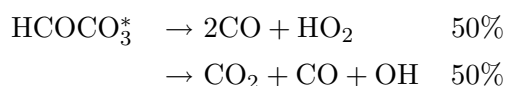
4.3.6.5   HOCH$_2$CO$_3^*$ radical

Butkovskaya et al. (2006a) explained the fate of this excited peroxy radical looking at the O$_2$-adducts that are formed with two conformers of the HOCH$_2$CO radicals. They estimated HOCH$_2$CO$_3^*$ radicals complete decomposition with the two following channels:

$$
\begin{aligned}
\text{HOCH}_2\text{CO}_3^* \quad &\rightarrow \text{OH} + \text{HCHO} + \text{CO}_2 \qquad 63\% \\
&\rightarrow \text{HCOOH} + \text{HO}_2 + \text{CO}_2 \quad 37\%
\end{aligned}
$$
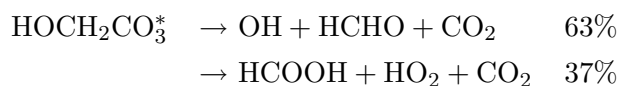
4.3.6.6   HOCH(O$_2$)CHO* radical

The HOCH(O$_2$)CHO* is produced during the OH-initiated oxidation of glycolaldehyde and the decomposition of some alkoxy radicals and the Criegee intermediate HOCH$_2$CH=O$^+$O$^-$
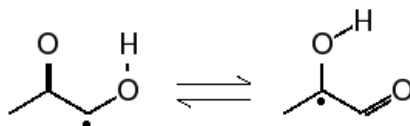
FIGURE 4.3: Tautomeric equilibrium between the two forms for the radical from the reaction of OH with hydroxyacetone.

(4.4.2.4). Butkovskaya et al. (2006a) inferred its fate to involve a 1,4-H shift followed by decomposition:

$$HOCH(O_2)CHO^* \rightarrow CO + HCOOH + OH$$
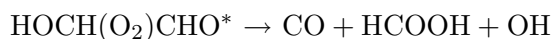
4.3.6.7 Vinyl peroxy radical $(CH_2{=}CHO_2^*)$

This radical comes from the degradation of acrolein $(CH_2{=}CHCHO)$ and the photolysis of MVK (Sec. 4.5.3). Its fate is represented according to the results of Feng and Wang (2002) and Orlando (pers. comm.):

$$
\begin{aligned}
CH_2CH + O_2 \quad &\rightarrow CH_2CHO_2^* \\
CH_2CHO_2^* \quad &\rightarrow HCHO + HO_2 + CO \quad 94\% \\
&\rightarrow CH_3O_2 + CO_2 \qquad\quad\; 6\%
\end{aligned}
$$
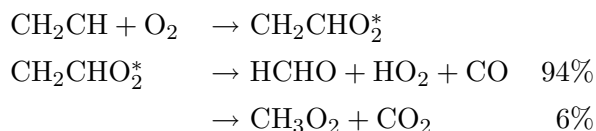
4.3.6.8 $CH_3COCH(O_2)OH^*$ and $CH_3CO_2(OH)CHO^*$ radicals

The reaction of hydroxyacetone with OH produces the alkyl radical $CH_3COC^\bullet HOH$. This radical can exist in two tautomeric forms [3] that equilibrates very quickly (see Fig. 4.3). Therefore, reaction with O_2 produces two excited peroxy radicals. Their chemistry has been determined by Butkovskaya et al. (2006b) as producing formic and acetic acid along with some OH. Their fate is presented below:

---

[3]Tautomerism - the existence of two or more chemical compounds that are capable of facile inter-conversion, in many cases merely exchanging a hydrogen atom between two other atoms, to either of which it forms a covalent bond. Unlike other classes of isomers, tautomeric compounds exist in mobile equilibrium with each other, so that attempts to prepare the separate substances usually result in the formation of a mixture that shows all the chemical and physical properties to be expected on the basis of the structures of the components (Encyclopaedia Britannica).

$$CH_3COCH(O_2)OH^* \rightarrow HCOOH + OH + CH_2=C=O \quad 44\%$$
$$\rightarrow HCOOH + CH_3O_2 + CO_2 \quad 56\%$$
$$CH_3CO_2(OH)CHO^* \rightarrow CH_3CO_2H + OH + CO \quad 44\%$$
$$\rightarrow CH_3CO_2H + HO_2 + CO_2 \quad 56\%$$
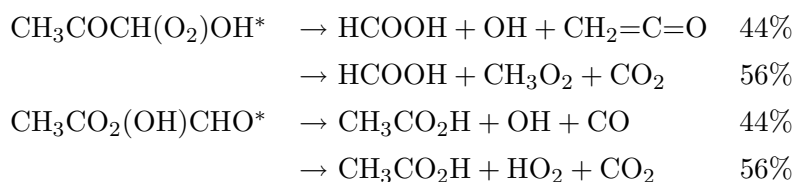
An analogy is assumed for C_3 radicals for which the CH_3- is substituted by $HOCH_2$-, $HOOCH_2$ and HCO-. In light of many experimental results it seems likely that C_4 and C_5 excited peroxy radicals do not undergo such decomposition but rather fast stabilization.

4.3.6.9 Methyl vinyl peroxy radical $\left(CH_3C(O_2)=CH_2^*\right)$

This alkyl radical is originated by loss of CO_2 from the acyl RO_2 of methacrolein (see Sec. 4.3.9.1). The mechanism of its formation and degradation is given below (Orlando et al., 1999).

$$CH_2=C(CH_3)CO_3 + NO \rightarrow CH_2=C(CH_3)CO_2 + NO_2$$
$$CH_2=C(CH_3)CO_2 \rightarrow CH_2=CCH_3 + CO_2$$
$$CH_2=CCH_3 + O_2 \rightarrow CH_2=C(O_2)CH_3^*$$
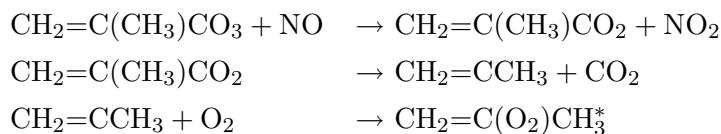
The way the resulting RO_2^* radicals dissipate the excess energy has also been inferred. About 65% is by decomposition. The remaining 35% is thought to be either another decomposition or a collisional stabilization. However, the second decomposition proposed is unlikely to happen because of the higher number of atoms that makes the stabilization easier as in the case of RO_2^* from glycolaldehyde and hydroxy acetone oxidation (Sec. 4.3.6). Therefore, the degradation mechanism is likely to be the following.

$$CH_2=C(O_2)CH_3^* \rightarrow CH_3CO^* + HCHO \quad 65\%$$
$$CH_2=C(O_2)CH_3^* + M \rightarrow CH_2=C(O_2)CH_3 + M \quad 35\%$$
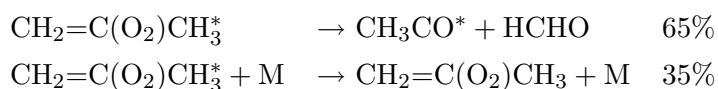
where $CH_2=C(O_2)CH_3$ undergoes the standard reactions of stabilized RO_2 and the species CH_3CO^* decomposes into $CH_3 + CO$ because it is produced in vibrationally hot state. The fate of the corresponding alkoxy radical $(CH_2=C(O)CH_3)$ is understood by writing its second and more important resonance structure [4], $CH_3C(=O)CH_2$, that is a closer representation of its actual structure. This resonance form turns out to be the same alkyl radical from the reaction of acetone with OH.

$$CH_2=C(O)CH_3 \leftrightarrow CH_3C(=O)CH_2$$
$$CH_3C(=O)CH_2 + O_2 \rightarrow CH_3C(=O)CH_2O_2^*$$

---
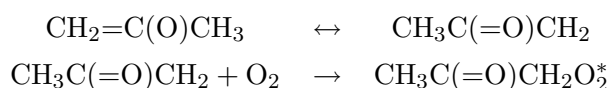
[4]Theory of resonance - in chemistry, theory by which the actual normal state of a molecule is represented not by a single valence-bond structure but by a combination of several alternative distinct structures. The molecule is then said to resonate among the several valence-bond structures or to have a structure that is a resonance hybrid of these structures (Encyclopaedia Britannica).

Finally, the species CH_3CO^* is produced in vibrationally hot state and decomposes into $CH_3 + CO$.

4.3.7 Stabilised RO_2

4.3.7.1 Reaction with HO_2

Until recently, $RO_2 + HO_2$ reactions were thought only to be radical terminating reactions yielding stable products. Some experimental studies have shown that the reaction between RO_2 and HO_2 is often a radical propagating reaction. In fact, alkoxy radicals along with OH are produced in significant fractions. Below I describe the new branching ratios for the reactions of some important peroxy radicals.

Elrod et al. (2001) studied the reaction of methyl peroxy radical (CH_3O_2) with HO_2 and found a 10% yield of HCHO. They also found this yield to increase as the temperature decreases reaching about 30% at 218 K. This new channel is expected to significantly modify the modeled HCHO mixing ratios and to accelerate the HO_x production due to photolysis of HCHO itself. The two channels are described below.

$$
\begin{array}{lccc}
 & & MCM & new \\
CH_3O_2 + HO_2 & \rightarrow O_2 + CH_3OOH & 100\% & 90\% \\
 & \rightarrow O_2 + HCHO + H_2O & 0\% & 10\%
\end{array}
$$
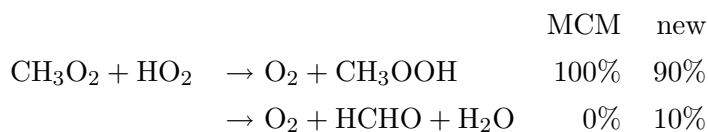
The reaction of $HOCH_2O_2$ with HO_2 at 296 K was recently studied by Jenkin et al. (2007). OH and formic acid (HCOOH) were found to be produced with a 20% and 50% yield, respectively. A complete description of all the channels is presented below.

$$
\begin{array}{lcc}
HOCH_2O_2 + HO_2 & \rightarrow O_2 + HOCH_2OOH & 50\% \\
 & \rightarrow O_2 + HCOOH + H_2O & 30\% \\
 & \rightarrow O_2 + HOCH_2O + OH & 20\%
\end{array}
$$
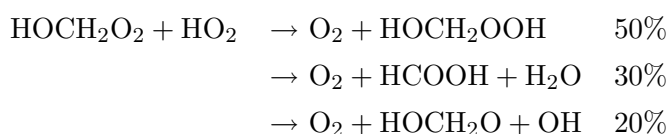
where the radical $HOCH_2O$ reacts with O_2 to give $HCOOH + HO_2$.

The reaction of peroxy acetyl radical (CH_3CO_3) with HO_2 was investigated in great detail by three studies (Dillon and Crowley (2008), Hasson et al. (2004), Jenkin et al. (2007)). Contrary to previous knowledge, OH was found to be the major product (44%). The reaction undergoes three channels described as:

$$
\begin{array}{lcc}
CH_3CO_3 + HO_2 & \rightarrow O_2 + CH_3CO_3H & 41\% \\
 & \rightarrow O_3 + CH_3CO_2H & 15\% \\
 & \rightarrow O_2 + CH_3CO_2 + OH & 44\%
\end{array}
$$
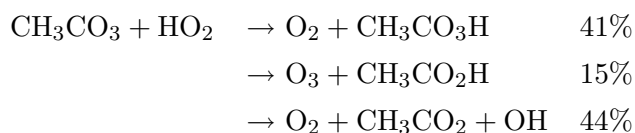
where CH_3CO_2 decomposes to CH_3 and CO_2.

The reaction of acetonoxy radical ($CH_3COCH_2O_2$) with HO_2 was recently studied by Hasson et al. (2004), Jenkin et al. (2007) and Dillon and Crowley (2008). Only two channels were identified:

$$CH_3COCH_2O_2 + HO_2 \quad \rightarrow O_2 + CH_3COCH_2OOH \qquad 85\%$$
$$\rightarrow O_2 + CH_3COCH_2O + OH \quad 15\%$$
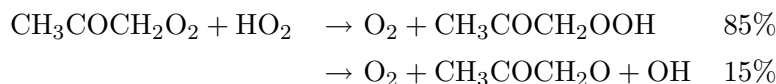
In light of the experimental results presented above, I apply a structure-reactivity analogy for all RO_2 produced in the oxidation of isoprene. In particular, I assume that RCO_3 and $RCOCH_2O_2$ peroxy radicals react with HO_2 in the same way as CH_3CO_3 and $CH_3COCH_2O_2$, respectively. However, due to the large size of the mechanism being developed, the formation of many $C_{4-5}-RCO_2H$ has often been neglected.

4.3.7.2 Reaction with NO

The reaction rates as estimated by the MCM protocol (Saunders et al. (2003)) are maintained. These reactions mostly convert peroxy to alkoxy radicals. Often other products such as alkyl nitrates are produced in which the NO radical adds to the RO_2 molecule. The MCM makes use of a well established method (a SAR) to determine the branching ratio of these two channels. Recently, new alkyl nitrates yields from the first peroxy radicals from isoprene, MVK and MACR have been estimated in a very detailed chamber study (Paulot et al. (2009a)). These yields have been determined to be significantly different from the ones used in the MCM. For instance, the internally double bonded RO_2 from OH addition to isoprene has been estimated to yield about 24% of alkyl nitrate in the reaction with NO. For the same species MCM assigns a much lower yield of 8.9%. On the other hand, the externally double bonded RO_2 have a alkyl nitrate yield of 6.7% was estimated. However, the total average alkyl nitrate yield from Paulot et al. (2009a) and MCM are 11.7 and 10% , respectively. Furthermore, the MCM does not consider any alkyl nitrate deriving from MACR and only one isomer of alkyl nitrate from MVK with a 1.7% yield. Paulot et al. (2009a) reports alkyl nitrate yields of 15 and 11% for MACR and MVK, respectively. Hence, these higher and new alkyl nitrate yields are adopted.

The MCM treatment of the unsaturated C_5-nitrates neglects OH-addition to double bonds is considered. Instead, only OH abstraction is considered leading to a 100% NO_2-recycling in one-step. This has important consequenses for the NO_x recycling efficiencies in isoprene chemistry under polluted regimes (Ito et al. (2009)). Paulot et al. (2009a) also gained mechanistic information about the fate of these alkyl nitrates establishing that OH addition is the dominant pathway. This implies a much lower NO_x recycling efficiency (55%) in comparison to MCM (100%). However, this new chemistry is beyond
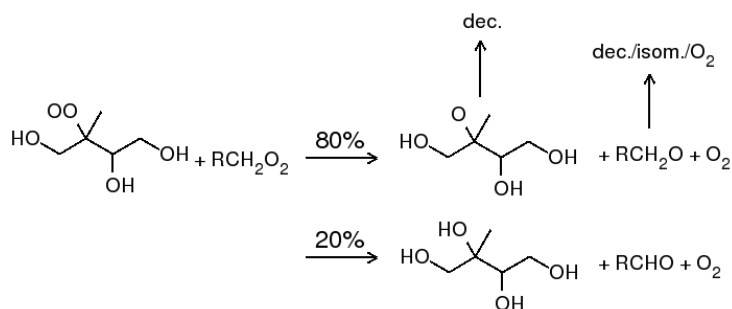
FIGURE 4.4: Example of homogeneous gas-phase production of tetrols in isoprene
oxidation involving reactions between peroxy radicals.

the scope of this study and will be implemented in the future in order to study the ozone
production due to isoprene in polluted environments.

4.3.7.3   Reaction with other RO_2 and NO_3

The reactions with other peroxy radicals and with nitrate radical are treated following
the MCM protocol (Saunders et al. (2003)). Applying the development protocol to the
RO_2 from isoprene hydroperoxides led to the production and treatment of tetrols [5] that
were recently measured in the atmosphere (Claeys et al. (2004a,b)). Heterogeneous
reaction mechanisms involving organic aerosols have been proposed by Edney et al.
(2005) and Böge et al. (2006b). The homogeneous gas-phase mechanism here developed
involves reactions of RO_2 bearing 3 hydroxy groups with all other peroxy radicals. For
one of the four possible C_5-RO_2 the tetrol is produced with a 20% yield as described
in Fig. 4.4.

4.3.7.4   Peroxy ring-closure

Under very low-NO_x regimes peroxy radicals have a lifetime of about $1 - 3 \times 10^{-2} s^{-1}$
against the traditional reactions with NO, HO_2 and RO_2. For these conditions, Vereecken
and Peeters (2004) predicted that some unsaturated RO_2 from terpenes may undergo a
non-traditional peroxy ring-closure. The mechanism is the intramolecular version of the

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[5]Compounds bearing four hydroxy groups (-OH).
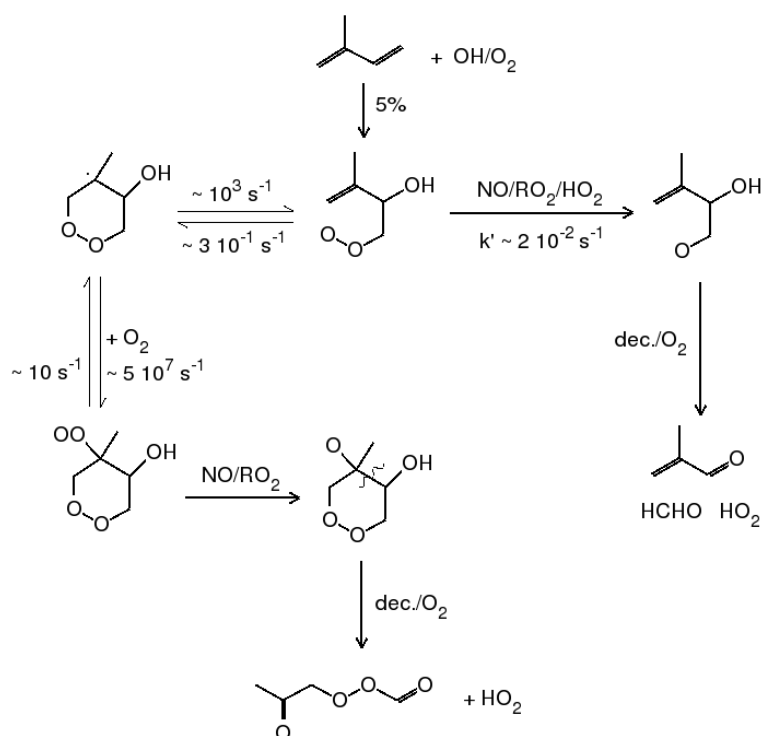
FIGURE 4.5: Competition between peroxy ring-closure and reactions with other radicals for one isomer of the peroxy radicals from isoprene under very low-NO_x. Numbers close to arrows are the (pseudo-)unimolecular rate constants for the reactions indicated.

RO_2 addition to double bonds that are well-known from cool-flame combustion science (Stark (1997, 2000)). This non-traditional route has been successfully used in developing the oxidation mechanism of α-pinene, whereby acetone yields could be better explained (Capouet et al. (2004), Vereecken et al. (2007)). Among the first isoprene RO_2, two isomers can undergo such peroxy ring-closure. Its competition with the traditional pathways is shown in Fig. 4.5 for one peroxy radical. Soon after the peroxy ring-closure, very fast reaction with O_2 takes place forming an heterocyclic RO_2. The mechanism for the subsequent chemistry has been developed. The fate of the resulting heterocyclic alkoxy radical has been predicted with the help of the SAR described in the next section (Sec. 4.3.8).

4.3.8   Fate of alkoxy radicals $RO^{\cdot}$

The alkoxy radicals can usually undergo reaction with O_2, decomposition and isomerization. The last reaction is competitive only if the radical forms a 6-membered ring while abstracting an H atom (1,5 H-shift). This is the case for C_4 radicals. The reactions are illustrated each with their respective frequencies in Fig.4.6 for a particular alkoxy radical. The competition of the three reactions determines the number of NO to NO_2 conversions
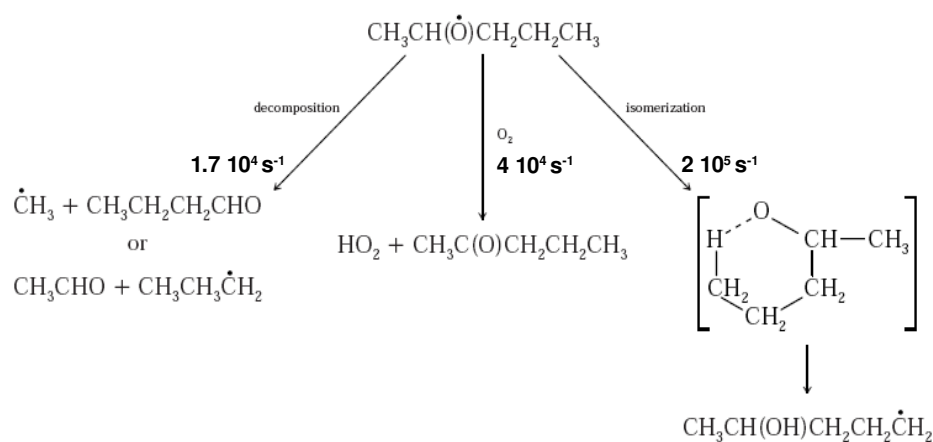
FIGURE 4.6: General fate of alkoxy radicals from VOC oxidation (Atkinson, 1997a).
The reaction frequencies shown are for atmospheric conditions at 298 K and 1 bar.

in the atmospheric oxidation of organic molecules. However, this competition takes place only for radicals which are produced with little or no excess energy. This is not the case for alkoxy radicals resulting from RO_2 + NO reactions (Sec. 4.3.7.2). In fact, these reactions are calculated to be exothermic by ca. 11 kcalmol^{-1} (Mereau et al. (2000)), which is higher than decomposition barriers for all β-hydroxy and many other oxygenated $RO^.$ species. Such activated radicals undergo prompt decomposition to significant extents prior to thermalization. For instance, Orlando et al. (2000) calculated that 80% of the acetonoxy radicals $CH_3C(=O)CH_2O^.$ from $CH_3C(=O)CH_2O_2$ + NO reactions have sufficient energy to decompose promptly under tropospheric conditions. In the same study the decomposition barrier was also estimated to be lower than 7.5 kcalmol^{-1}. Furthermore, Johnson et al. (2004) proposed a SAR to estimate the fraction of alkoxy radicals from RO_2 + NO reactions that are activated and undergo prompt decomposition. However, in most cases decomposition also dominates the fate of thermalized alkoxy radicals. Given the focus of my development for low-NO_x regimes, I treat the alkoxy radicals as being all thermalized. Discrimination of activated and thermalized ones will be subject of development in the near future. In order to estimate the dominant fate of the alkoxy radicals I make use of SARs. For the reactions with O_2 and the isomerization I make use of the updated SARs by Atkinson (2007). The rate constants for these two processes do not vary much with changing molecules. However, the frequency for decomposition

of alkoxy radicals can vary a lot and ranges from $< 1s^{-1}$ to 10^{12} s^{-1}. Therefore, it is critical to make good estimates of these rates. For the decomposition I use the SAR developed by Peeters et al. (2004) and extended by L. Vereecken for the hydroperoxy (-OOH) and nitro (-ONO$_2$) groups (L. Vereecken, pers. comm.). This SAR estimates the activation energy for the β C-C fission with the relationship:

$$
\begin{aligned}
E_b(kcal/mol) = \quad & 17.5 - 2.1 \cdot N_\alpha(alk) - 3.1 \cdot N_\beta(alk) \\
& -7.5 \cdot N_{\alpha,\beta}(-OH) - 8.0 \cdot N_\beta(=O) - 12 \cdot N_\alpha(=O) \\
& -9.5 \cdot N_{\alpha,\beta}(-OOH) - 3.1 \cdot N_\alpha(-ONO_2) - 2.7 \cdot N_\beta(-ONO_2)
\end{aligned}
$$

where N is the number of substituents of one kind in position α or β relative to the alkoxy and "alk" stands for alkyl group.

If $E_b \leq 7kcal/mol$ then a correction must be applied:

$$E'_b = E_b + 0.027 \cdot (9 \ kcal/mol - E_b)^2$$

To calculate the rate coefficient one needs to put the value of E_b in the following formula:

$$k(s^{-1}) = 1.8 \cdot 10^{13} exp(-E_b/RT)$$

The SAR for the decomposition confirms experimental results that contradict the MCM for the fate of the alkoxy radical HOCH$_2$CO(CH$_3$)CH=CH$_2$ from isoprene. In MCM this radical is named ISOPBO and is predicted to lose a methyl group with a 25% yield of a species named MVKOH (HOCH2COCH=CH$_2$). However, Benkelberg et al. (2000) determined that the detection of MVKOH was an erroneous identification of a peak obtained with a mass spectrometer. Therefore, HOCH$_2$CO(CH$_3$)CH=CH$_2$ very likely decomposes yielding 100% of MVK and HCHO.

4.3.9   Reaction of OH with major compounds

4.3.9.1   Methacrolein

The OH-initiated oxidation of methacrolein under high-NO$_x$ has been studied in detail by Orlando et al. (1999). However, the mechanistic results of this valuable study have not been incorporated in MCM yet. The branching ratios in MCM and Orlando et al. (1999) are compared:

		MCM	new
CH$_2$=C(CH$_3$)CHO + OH	$\rightarrow$ CH$_2$=C(CH$_3$)CO + H$_2$O	57%	45%
	$\rightarrow$ HOCH$_2$CO$_2$(CH$_3$)CHO	43%	$\alpha \cdot$55%
	$\rightarrow$ CH$_2$O$_2$C(OH)(CH$_3$)CHO	0%	$(1-\alpha) \cdot$55%
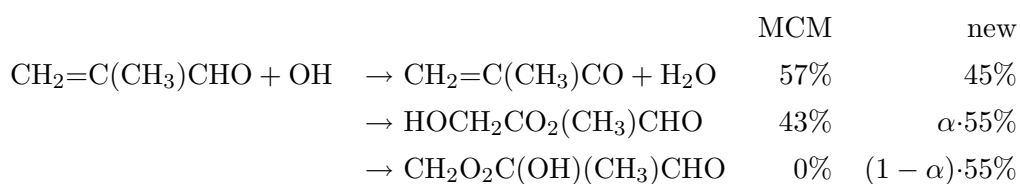
where $\alpha < 1$.

Using the site-specific SAR (Sec. 4.3.2) α is estimated to be about 0.92. Furthermore, Orlando et al. (1999) gave a lower bound of 0.85 for α. The degradation of $CH_2O_2C(OH)(CH_3)CHO$ should produce the radical $CH_3COHCHO$. Subsequent reaction with O_2 produce methylglyoxal with a 85% yield (Sec. 4.3.6.8). The alkoxy radical from $HOCH_2CO_2(CH_3)CHO$ is predicted to yield hydroxyacetone and methyl glyoxal in a 66:34 ratio. However, the uncertainties of the SAR make this calculated ratio not robust. On the other hand, I can assume the 8% yield of methyl glyoxal (Tuazon and Atkinson (1990b)) to be only from the internal OH addition. Under high-NO_x, Paulot et al. (2009a) determined a 15% alkyl nitrate yield. Using these data and assumptions together I can calculate the branching ratio α:

$$(1 - \alpha) \cdot Y_{MGLYOX}^{CH_3COHCHO} \cdot (1 - Y_{ROONO_2}) = Y_{MGLYOX}^{MACR} \;\Rightarrow\; \alpha = 0.89$$

It follows that the hydroxyacetone yield (only from $HOCH_2CO_2(CH_3)CHO$ degradation) is $0.89 \cdot 0.55 \cdot (1-0.15) = 0.42$, consistent with $45\pm5\%$ estimated by Tuazon and Atkinson (1990b) and Orlando et al. (1999).

4.3.9.2 isoprene

Under daylight conditions, isoprene oxidation is initiated by OH to a very large extent. Its reaction with OH has little activation energy and the relative rate constant at 298 K is 1×10^{-10} $cm^3\,molec^{-1}\,s^{-1}$, close to the kinetic limit[6]. OH-addition to its double bonds is the dominant pathway with H-abstraction being negligible (Atkinson et al. (1989)). The latter one is not considered by nearly all oxidation mechanisms in use. The first isoprene products to be considered should be hydroxy alkyl radicals. However, under the widely accepted assumption that stable RO_2 are produced, they are not explicitly represented and assumed to undergo fast O_2 addition. The MCM considers only four isomeric RO_2, though eight are possible (see Fig. 4.7). In this work the RO_2 production branching ratios from isoprene + OH is taken from the recent detailed study under high-NO_x conditions (Paulot et al. (2009a)). However, due to limitations of time I treat the six structural isomers[7], for which the relative product yields are shown in Fig. 4.7. Two of these structural isomers can be present in two stereoisomers[8] E and Z. Although Paulot

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[6]The kinetic limit for a bimolecular reaction can be estimated making use of the collision frequency from the kinetic theory of gases. For a barrierless reaction ($E_a = 0$), every collision should result in a reactive event. Thus, at 298K and 1 atm, molecules having a radius of 0.2nm and molecular weight of 50 $gmol^{-1}$ would react with a rate constant $k = 2.51 \times 10^{-10}$ $cm^3\,molec^{-1}\,s^{-1}$ (Finlayson-Pitts and Pitts, Jr. (2000))

[7]In structural isomers, the atoms and functional groups are joined together in different ways.

[8]In stereoisomers the bond structure is the same, but the geometrical positioning of atoms and functional groups in space differs.
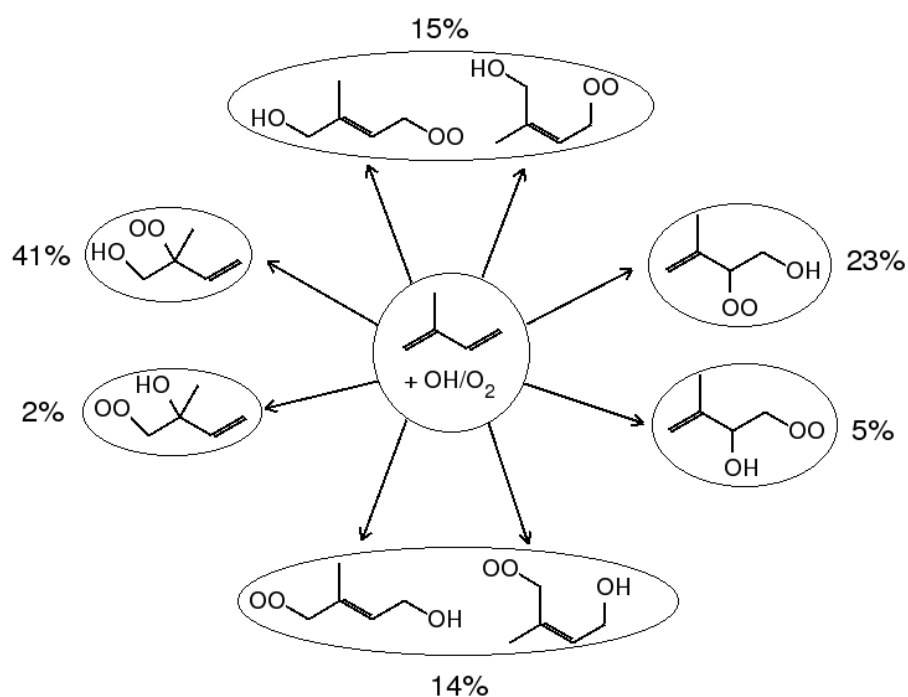
FIGURE 4.7: OH addition to isoprene, subsequent O_2 addition and RO_2 with relative yields for each isomer taken from Paulot et al. (2009a). The two pairs of RO_2 in the upper and lower part of the graph are geometric isomers and treated in the mechanism as single species.

et al. (2009a) established experimentally the E and Z isomers undergo very different pathways, their chemistry should not be crucial in explaining the high OH-recycling mechanisms and I, therefore, maintained the MCM treatment. Implementation of the new chemistry for these geometric RO_2 isomers will be implemented at a later stage. The six RO_2 here considered and their relative alkoxy radicals are treated according to the latest SARs as described in Sec. 4.3.7 and 4.3.8.

4.4 Reactions of O_3 with unsaturated VOC

4.4.1 General mechanism

The atmospheric reactions of O_3 with VOC bearing double bonds has been reviewed recently (Johnson and Marston (2008)). As shown in Fig. 4.8, they go through a [3+2] cycloaddition of ozone to the double bond to form a primary ozonide (POZ). This reaction is highly exothermic (48-60 kcalmol^{-1}) and this excess energy is retained within the adduct, leading to a very rapid decomposition of the POZ to a carbonyl and a diradical compound called Criegee intermediate. When the alkene is asymmetric
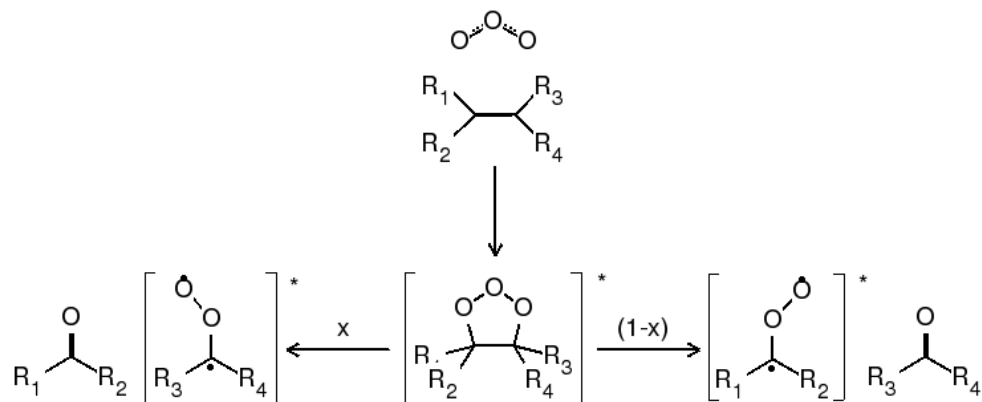
FIGURE 4.8: General mechanism of ozonolysis. The diradical species are the Criegee intermediates. R_i ($i = 1, 4$) can be either an alkyl radical or a H atom.

two channels for the POZ decomposition are possible. The Criegee intermediates are excited and very short-lived. They are usually represented as diradicals although having most of the times a more zwitterionic character (see Fig. 4.9a). The diradical and the zwitterionic form are used here interchangeably. These intermediates can exist as two conformers[9] (Fig. 4.9b), *syn* and *anti*, that do not interconvert because the C-O bond has a significant π character (double bond). The conformation of the Criegee intermediates is very important in determinining the their fate (see Sec. 4.4.2).

4.4.2   Fate of Criegee intermediates

4.4.2.1   General

Criegee intermediates have a rather complex fate which involves other short-lived intermediates. They can undergo either collisional stabilization or decomposition. The latter can go *via* the "hot acid" and "hydroperoxide" channel (see Fig. 4.10). Whether one channel or the other is preferred depends critically on the size, the availability of H atoms to migrate to the external O atom and the conformation. For instance, the $^\bullet CH_2OO^\bullet$

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[9]One of a set of stereoisomers, each of which is characterized by a conformation corresponding to a distinct potential energy minimum (IUPAC Goldbook).
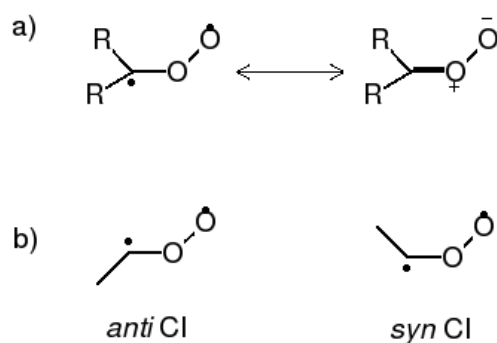
FIGURE 4.9: Criegee intermediates. a) Resonance between the diradical and the zwitterionic form. b) The conformers *syn* and *anti*.
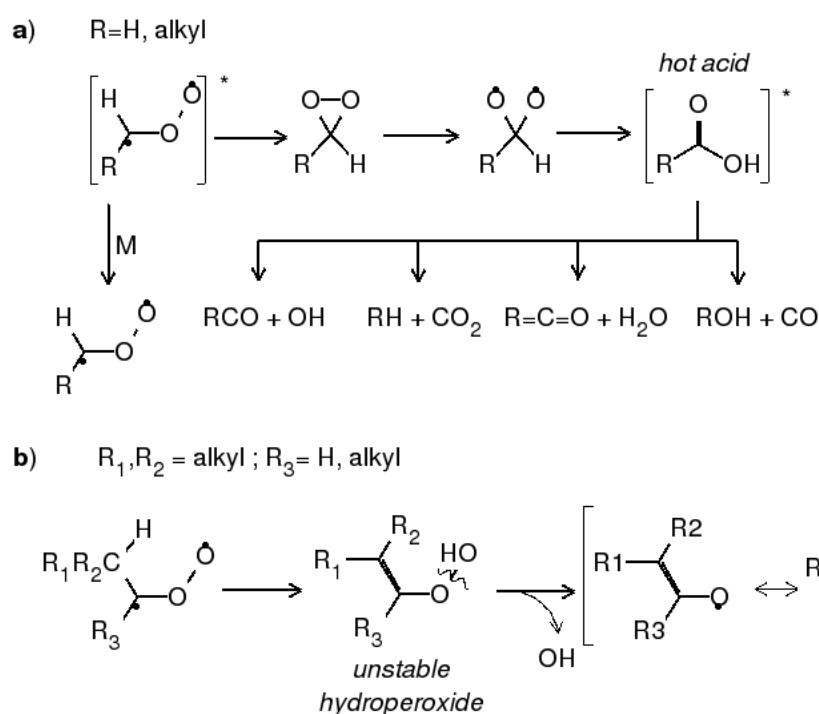
FIGURE 4.10: Possible fates of Criegee intermediates that are *anti* monosubstituted conformers (a) and *syn* monosubstituted and disubstituted conformers (b).

and *anti* monosubstituted Criegee intermediates decompose solely *via* the "hot acid" channel or under go stabilisation (see Fig. 4.10a). Instead, *syn* monosubstituted or disubstituted Criegee intermediates decompose *via* the "hydroperoxide" channel. This channel was first proposed by Niki et al. (1987) and has been corroborated by more than 20 years of research (Johnson and Marston (2008) and references therein). Recently,

time-resolved studies of OH formation from ozonolysis gained valuable mechanistic insights (Kroll et al. (2001a,b)). At atmospheric pressure OH yields were consistent with previously reported yields only at reaction times of around 1 s^{-1}, indicating the involvement of stabilized Criegee intermediates in the OH formation. The key intermediate appears to be an α, β unsaturated hydroperoxide, either excited or thermalized, that decompose producing OH and a vinoxy radical (see Fig. 4.10b). Kuwata et al. (2003) calculated that the O-O bond in vinyl hydroperoxide has a dissociation energy (D(O-O)) of about 20 kcalmol^{-1} compared to the one of CH$_3$OOH being about 45 kcalmol^{-1}. The significant difference lies in the resonance stabilization of the resulting vinoxy radical. Interestingly, using the low D(O-O) in the expression for the thermal decomposition of CH$_3$OOH (Baulch et al. (2005)), I estimate that vinyl hydroperoxide has slightly less than 1 s lifetime under atmospheric conditions. Recently, Nguyen et al. (2009) calculated for a vinyl hydroperoxide from β-pinene ozonolysis that D(O-O) is less than 17 kcalmol^{-1}. I consider these unsaturated hydroperoxides explicitly in the mechanism. Since their lifetime is likely always less than 1 s^{-1}, I let them decompose all at the same rate with a rate constant $k = 6. \times 10^{14} \ exp(-20000/(1.986 \ T))$. It is interesting to note that OH-initiated oxidation of MACR (Sec. 4.3.9.1) and photolysis of MVK and MACR (Sec. 4.5.3) also lead to vinyl hydroperoxides through production of vinyl radicals.

As a guide, I follow the SAR by Rickard et al. (1999) for the fate of Criegee intermediates. The SAR assumes that OH is produced *via* the "hydroperoxide" channel with a 100% efficiency, with the exception of $^\bullet$CH$_2$OO$^\bullet$. Consequently, (CH$_3$)$_2^\bullet$COO$^\bullet$ and *syn*-CH$_3^\bullet$CHOO$^\bullet$ should always give OH radicals, while *anti*-CH$_3^\bullet$CHOO$^\bullet$ should not. Assuming that the *syn* and *anti* are always produced in a 1:1 ratio, the OH yields for generic Criegee intermediates R$_1$R$_2$CHOO and RCHOO are 1 and 0.5, respectively. However, I integrate this SAR with the last recommendations by IUPAC. In the next sections the fate of many specific Criegee intermediates is illustrated.

4.4.2.2 $^\bullet$CH$_2$OO$^\bullet$

The simplest Criegee intermediate cannot decompose *via* the "hydroperoxide" channel. Compared to MCM, the three channels have similar branching ratios. It is worth noting that the latest recommended OH yield is slightly higher.

		MCM	new
[$^\bullet$CH$_2$OO$^\bullet$]* + M	$\rightarrow$ $^\bullet$CH$_2$OO$^\bullet$	0.37	0.37
[$^\bullet$CH$_2$OO$^\bullet$]*	$\rightarrow$ CO + H$_2$O	0.50	0.47
	$\rightarrow$ HO$_2$ + CO + OH	0.13	0.16

4.4.2.3 $CH_3^\bullet CHOO^\bullet$

It comprises both the *anti* and the *syn* conformers. The first one decomposes *via* the "hot acid" channel. The latter one is assumed to entirely rearrange to give the unstable hydroperoxide $CH_2{=}CHOOH$ and give OH and vinoxy radical. Below its detailed fate is shown.

		MCM	new
$[CH_3^\bullet CHOO^\bullet]^* + M \rightarrow CH_3^\bullet CH_2 OO^\bullet$		0.18	0.16
$[CH_3^\bullet CHOO^\bullet]^* \rightarrow CH_4 + CO_2$		0.125	0.15
$\rightarrow CH_3 + HO_2 + CO_2$		0.125	-
$\rightarrow CH_3 + CO + OH$		0.57	-
$\rightarrow CH_2{=}CHOOH$		-	0.50
$\rightarrow CH_2 CO + H_2 O$		-	0.06
$\rightarrow CH_3 OH + CO$		-	0.09
$\rightarrow CH_3 CO + OH$		-	0.04

The MCM has actually three different kinds of excited $[CH_3^\bullet CHOO^\bullet]^*$. For comparison I took the one that was closer to the SAR by Rickard et al. (1999) that is used by the MCM as stated by Saunders et al. (2003). I find, however, the inconsistency between the SAR and the MCM treatment regarding the "hydroperoxide" channel set to have a branching ratio of 0.57 in the latter. Taking into account the fate of the decomposition products, the new effective OH yield is about 0.59, that is very similar to the yield in MCM.

4.4.2.4 $HOCH_2^\bullet CHOO^\bullet$

This intermediate is produced from the ozonolysis of C_5 unsaturated β-hydroxy compounds. Its fate is shown below.

		MCM	new
$[HOCH_2^\bullet CHOO^\bullet]^* + M \rightarrow HOCH_2^\bullet CHOO^\bullet$		0.18	0.16
$[HOCH_2^\bullet CHOO^\bullet]^* \rightarrow CH_3 OH + CO_2$		0.125	0.15
$\rightarrow 2HO_2 + HCHO + CO_2$		0.125	-
$\rightarrow HCHO + CO + HO_2 + OH$		0.57	-
$\rightarrow HOCH{=}CHOOH$		-	0.50
$\rightarrow CH_3 OH + CO$		-	0.15
$\rightarrow HOCH_2 CO + OH$		-	0.04

The formation of HOCHCO, analogous of chetene, is neglected and its branching ratio assigned to the channel producing $CH_3 OH + CO$. The unsaturated hydroperoxide

HOCH=CHOOH decomposes giving OH and the radical HOCHCHO. The latter produces OH with a 19% yield after reacting with O_2 (see Sec. 4.3.6.6). Considering the fate of the other products I estimate a new effective OH yield of about 0.61.

4.4.2.5 $HCO^\bullet CHOO^\bullet$

This intermediate is produced from the ozonolysis of C_5 unsaturated β-hydroxy compounds. Its fate is shown below.

		MCM	new
$[HCO^\bullet CHOO^\bullet]^* + M$	$\rightarrow HCO^\bullet CHOO^\bullet$	0.18	0.16
$[HCO^\bullet CHOO^\bullet]^*$	$\rightarrow HCHO + CO_2$	0.125	0.15
	$\rightarrow 2HO_2 + HCHO + CO_2$	0.125	-
	$\rightarrow 2CO + HO_2 + OH$	0.57	-
	$\rightarrow HOOCH=CHO$	-	0.50
	$\rightarrow HCOOH + CO$	-	0.15
	$\rightarrow HCOCO + OH$	-	0.04

4.4.2.6 $HOOCH_2^\bullet CHOO^\bullet$

This intermediate is produced from the ozonolysis of a C_5 unsaturated hydroperoxide (see Sec.4.4.5) and is not considered in MCM. Assuming the branching ratios for $[CH_3^\bullet CHOO^\bullet]^*$ to be a good approximation, I implemented the following reactions.

$[HOOCH_2^\bullet CHOO^\bullet]^* + M$	$\rightarrow HOOCH_2^\bullet CHOO^\bullet$	0.16
$[HOOCH_2^\bullet CHOO^\bullet]^*$	$\rightarrow CH_3OOH + CO_2$	0.15
	$\rightarrow HOOCH=CHOOH$	0.50
	$\rightarrow HOOCH=CO + H_2O$	0.06
	$\rightarrow HOCH_2OOH + CO$	0.09
	$\rightarrow HOOCH_2CO + OH$	0.04

The unsaturated hydroperoxide HOOCH=CHOOH decomposes giving glyoxal and 2 OH. Considering the fate of the other products I estimate an effective OH yield of about 1.14.

4.4.2.7 $HOCH_2^\bullet C(OO^\bullet)CH_3$

According to the SAR by Rickard et al. (1999), both conformers of R_1R_2CHOO (*anti* and *syn*) decompose *via* the "hydroperoxide" channel giving OH. The mechanism is illustrated in Fig. 4.11. It is worth noting that the product of the *anti* conformer is a
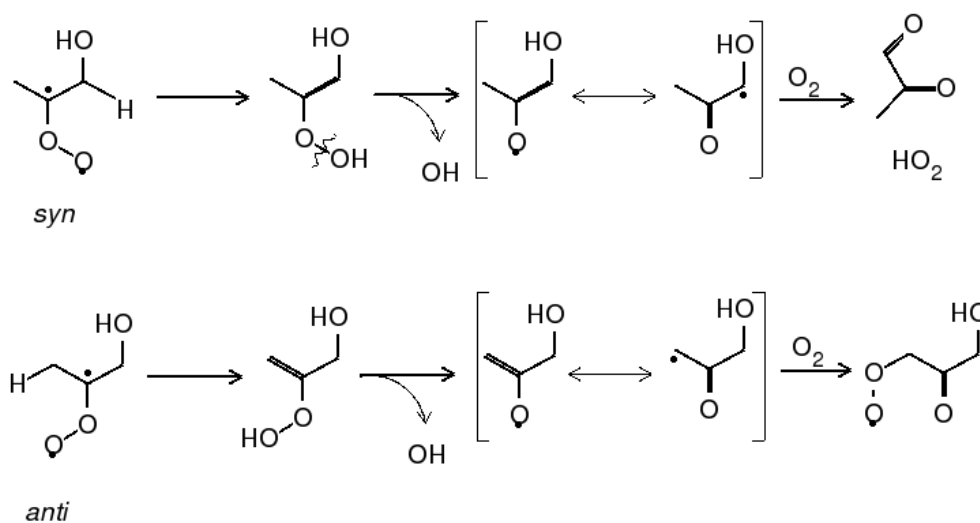
FIGURE 4.11: Quantitative decomposition of a simple Criegee intermediate.

β-keto RO_2 whose further degradation results in significant OH production. In contrast, the MCM treatment is inconsistent with its own development protocol (Saunders et al. (2003)) considering an 11% yield of the stabilised Criegee intermediate and the rest (89%) methylglyoxal as if only *syn* conformers were produced.

4.4.2.8 $HOOCH_2^{\bullet}C(OO^{\bullet})CH_3$

This Criegee intermediate results from the ozonolysis of a C_5 unsaturated hydroperoxide that is not considered in the MCM. I developed the mechanism for the decomposition of both conformers (se Fig. 4.12). It can be seen that $HOOCH_2^{\bullet}C(OO^{\bullet})CH_3$ decomposition is predicted to give OH with a 1.5 yield. Normally, the OH yields from Criegee intermediates are below or equal to unity. The potential implications of this very OH yield are discussed in Sec. 4.4.5.

4.4.2.9 $HCO^{\bullet}C(OO^{\bullet})CH_3$

This Criegee intermediate is produced from the ozonolysis of MACR and a C_5 hydroxy carbonyl. Omitting the intermediate species likely involved in the decomposition, its fate can be described as follow.
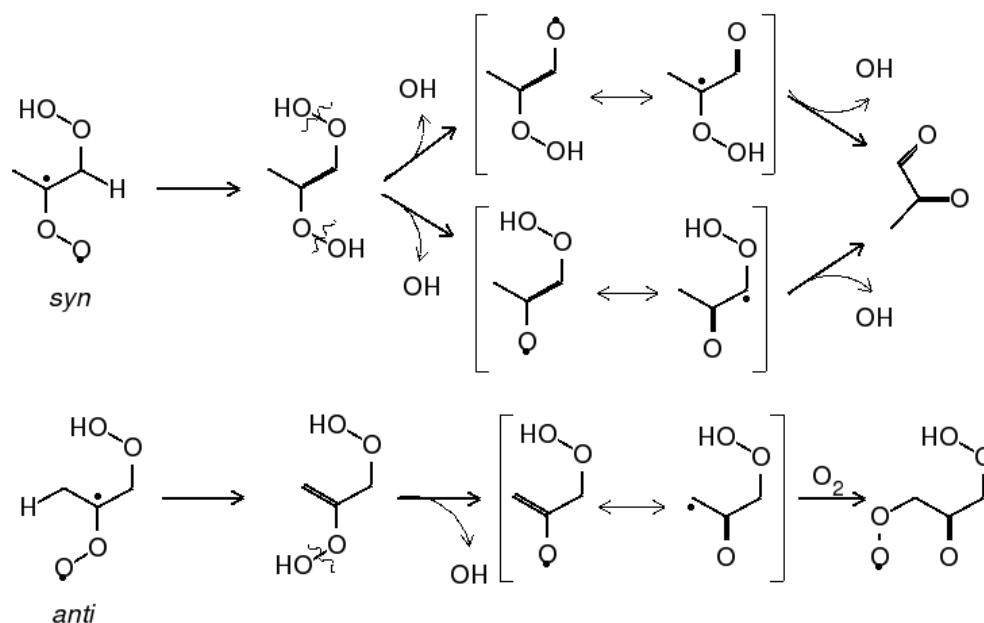
FIGURE 4.12: Decomposition of a Criegee intermediate from ozonolysis of an isoprene hydroperoxides. The *syn* and *anti* conformers have final OH yields of 2 and 1, respectively.

$$[HCO^\bullet C(OO^\bullet)CH_3]^* \quad \rightarrow OH + CH_3CO + CO \qquad 0.50$$
$$\rightarrow OH + HCOCOCH_2O_2 \quad 0.50$$
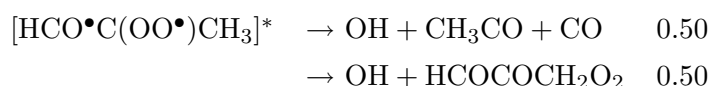
Thus an OH yield of 1 is predicted. However, the degradation of the other products (CH_3CO and $HCOCOCH_2O_2$) leads to additional OH production. Comparison with the MCM is not meaningful because the MCM has two "ad hoc" intermediates whose fate is inconsistent with the MCM development protocol (Saunders et al. (2003)).

4.4.2.10 $CH_3C(O)^\bullet CHOO^\bullet$

In isoprene oxidation the species $CH_3C(O)^\bullet CHOO^\bullet$ is produced only in the ozonolysis of MVK. This Criegee intermediate cannot undergo the usual "hydroperoxide" channel for the lack of H atoms allowing a 1,5-H shift. I find the MCM treatment of this intermediate to be a good guess of its fate. It can be described as below.

$$[CH_3C(O)^\bullet CHOO^\bullet]^* + M \quad \rightarrow CH_3C(O)^\bullet CHOO^\bullet \qquad 0.24$$
$$[CH_3C(O)^\bullet CHOO^\bullet]^* \qquad \rightarrow OH + CO + HOCH_2CO \qquad 0.36$$
$$\rightarrow HOCH_2CHO + CO_2 \qquad 0.20$$
$$\rightarrow HOCH_2CO + HO_2 + CO_2 \quad 0.20$$
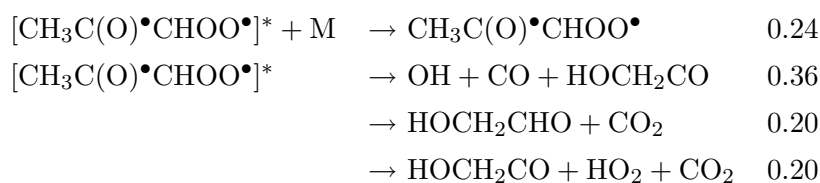
Considering further OH production in the reaction $HOCH_2CO + O_2$ (26%), an effective OH yield of about 0.51 is estimated for the present Criegee intermediate.

4.4.3   Fate of stabilised Criegee Intermediates

As shown above, Criegee intermediates are stabilized by collisions to a significant extent. The *syn* conformers undergo likely decomposition, either thermal or prompt, *via* the "hydroperoxide" channel as explained in Sec. 4.4.2.1. The *anti* conformers are precluded this pathway and undergo bimolecular reactions. The atmospheric fate of the stabilized Criegee intermediates have been investigated in a number of studies (Hasson et al. (2001a,b, 2003), Neeb et al. (1997), Sauer et al. (1999) and references therein). The most important bimolecular reaction in the atmosphere is the reaction with H_2O. A remarkable finding was that the sole product of $^\bullet CH_2OO^\bullet$ is hydroxymethyl hydroperoxide (Neeb et al. (1998)). This is in contrast with the MCM that considers the formation of $HCOOH$ and $HCHO + H_2O_2$. Neeb et al. (1997) studied the fate of the stabilized $^\bullet CH_2OO^\bullet$ and $CH_3^\bullet CHOO^\bullet$ with H_2O. I assume that intermediates with analogous structure to the latter have the same branching ratios for each channel. With the exception of C_4 Criegee intermediates, the fate of stabilized Criegee intermediates, not decomposing *via* the "hydroperoxide" channel, is illustrated below.

		MCM	new
$^\bullet CH_2OO^\bullet + H_2O$	$\rightarrow HOCH_2OOH$	0	1
	$\rightarrow HCHO + H_2O_2$	0.375	0
	$\rightarrow HCOOH + H_2O$	0.625	0
$R^\bullet CHOO^\bullet + H_2O$	$\rightarrow RCH(OH)OOH$	0	0.15
	$\rightarrow RCHO + H_2O_2$	0.375	0.77
	$\rightarrow RCOOH + H_2O$	0.625	0.08

4.4.4   Branching ratios and rate constants

In order to predict the decomposition of the POZ I use again the SAR by Rickard et al. (1999). The branching ratios for three differently substituted alkenes are shown in Fig. 4.13. They can be rationalized looking at stability of the radical species of each channel. A channel producing a more stable radical , e.g. a tertiary radical, should be favoured in comparison to other one producing a less stable radical, e.g. a secondary radical. This SAR by Rickard et al. (1999) was based on old IUPAC recommendations regarding Criegee intermediates and developed to predict OH yield for alkene ozonolysis. However, the IUPAC recommendations about the OH yields changed slightly. A fundamental assumption is that the chemistry of oxygenated unsaturated compounds from
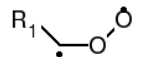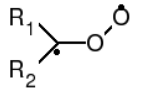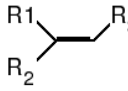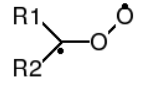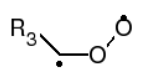
FIGURE 4.13: Branching ratios for ozonolysis of generic alkenes.

isoprene oxidation can be reasonably well approximated by this SAR for alkenes. The reason for that is the presence of heteroatoms that can alter the stability of the radicals forming. Furthermore, this SAR is not for conjugated dienes like isoprene. In this case I continue the MCM treatment of isoprene ozonolysis because it accurately reproduces the experimentally available data (Atkinson (1997b)). Substituents around the double bonds affect the rate constants modifying the bonding and anti-bonding molecular orbitals. I maintain the MCM rate constants unless new specific IUPAC recommendations are made. New ozonolysis reactions involving unsaturated C_5 hydroperoxides, diols and hydroxy alkyl nitrates are considered. The rate constants of the parent alkenes are taken representing likely a lower limit. In fact, the substituent group $HOCH_2$- has the tendency to enhance the rate constant with respect to the parent alkene (Grosjean and Grosjean (1994)). The predicted chemistry for the two internally double bonded C_5 hydroperoxides is described in Sec. 4.4.5.

4.4.5 Unsaturated hydroperoxides

The ozonolysis of many C_5 unsaturated isoprene oxidation products is not considered in MCM. Applying the SAR described above led to a notable discovery. All alkenes and many oxygenated analogues have OH yields to be lower than one. However, the Criegee
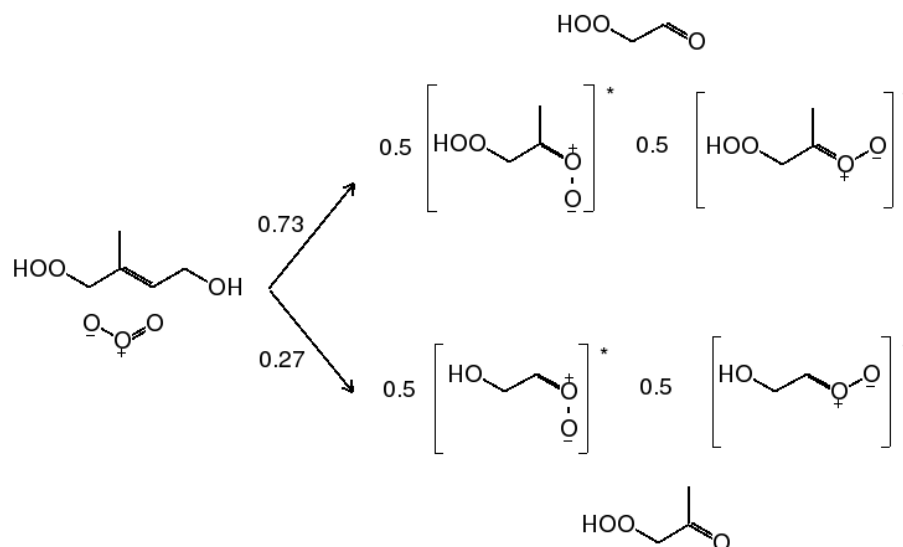
FIGURE 4.14: Ozonolysis of one internally double bonded hydroperoxide for which the total OH yield is estimated to be higher than one (see text).

intermediates from internally double bonded hydroperoxides contain $-CH_2OOH$ groups that provide an addtional source of OH radicals during their decomposition (see Sec. 4.4.2.1). The best example is shown in Fig. 4.14. The C_3 Criegee intermediate in this case is predicted to produce 1.5 OH by decomposition. Considering the branching ratio, this channel alone may yield 1.1 OH. When the OH production from the other channel is accounted for, a total OH yield of about 1.3 is predicted. Such high OH yields may be important in explaining recent findings of elevated non-stomatal O_3 losses within the forest canopy (Goldstein et al. (2004), Kurpius and Goldstein (2003)). The radiation intensity in canopies is usually reduced causing a higher O_3/OH ratio compared to above-canopy conditions. Reactions with O_3 with unsaturated hydroperoxides may be important in sustaining OH levels and protecting plants from O_3 damages. In Sec. 5.1.4 hypothesis is tested.

4.5 Photolysis reactions

4.5.1 PAN

The photolysis of PAN and PAN-like compounds is not very important in the lower troposphere. In fact, it starts to become important above about 7 km altitude. In all models it is represented with one channel that yields its precursors. However, Harwood et al. (2003) found that there is a second channel in which the precursors are not formed and that is a net sink of PAN. The new IUPAC recommendation for PAN at 308 nm,compared to the MCM assumption, is:

		MCM	IUPAC
$CH_3C(O)OONO_2 + h\nu$	$CH_3CO_3 + NO_2$	100%	60%
	$CH_3CO_2 + NO3$	0%	40%

The branching ratios are used for PAN and its homologues.

4.5.2 Glycolaldehyde

The IUPAC recommendations regarding glycolaldehyde photolysis have not been updated since 2002. Meanwhile two recent studies appeared in the literature shedding more light on the relative importance of thermodynamic possible channels. Magneron et al. (2005) detected OH directly and estimated that a 7% branching ratio for the channel that produces OH and CH_2CHO. Karunanandan et al. (2007) obtained complementary information on the other channels. Combining the results of the studies the photolysis of glycolaldehyde can be described as follows.

		MCM	this work
$HOCH_2CHO + h\nu$	$\rightarrow HOCH_2 + HCO$	100%	83%
	$\rightarrow OH + CH_2CHO$	-	7%
	$\rightarrow CH_3OH + CO$	-	10%

By analogy, the photolysis of species like $CH_3CHOHCHO$ are implemented taking the branching ratios for $HOCH_2CHO$ as a first-order approximation.

4.5.3 Methyl vinyl ketone and methacrolein

The current IUPAC recommendations for MVK photolysis are significantly different from the MCM as detailed below.

TABLE 4.4: Number of reactions and species for the MCME mechanism and comparison to the other ones considered in this study.

Mechanism	Species	Reactions
MIM	15^a	44
MIM2	68^a	199
MCM	180^a	595
MCME	≈ 850	≈ 3800

[a] Note that only C_2-C_5 species have been taken into account.

		MCM	IUPAC
$CH_3COCH=CH_2 + h\nu$	$\rightarrow CH_2=CHCH_3 + CO$	50%	60%
	$\rightarrow CH_3CO_3 + HCHO + CO + HO_2$	50%	-
	$\rightarrow CH_3CO + CH_2=CH$	-	20%
	$\rightarrow CH_2=CHCO + CH_3$	-	20%

The branching ratios for the propene producing channel are similar. The second MCM channel is to be considered an approximation of the channel producing CH_3CO and $CH_2=CH$ radicals. In fact, the main degradation products under high-NO_x of these radicals are CH_3CO_3, HCHO, CO and HO_2 (see Sec. 4.3.6.2 and 4.3.6.7). However, a significant amount of OH can be produced during the reactions these alkyl radical undergo.

Regarding MACR photolysis, quantitative information about reaction channels are scarce (Raber and Moortgat (1995)). I take, therefore, the MCM channels and substitute one channel with the more appropriate production of methyl vinyl radical whose atmospheric fate is described in Sec. 4.3.6.9.

		MCM	this work
$CH_2=C(CH_3)CHO + h\nu$	$\rightarrow CH_3CO_3 + HCHO + CO + HO_2$	50%	-
	$\rightarrow CH_2=CCH_3 + CO + HO_2$	-	50%
	$\rightarrow CH_2=C(CH_3)CO + HO_2$	50%	50%

According to Pinho et al. (2005), the photolysis frequencies as used in the MCM are lowered by a factor of 0.12 and 0.168 for MACR and MVK, respectively.
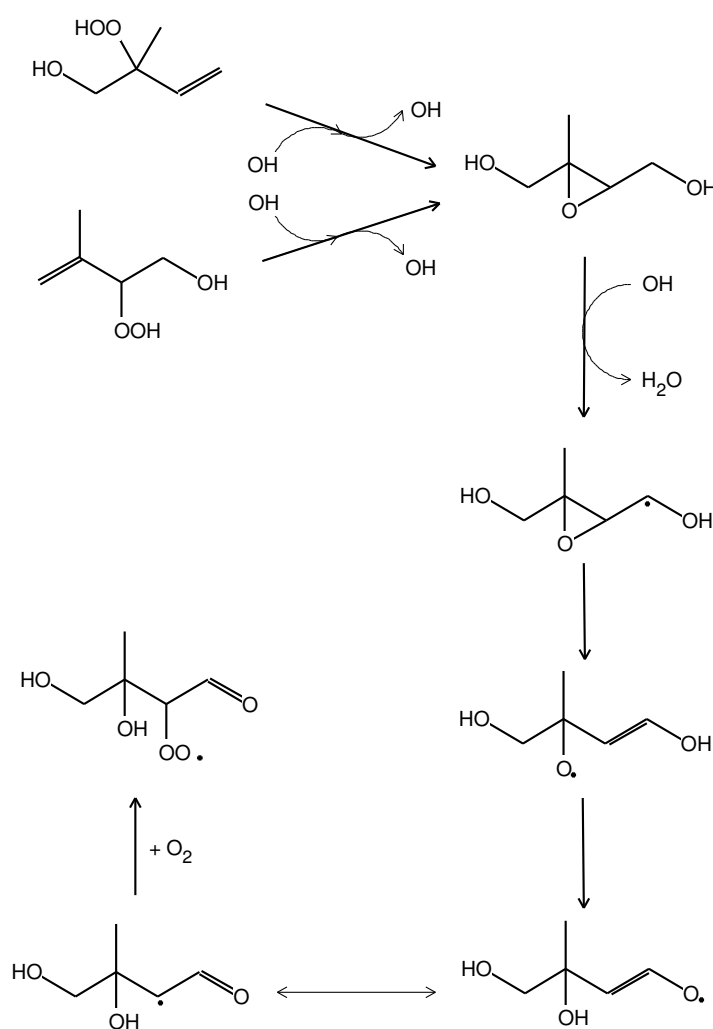
FIGURE 4.15: A general representation of epoxide formation from β hydroperoxide
alkyl radicals above a tropical pristine forest.

4.6   MCM extended

4.6.1   Version 1

The update and substantial extension of the MCM mechanism for isoprene described in
this chapter has led to the development of a highly explicit oxidation mechanism, called
MCME v1, in which many intermediates are treated. New pathways have been included
and new SAR for the OH- and O_3-pathway have been developed. The new mechanism
conserves mass with respect with carbon and has about 850 species and 3800 reactions.
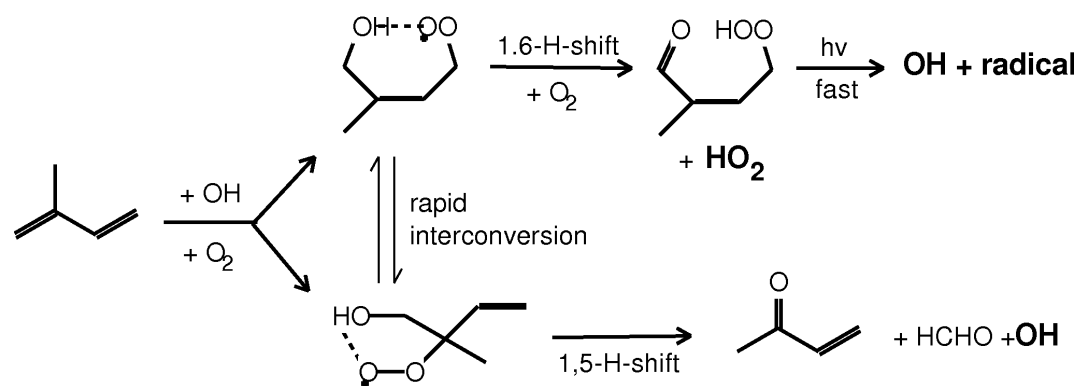
FIGURE 4.16: 1,5- and 1,6-H-shifts for isoprene derived peroxy radicals as proposed by
Peeters et al. (2009).

A comparison with MCM and the two reduced mechanisms MIM and MIM2 is shown
in Tab. 4.4.

4.6.2   Version 2

The first version of MCME is highly explicit and allows inclusion of new oxidation
routes with relatively little effort. This made it possible in the framework of this thesis
to include two recently published breakthroughs (Paulot et al. (2009b), Peeters et al.
(2009)), adding about 20 reactions. These breakthroughs encompass three new efficient
routes for the recycling of both OH and HO_2. They are briefly described below.

Unexpected epoxide formation (Paulot et al. (2009b))
NO_x-free experiments on isoprene oxidation in the CALTECH environmental chamber
have revealed the production of epoxydiols. The likely formation route is the reaction of
unsaturated hydroperoxides with OH that form an excited alkyl radical with a $-OOH$
group in the β position (Fig. 4.15). The ring closure and the simultaneous OH elimi-
nation should be a process faster than O_2 addition to form RO_2 . This mechanism is
known in combustion chemistry, and according to calculations, a tertiary β-OOH alkyl
radical in thermal equilibrium is estimated to undergo ring closure with an activation
energy of about 14 kcal/mol at a frequency of about 600 s^{-1} at 298 K (Wijaya et al.
(2003, and references therein)). However, in isoprene oxidation the epoxide precursor is
formed with about 30 kcal/mol excess energy. Therefore, prompt ring closure and OH
elimination is expected. The resulting epoxydiol reacts with OH with a rate constant of
1.5 10^{-11}. The chemistry of products is unknown and a tentative mechanism is drawn
in Fig. 4.15.

H-shifts and fast ROOH photolysis (Peeters et al. (2009))

Theoretical calculations have been carried out on potentially important H-shifts which isoprene related RO_2 can undergo. A very efficient 1,6-H-shift ($k_{298} > 1 \ s^{-1}$) has been identified for Z geometric isomers of 1-hydroxy-4-peroxy radicals (see Tab. 4.16). The resulting alkoxy radical will readily react with O_2 leading to the production of HO_2. The stable product, an unsaturated carbonyl hydroperoxide, has been estimated to photo-dissociate with a $J = 3 \cdot 10^{-4} \ s^{-1}$ that under atmospheric conditions results in about 100% OH radical generation. Furthermore, 1,5-H-shifts for β-hydroxy RO_2 from isoprene, methacrolein and methyl vinyl ketone have been estimated to be competitive with the standard RO_2 sinks under pristine conditions.

In the next chapter (Chapter 5) both versions of MCME are evaluated against MCM in a box model under a variety of case scenarios and against field data from the GABRIEL campaign (Lelieveld et al. (2008)).

Chapter 5

Enhanced isoprene oxidation

5.1 Unconstrained simulations

5.1.1 Simulation parameters

The two versions of MCME are compared to MCM with a box model setup similar to the one used for the MIM2 evaluation (see Sec. 3.1). However, many more species are initialized since all mechanisms compared here are explicit. The full list of initialized species is shown in Tab. 5.1. It can be seen from the table that, unless NO emissions are prescribed, the simulations are NO_x-free. In order to make the evaluation more representative of tropical boundary layer conditions, the photolysis frequencies have been increased with $J(O^1D)_{max} \approx 7 \cdot 10^{-5} s^{-1}$. The maximum isoprene flux in the simulations is about $4 \cdot 10^9$ molecule $cm^{-2} s^{-1}$. No dry deposition is taken into account and therefore species like H_2O_2, O_3 and NO_x eventually reach very high and unrealistic mixing ratios.

5.1.2 Case 1: NO_x-free boundary layer

A substantial fraction of the global isoprene emission occurs in the southern tropics where NO mixing ratios are below 60 pmol/mol (Emmons et al. (1997), Müller et al. (2008), Torres and Buchan (1988)). After being emitted, most of isoprene is oxidized in the continental boundary layer. Therefore, the first set of simulations is for conditions representative of a boundary layer above a pristine tropical forest. The results for the most important species is shown in Fig. 5.1. Each mechanism significantly differs from the other two. As expected, the highest HO_x concentrations are computed by MCMEv2. At noon of the 2nd model day the OH (HO_2) concentration is 7 (1.8) times higher than
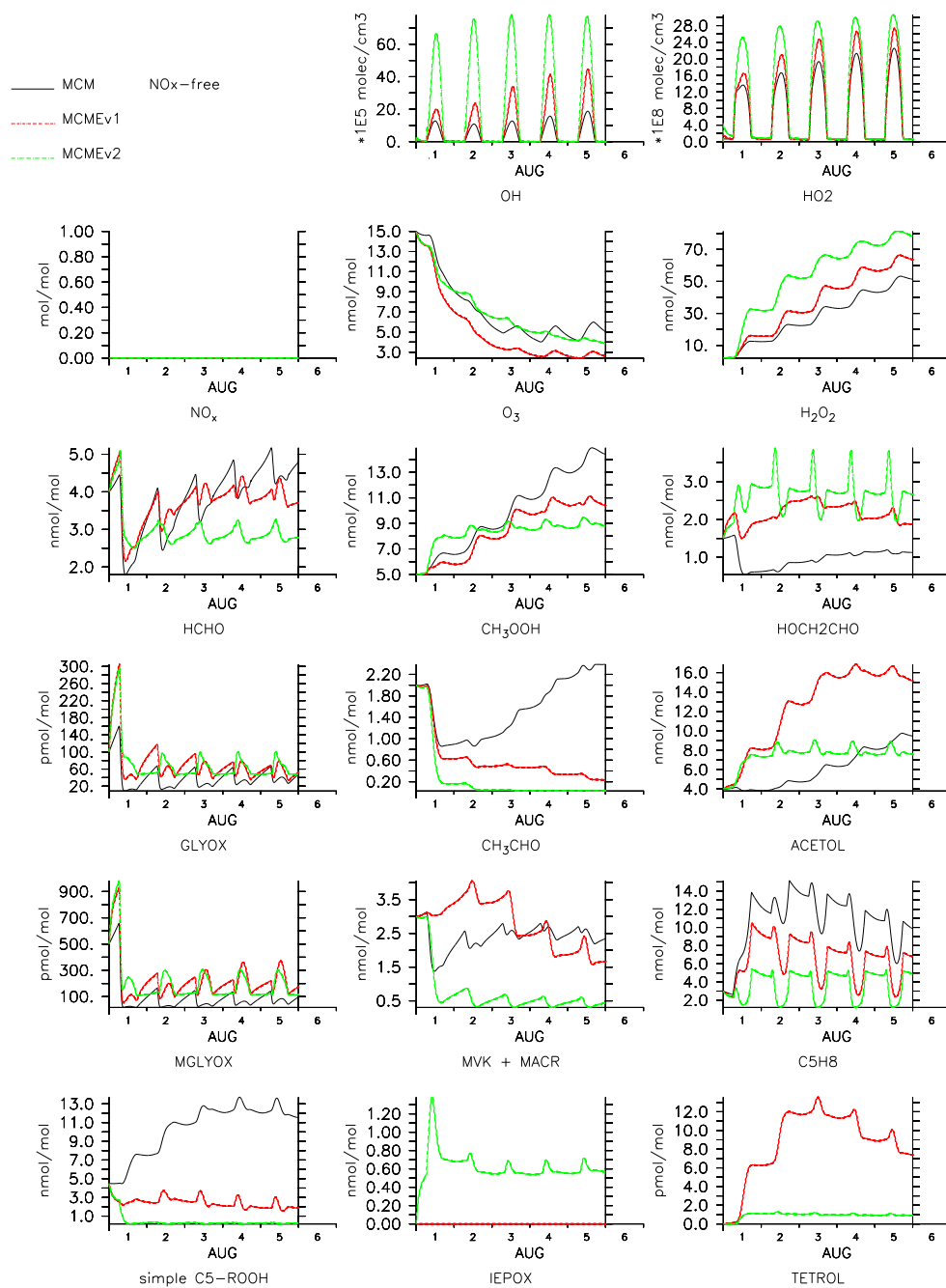
FIGURE 5.1: Comparison of MCME v1 and v2 with MCM for a NOx-free boundary layer.

TABLE 5.1: Initial mixing ratios of species under the three scenarios here used.

Species formula	initial mole fraction $(\mathrm{mol}\,\mathrm{mol}^{-1})$
H_2O	0.01851
O_3	15×10^{-9}
H_2O_2	2×10^{-9}
NO_2	0
NO	0
CH_4	1.8×10^{-06}
HCHO	4.0×10^{-09}
CO	100×10^{-09}
CH_3OH	3.0×10^{-09}
CH_3OOH	5.0×10^{-09}
HCOOH	350×10^{-12}
$CH_3C(O)O_2NO_2$ (PAN)	0
CH_3CHO	2.0×10^{-09}
$HOCH_2CHO$	1.5×10^{-09}
GLYOX	100×10^{-12}
CH_3CO_2H	2.0×10^{-09}
CH_3CO_3H	1.5×10^{-09}
CH_3COCH_2OH	4.0×10^{-09}
CH_3COCHO	500×10^{-12}
MVK	1.5×10^{-09}
MACR	1.5×10^{-09}
ISOPAOOH	500×10^{-12}
ISOPBOOH	2.0×10^{-09}
ISOPCOOH	500×10^{-12}
ISOPDOOH	1.5×10^{-09}
HC4ACHO	600×10^{-12}
HC4CCHO	600×10^{-12}
C_5H_8 (isoprene)	3.0×10^{-09}

computed by MCM. Despite the substantial extensions to MCM, MCMEv1 computes a OH concentration that is only 2.5 times higher. On the 5th model day most of the secondary OH production in MCMEv1 (and MCM) comes from the photolysis of organic hydroperoxides (ROOH) whose mixing ratios significantly build up in contrast to the GABRIEL field measurements of about 1 nmol/mol (Lelieveld et al. (2008), Stickler et al. (2007)). However, mixing ratios of simple C_5-hydroperoxides computed with MCMEv2 are a factor of 20 lower than with MCM. The daytime isoprene mixing ratio mirrors the corresponding OH concentrations for each mechanism. MCMEv2 computes a noon isoprene minimum of 1.5 nmol/mol, that is quite close to the average value of 2 nmol/mol measured during GABRIEL in the boundary layer (Lelieveld et al. (2008)), in contrast to the 6 nmol/mol computed by MCM. HCHO is substantially lower in the simulation with MCMEv2, while MCMEv1 significantly diverges from MCM on the 4th model day. This is also the case with respect to the sum of MVK and MACR that is greatly reduced in MCMEv2 compared to both MCM and MCMEv1. This is mainly the consequence of the new routes discovered by Peeters et al. (2009) which do not lead to MVK and MACR production. As a result mixing ratios of HCHO, MVK and MACR are substantially

reduced being more consistent with field measurements. For instance, Butler et al. (2008) showed that 3D simulations with MIM2 overestimate the measured HCHO and MVK+MACR mixing ratios by 1-2 nmol/mol. Butler et al. (2008) also showed a large underestimation of the model (MIM2) with respect to CH_3CHO. This underestimation is larger for MCMEv2 mainly because of the much higher OH mixing ratios. Provided that no substantial CH_3CHO source could be identified in the isoprene oxidation, it is likely that the major atmospheric sources are ozonolysis of higher terpenes and/or decomposition of dissolved organic matter in the ocean, followed by sea-air transfer of CH_3CHO (Kieber et al. (1990), Millet et al. (2008a)). The species denoted as IEPOX is the epoxydiol identified by Paulot et al. (2009b). It is formed in the reaction of C_5-hydroperoxides with OH in which after addition OH is eliminated by the $-OOH$ group. IEPOX turns out to be a major isoprene oxidation product with mixing ratios higher than 0.5 nmol/mol throughout the simulation. This implies a substantial OH recycling. Moreover, IEPOX has been indicated as the missing link in SOA formation from isoprene, via the heterogeneous production on aerosols of tetrols which have been measured in SOA (Claeys et al. (2004a)). Inclusion of IEPOX in the model makes the tetrol mixing ratios computed by MCMEv1 decrease from 13 (max. value) to 1 pmol/mol in MCMEv2. This indicates the likely predominance of the heterogeneous acid-catalyzed hydrolysis of IEPOX on the homogeneous gas-phase mechanism to form tetrols in aerosols (Böge et al. (2006b), Edney et al. (2005)).

5.1.3 Case 2: NO_x-rich boundary layer

The three oxidation mechanisms considered here are also tested under "mid-NO_x" conditions in which the NO emissions have been set to be 3.33×10^{10} molecule $cm^{-2} s^{-1}$. Depending on the mechanism used, the NO_x mixing ratios oscillates between 100 and 650 pmol/mol (see Fig. 5.2). MCMEv1 and v2 show significantly lower NO_x mixing ratios, reflected in the lower O_3 production compared to MCM. The reason lies in the different capacity of the two versions of MCME and MCM to store nitrogen in the form of alkyl nitrates (see Sec. 4.3.7.2). The patterns of differences between the mechanisms are similar to those in the NO_x-free scenario. The highest HO_x concentrations are again computed by MCMEv2. Both MCME versions compute lower mixing ratios of CH_3OOH with differences reaching 3 nmol/mol though the difference is much less than in the NO_x-free scenario. At noon of the 2nd model day the OH concentration is 2.5 times higher than computed by MCM. Under this scenario the epoxide (IEPOX) appears still to be a relatively important product.
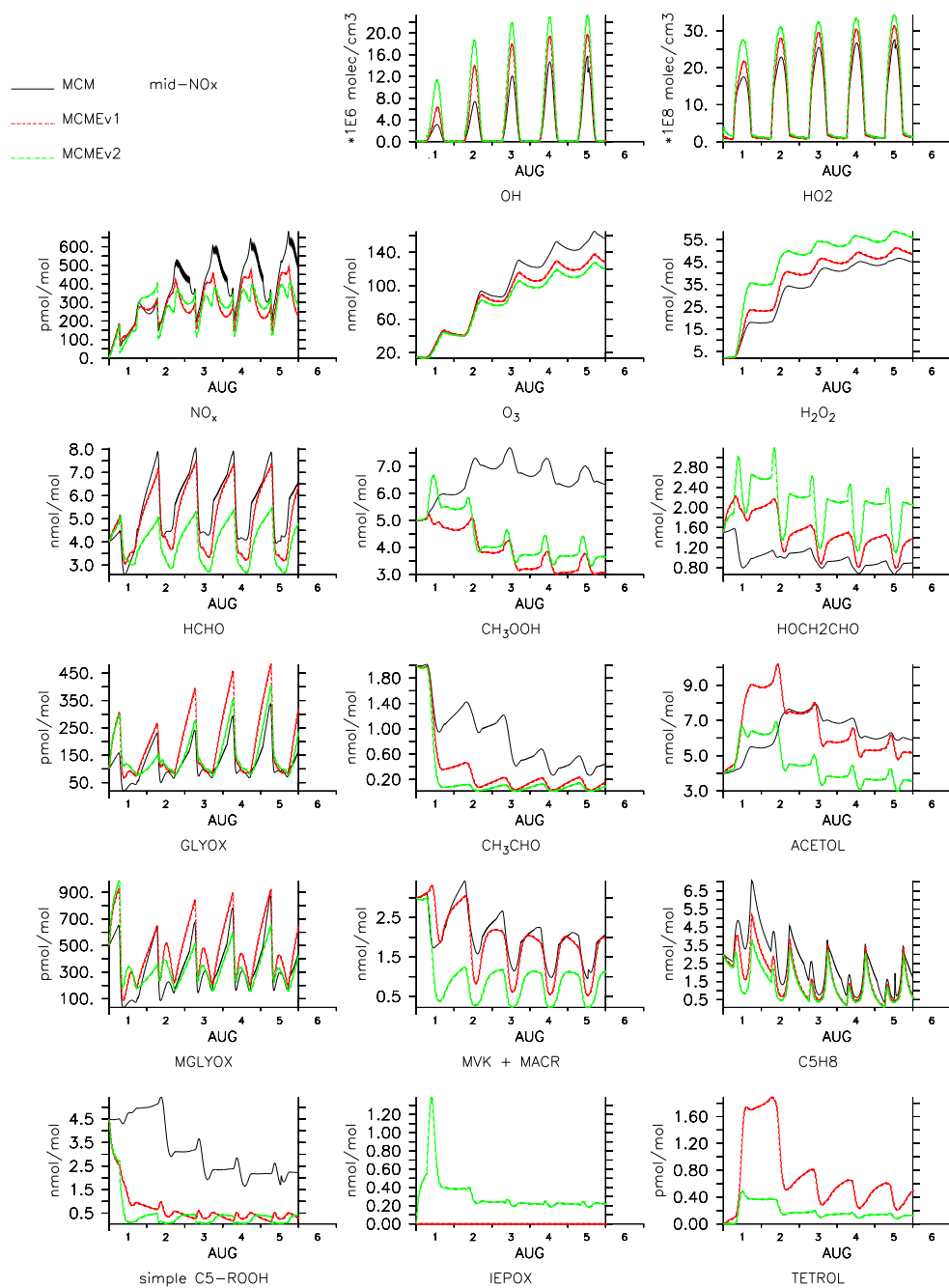
FIGURE 5.2: Comparison of MCME v1 and v2 with MCM for a NO_x-rich boundary layer.
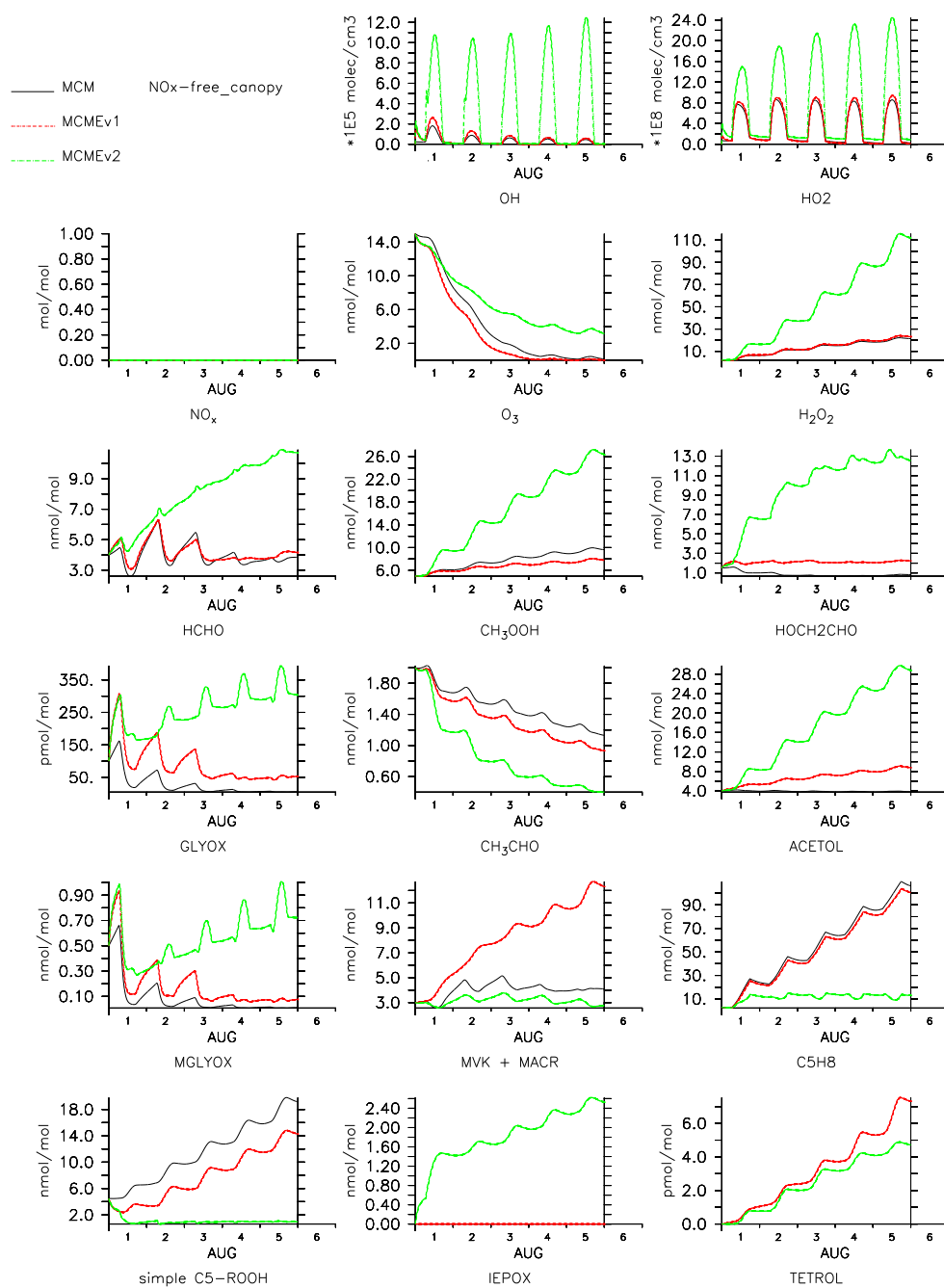
FIGURE 5.3: Comparison of MCME v1 and v2 with MCM for a within-canopy scenario.

5.1.4 Case 3: within the canopy

The enhanced HO_x levels shown by field measurements and these simulations might significantly affect the emissions of biogenic VOC. In fact, fast oxidation within the canopy affects the net amount of VOC that is emitted into the overlying atmosphere. For instance, Stroud et al. (2005) estimated β-caryophyllene to escape the canopy with an efficiency lower than 40% under all conditions. In that study traditional chemistry with little OH-recycling under low-NO_x was used. Isoprene was estimated to escape the canopy with an efficiency greater than 90%. Therefore representing the enhanced isoprene oxidation in canopies will reduce this efficiency and might help reconciling the large discrepancies between "top-down" and "bottom-up" VOC emissions estimates (Guenther et al. (2007)).

Box model simulations are not well suited to estimate the effect of chemistry on the net isoprene emissions from a canopy. However, they can be used to get an idea of the order of magnitude of such potential effect. For this purpose another set of simulations is shown in Fig. 5.3 in which all photolysis frequencies have been reduced by 80%. This reduction represents the maximum intensity reduction of the photosynthetic active radiation (PAR) in a canopy (Grant (1997)). Under these conditions on the 2nd model day the OH concentrations computed by MCMEv2 are 10 times higher than the ones computed by both MCM and MCMEv1. Correspondingly, the isoprene mixing ratios computed by MCMEv2 are 2 times lower than by both MCM and MCMEv1 on the first model day and 3 times lower on the second model day. This might well explain why local "bottom-up" estimates of isoprene emission can exceed the "top-down" estimates by a factor of 2 or more (Guenther et al. (2007)).

5.2 Box model constrained with field measurements

5.2.1 Simulation setup

In order to assess which oxidation mechanism better reproduces the measurements, the box model has been constrained with actual measurements taken during the GABRIEL field campaign. They comprise radical species like OH, HO_2 and NO and long-lived species like H_2O_2, HCHO, isoprene, acetone, methanol, pinene and the sum of MVK and MACR. Furthermore, the mixing ratio of the total organic hydroperoxides has also been measured. In the free troposphere this quantity corresponds approximately to the CH_3OOH mixing ratio. Besides the basic physical quantities like temperature and pressure, $J(NO_2)$ was also measured. Further details on the preparation of data for constrained box model simulations have been reported by Madronich and Flocke (1998).

For a given location and time, the species mixing ratios were initialized with either the measured value or with a typical one taken from preliminary simulations. In the case of organic hydroperoxides, simulations with MCMEv1 showed that in an isoprene-rich scenario about 70% is made of CH_3OOH and the rest made mainly of the MCM species ISOPBOOH. The organic hydroperoxides mixing ratios where assigned according to this ratios. For simplicity this initial mixing ratios are used for the isoprene-poor simulations in which the measured value should be assigned only to CH_3OOH. However, since the C_5 organic hydroperoxides disappear quickly this assumption does not significantly affect the results. The pinene mixing ratio was set to its average measured value in the boundary layer during the campaign (300 pmol/mol). In the simulations pinene represents a simple OH sink as only the first oxidation step is represented.

Photolysis frequencies are as in Kubistin et al. (2008) and kept constant during each simulation. They were calculated with the TUV model using a total ozone column of 265 D.U. (GOME satellite data). The photolysis frequencies were then corrected for cloud and aerosol effects by scaling to the measured $J(NO_2)$ (Madronich and Flocke (1998)). The simulations were performed constraining only a limited number of species to the measured values and letting the model run for 2 simulation hours. The constrained species were NO, O_3, CO, CH_4, CH_3COCH_3, pinene and isoprene. No dry deposition was included since the simulations were short and partly representative of the free troposphere.

5.2.2 Case 1: isoprene-poor troposphere

In order to first examine the differences in C_1-chemistry, before going in to the more complex ones the oxidation mechanisms were first compared to a set of measurements for an isoprene-poor region at specific location and time (Fig. 5.4). Despite the mixing ratios for pinene and the simple C_5 ROOH being unrealistically set to non-zero values, all mechanisms overestimate the OH concentration by about a factor of 4.5. These simulations do not include significant contributions by other VOC that the forest may emit. For example, the contributions by monoterpenes other than pinene, sesquiterpene oxidation products and in general directly emitted oxygenated VOC may well bring the modeled OH concentrations close to the measurements. Since the detection limit for the isoprene measurements was 100 pmol/mol (Eerdekens et al. (2009)) a sensitivity simulation with that amount of isoprene was performed. The overestimation of the OH concentration by all mechanisms is thereby reduced to a factor of 4. On the other hand, the HO_2 concentration is underestimated by a factor of 6.4. Under very low-NO_x conditions, 14 pmol/mol in this case, HO_2 and OH are chemically "decoupled" because of the negligible role of the $NO + HO_2 \rightarrow OH + NO_2$ reaction. Therefore, the discrepancy
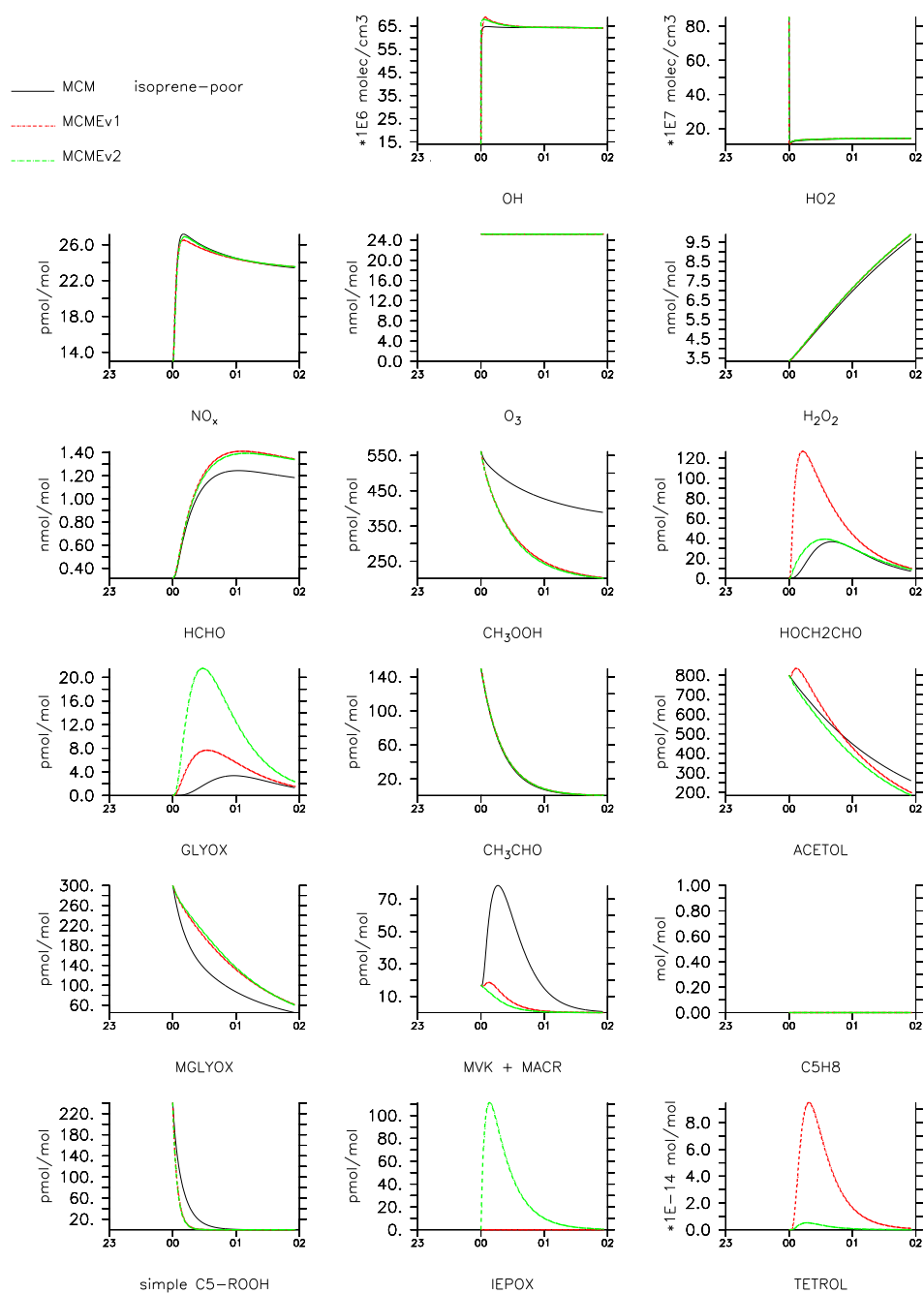
FIGURE 5.4: Results for simulations constrained with GABRIEL measurements in the free troposphere for which isoprene is below the detection limit and assumed to be not present.

TABLE 5.2: Measured OH concentrations and modeled-to-measured ratios for the different mechanisms after 20 minutes simulations time. MCMEv2seg include a 50% reduction in the rate constant of isoprene + OH.

altitude	C_5H_8	OH	OH_{meas}/OH_{mod}		
(m)	(nmol/mol)	(molecule cm^{-3})	MCM	MCMEV2	MCMEv2seg
1264	< 0.10	1.18×10^7	0.23	0.23	0.23
735	3.19	6.18×10^6	3.1	1.1	0.94

concerning HO_2 may be likely due to too low mixing ratios of VOC other than isoprene whose oxidation produces HO_2. The substantial model overestimation of HCHO mixing ratio is difficult to pin down without a budgeting analysis. However, a likely explanation is an increased HCHO production due to the overestimation of the OH concentration. On the other hand, the differences between MCM and MCME are easier to identify. One reason is that, compared to MCM, the last IUPAC recommendations include a much higher rate constant of the HCHO-producing channel in the $CH_3OOH + OH$ reaction and a direct HCHO production in the reaction of glycolaldehyde and hydroxyacetone with OH. In addition, the reaction $CH_3CO + O_2$ should significantly contribute as well (see Sec. 4.3.6.2). With respect to hydroxyacetone (ACETOL in the plot) the differences between MCM and MCME are likely due to the new IUPAC recommendations for the rate constant for the $ACETOL + OH$ being a factor of 1.5 higher than in MCM at 298 K. As mentioned in Sec. 5.2.1 the initialization of simple C_5 hydroperoxides causes transient production for intermediates like glycolaldehyde and glyoxal.

5.2.3 Case 2: isoprene-rich boundary layer

MCM and MCMEv2 have been compared for a region in which the isoprene mixing ratio was about 3 nmol/mol. MCMEv2 has also been modified (MCMEv2seg) by reducing the rate constant for the reaction of isoprene with OH by 50%. This is because the heterogeneity of isoprene emissions and the short OH lifetime result in a species segregation whose effect is the reduction of the effective rate constant (Krol et al. (2000)). A reduction of 50%, together with a 40-50% OH-recycling, was found necessary in order to match the GABRIEL and OP3 field measurements (Butler et al. (2008), Pugh et al. (2009)). The results from the three mechanisms, MCM, MCMEv2 and MCMEv2seg, are shown in Fig. 5.5. MCMEv1 is not shown since it produces similar results to MCM with respect to HO_x and many other species. Under these conditions intermediate species mostly accumulate with time decreasing OH in the long term. A fair compromise is to look at the HO_x levels at about 20 minutes simulation time when NO_x has reached the stationary state. MCM underestimates the observed OH concentration of 6.18×10^6 molecule cm^{-3}
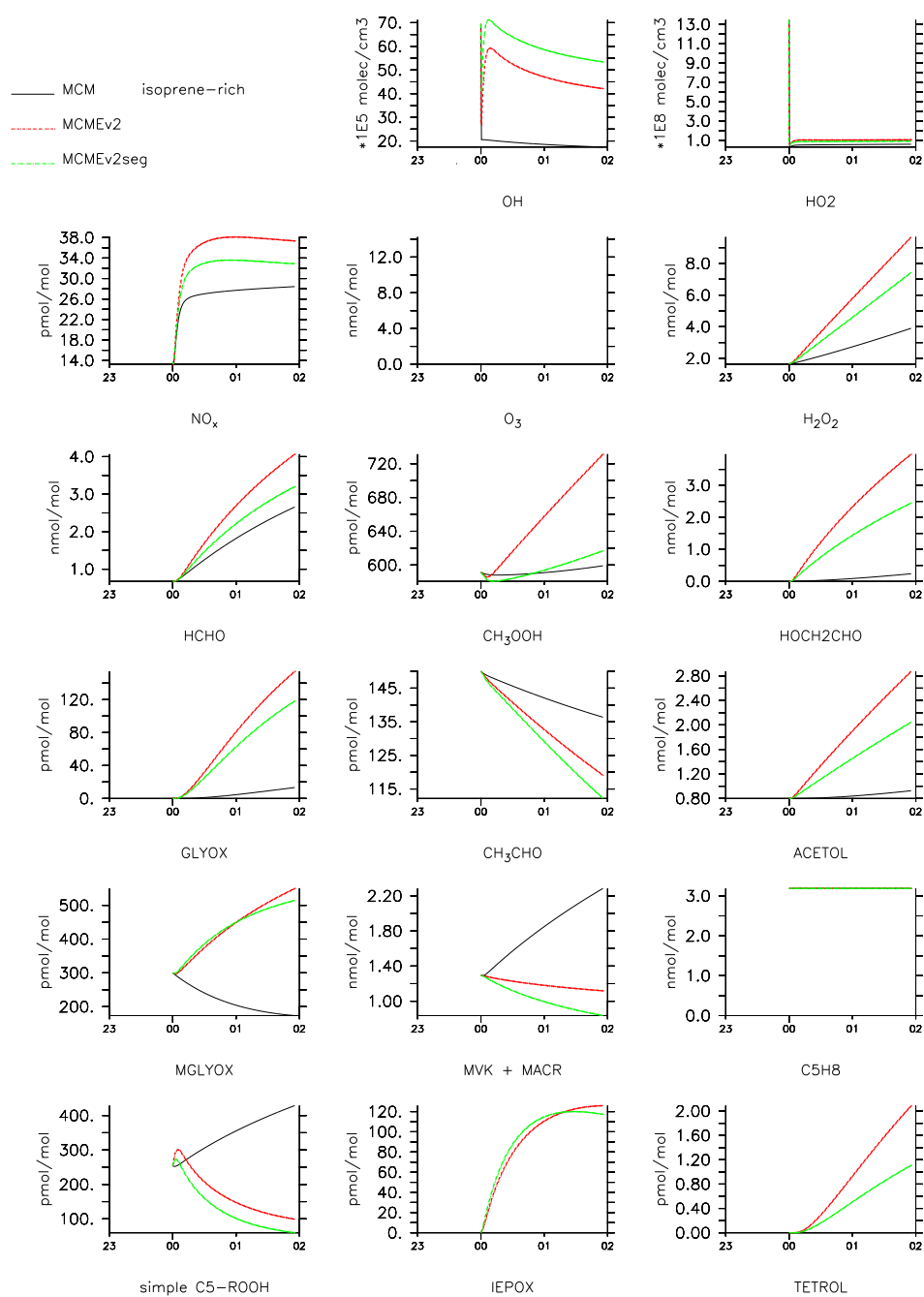
FIGURE 5.5: Results for simulations constrained with GABRIEL measurements in the boundary layer for which isoprene is about 3 nmol/mol. MCMEv2seg includes a 50% reduction of $k_{OH+C_5H_8}$.

by a factor of 3.1 while MCMEv2 by a factor of about 1.1 and MCMEv2seg agrees very well (Tab. 5.2). The new routes proposed by Paulot et al. (2009b) and Peeters et al. (2009) together with the segregation effect appear to be crucial in reconciling the model with the field data. Despite these breakthroughs, the underestimation of HO_2 remains substantial, although halved by MCMEv2. One of the possible causes for this persisting underestimation might be presence in the air of VOC that are not related to isoprene, whose oxidation produce HO_2 and consume OH. After 1-2 hours simulation time, the mixing ratios of species with a lifetime of a day or more are not very representative and normally expected to accumulate because of the absence of dry deposition and transport in the simulation setup. However, some negative trends provide further support for the new chemistry in MCMEv2. In contrast to MCM, MCMEv2 computes mixing ratios for the sum MVK+MACR and the simple C_5 hydroperoxides that decrease rather than accumulate with time. In fact, it was found that the MCM isoprene chemistry greatly overestimates the mixing ratios for the sum MVK+MACR and the organic hydroperoxides (Butler et al. (2008), Pugh et al. (2009)). It is worth noting that the isoprene epoxydiol discovered by Paulot et al. (2009b) reaches a mixing ratio of 100 pmol/mol in one simulation hour.

Chapter 6

Conclusions and outlook

6.1 Conclusions

6.1.1 A new oxidation mechanism for 3D models

With a simple set of mechanism reduction principles, the development of a new isoprene oxidation mechanism for regional and global atmospheric models was possible. It has been described and evaluated against the MCM in a box model representative of a tropical continental boundary layer. The mechanism, called MIM2, is mass conserving with respect to carbon, including CO_2. Compared to its predecessor MIM, MIM2 offers several improvements, as summarized below. The mechanism was found to compute small average relative biases ($<6\%$) for most of the intermediate species under all NO_x regimes studied (see Table 3.2). For instance, this is the case for C_5-alkyl nitrates, hydroperoxides and diols. The C_5-hydroperoxides are suggested to be precursors for organic aerosol nucleation and growth from isoprene oxidation (Kroll et al., 2006) and the C_5-diols are precursors of tetrols found recently in aerosols (Böge et al., 2006a, Claeys et al., 2004a). MIM2 (MIM) was found to compute relative biases for formic and acetic acid, which are important components of the gas and aqueous phase of the atmosphere (Chebbi and Carlier, 1996), reaching about -10% ($+300\%$) and $+10\%$ (-40%), respectively. HCHO nocturnal production is close to the rate in the MCM with the average relative bias being less than 1%. Chemical production of CH_3OH has been improved substantially under all NO_x conditions. The representation of the organic nitrogen has been improved remarkably due to the consideration of eight alkyl nitrates ($RONO_2$) and four peroxy acyl nitrates ($RC(O)OONO_2$), causing the NO_x relative bias to be always less than 10%. With respect to MIM, MIM2 represents many important new species like glycolaldehyde, α-nitrooxy acetone, two more peroxy acyl nitrates, as well as MVK and MACR, which were previously lumped. In comparison to the isoprene chemistry implemented

in MCM v3.1, the overall improvement in the computation of key atmospheric species and of the isoprene oxidation intermediates is substantial and it will be reflected in the applications with 3D atmospheric models. Because of its low level of species lumping, MIM2 is especially suitable for implementation of new results regarding the isoprene oxidation. An example was given with the modified mechanism, MIM2mod, in which a selection of recent results of VOC chemistry were easily implemented. This will make it straightforward to evaluate the global impacts of new oxidation routes, especially in low-NO_x regions.

MIM2 has been preliminarily implemented in a global atmospheric chemistry model. It has been compared to the modified version of MIM, here referred to as MIMvK, that is used in the EMAC model (Jöckel et al., 2006). Higher OH concentrations are computed compared to the previously implemented isoprene mechanisms. The overall increase in OH and the decrease in isoprene mixing ratios, however, are not enough to match the observations which were made during the GABRIEL campaign (Lelieveld et al., 2008). A more in-depth discussion of the model-measurement comparison during this campaign for OH, isoprene and many other intermediates is presented in Butler et al. (2008). Amongst the new species present in MIM2, the global chemical production of important species like acetaldehyde, propene and glyoxal has been found to be 7.3, 9.5 and 33.8 Tg/yr, respectively.

6.1.2   A new master oxidation mechanism

Lelieveld et al. (2008), based on field observations, proposed that isoprene could sustain the atmospheric oxidation capacity even in pristine environments. In order to test this hypothesis, the MCM for isoprene has been extended from about 600 to 3800 reactions with new rate constant estimates and experimental results. A second version of this extended mechanism, MCMEv2 which was slightly modified to include recent findings, has been shown to produce much higher OH concentrations under NO_x-free conditions. When used to reproduce a subset of the GABRIEL field measurements, MCMEv2 has been able to compute OH concentrations very close to the measurements. The major contributors to the enhanced OH concentration has been found to be the new oxidation routes discovered by Paulot et al. (2009b) and Peeters et al. (2009). However, their relative importance remains to be investigated with either a detailed budget analysis of the mechanism or by neglecting one route at a time. Furthermore, the MCMEv2 has been able to halve the substantial discrepancy with the HO_2 measurement. With respect to other species like organic hydroperoxides, MVK, MACR, HCHO and isoprene itself, model improvements have been achieved.

The great extent of OH recycling in isoprene oxidation may substantially affect estimates

of net VOC emissions from forest canopies. In fact, a significant part of the VOC emitted could be oxidized before it escapes the forest canopy. An attempt to estimate this effect has been made with the box model. The new isoprene chemistry might well explain why local "bottom-up" estimates of isoprene emission can exceed the "top-down" estimates by a factor of 2 or more (Guenther et al., 2007). This effect should be taken into account in global atmospheric studies.

Finally, the implementation of the dihydroxy epoxide production from isoprene hydroperodices oxidation (Paulot et al., 2009b) provides support for a crucial role of heterogeneous hydrolysis as major formation pathway of tetrols (Böge et al., 2006b, Edney et al., 2005). The gas-phase mechanism of tetrol production should only play a minor role.

6.2 Outlook

6.2.1 Budgeting of OH recycling routes

An important future step will be evaluation of the relative importance of the OH recycling routes. This may be accomplished by budgeting analysis for many species, especially HO_x (Butler, 2009). Suggestions for resolving other model-observation discrepancies may come from such an analysis.

6.2.2 New chemistry and the global atmospheric composition

It is planned to assess the impacts of the new isoprene oxidation routes in a global atmospheric model (Jöckel et al., 2006). Such a task is only feasible after a reduced mechanism with a performance close to MCMEv2 has been developed. MIM2 presents a good starting basis for such a development as demonstrated with MIM2mod (Sec. 3.12). The reduced mechanism will be evaluated against MCMEv2 in a box model in an analogous way to MIM2 versus MCM. An initial focus in the 3D model study will be how well the atmospheric composition in the continental boundary layer is simulated. Following this, the impact of the new oxidation mechanism on the global mean OH concentration and the methane lifetime will be examined. Other possible focal topics include the transport of oxidation products from isoprene emission hot spots, particularly to the upper troposphere, as well as the sensitivity to a simplistic representation of isoprene oxidation within the canopy, which could be implemented by replacing a fraction of the isoprene emission fluxes with a corresponding amount of products of its reaction with OH.

6.2.3 Further mechanism development

Despite much effort, still a few recent experimental results remain to be included in the detailed oxidation mechanism. Two of them are mostly relevant under NO_x-rich conditions.

Paulot et al. (2009a) reported that Z-1,4-hydroxyalkoxy radicals from isoprene undergo an isomerization (H-shift), forming enolic peroxy radicals. This and subsequent chemistry was firstly predicted by Dibble (2002) and Dibble (2004). The net effect of this new oxidation route should be the reduction of $NO \rightarrow NO_2$ conversions in the current mechanism.

The fate of alkyl nitrates affects the ozone production efficiencies of air masses. In fact, the fraction of NO_2 produced during the oxidation of the unsaturated C_5-alkyl nitrates from isoprene is uncertain and considered to be unity in MCM as well as in MCMEv2. Paulot et al. (2009a) also reported the branching ratios for the reaction of OH with all six isomers of C_5-alkyl nitrates from isoprene. This new chemistry results in about 50% NO_2 recycling efficiency and is expected to significantly affect the O_3 production.

The oxidation mechanism at 298 K for glycolaldehyde and hydroxyacetone as determined by Butkovskaya et al. (2006a) and Butkovskaya et al. (2006b) have already been implemented in MCMEv2. However, it has been established that the yields of products like OH, HCHO, HCOOH and CH_3CO_2H depend strongly on the temperature. At temperatures typical of the upper troposphere these yields are much greater than at 298 K. Therefore, inclusion of such temperature dependent product yields will be important in 3D model studies.

6.2.4 Investigation of new routes

Current computational tools, eg. GAUSSIAN09 (Frisch et al., 2009) and MULTIWELL (Barker, 2001), could be used in order to determine the likely fate of species whose fate is currently unknown. Two potential applications are shown in Fig. 6.1. One could be the fate of the isoprene-related epoxides discovered by Paulot et al. (2009b). After H-abstraction by OH, the heterocyclic three-membered ring could rearrange unimolecularly via cleavage of either a $C-C$ or $O-C$ bonds (see Fig. 6.1a). Estimates of the k_{a1} and k_{a2} would provide a valuable guide in the mechanism development. The second application could be the fate of isoprene-related alkyl nitrates. The extent to which they recycle NOx in the first degradation steps is thought to be important in determining the O_3 production potential of isoprene in air masses. Their gas phase fate was studied by Paulot et al. (2009a) in presence of 500 nmol/mol NO. Under these conditions the lifetime of the corresponding peroxy radicals (RO_2) is greatly reduced, precluding pathways that are
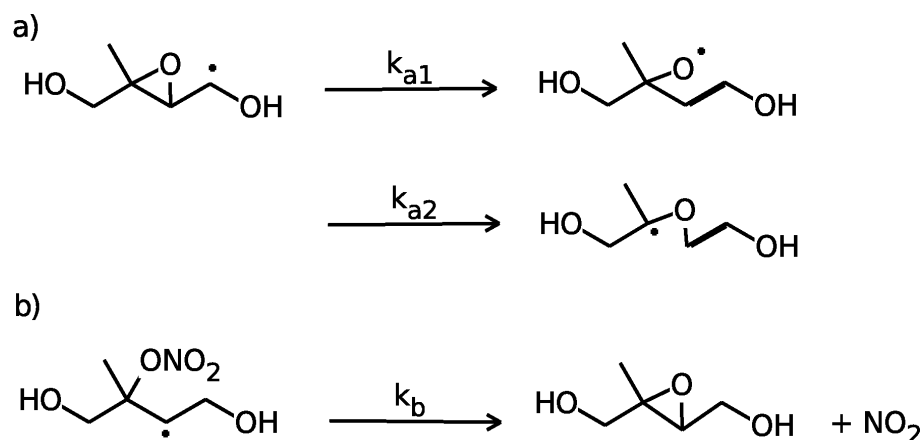
FIGURE 6.1: Molecular decompositions that could be theoretically investigated for further mechanism development.

potentially accessible under more typical (tropical forest) atmospheric conditions. For example, OH addition to one of the unsaturated isoprene nitrates produces a radical like the one shown on the lower left in Fig. 6.1b. In analogy with the formation of epoxides from isoprene hydroperoxides, NO_2 could be eliminated after formation of the three membered ring. Formation of epoxides has been reported in studies of isoprene + NO_3 in which similar radicals are formed (Berndt and Böge (1997)). If calculations were to support this newly hypothesized route, the implications for mechanism development and SOA formation would be significant. In fact, formation of epoxides (SOA precursors) under high-NO_x conditions would provide the missing link explaining the enhanced concentration of tetrols found in organic aerosols during biomass burning periods (Claeys et al., 2004b).

6.3 Catalytic oxidation in the atmosphere

The ultimate oxidant in the atmosphere is O_2 which is present in high concentrations ($\approx 21\%$). Over the last 500 million years the O_2 concentration remained in a relatively narrow range between 10 and 30% (Falkowski and Isozaki, 2008, and references therein). O_2 is continuosly produced biologically via the oxidation of water driven by the energy from the Sun. On time scales of millions of years more organic matter was buried in the Earth's crust than respired allowing a substantial accumulation of O_2 in the atmosphere. O_2 has a lifetime of 4 million years according to (Keeling et al., 1993) and is not able to initiate the oxidation of any non-radical atmospheric species. Therefore, atmospheric oxidation can only take place with the help of catalyzers like O_3 and OH. O_3 is produced primarily in the stratosphere via O_2-photolysis and in the upper troposphere

via lightning NO_x production. The second and most important catalyzer is OH that results from the photolysis of O_3 in the presence of water. An essential characteristic of a catalyzer is that it is recycled during the chemical processes. Although the atmosphere is not an idealized mono-phase system the current work shows that the extent of OH recycling is still substantial and can be higher than 50%. This has an impact on the abundance of OH that ultimately determines the speed at which oxidation proceeds in the troposphere. When added, this OH recycling makes the atmospheric models reconcile with the Earth system behaviour. Under pristine conditions the enhanced oxidation of isoprene, and possibly of other BVOCs, is in fact essential in allowing:

- a sustained self-cleansing capacity of the atmosphere

- BVOCs gradients whereby plant-plant and plant-insect interactions can take place

- protection at both leaf- and forest-level from damages caused by O_3

- a self-fertilizing mechanism for N-poor forests via foliar uptake of alkyl nitrates

- an enhanced formation aerosol precursors that might affect cloud formation and climate

It will be a challenge to elucidate the chemistry of complex mixtures of hydrocarbons emitted by the vegetation and assess the level of OH recycling and the driving mechanisms.

Appendix A

MIM2 mechanism
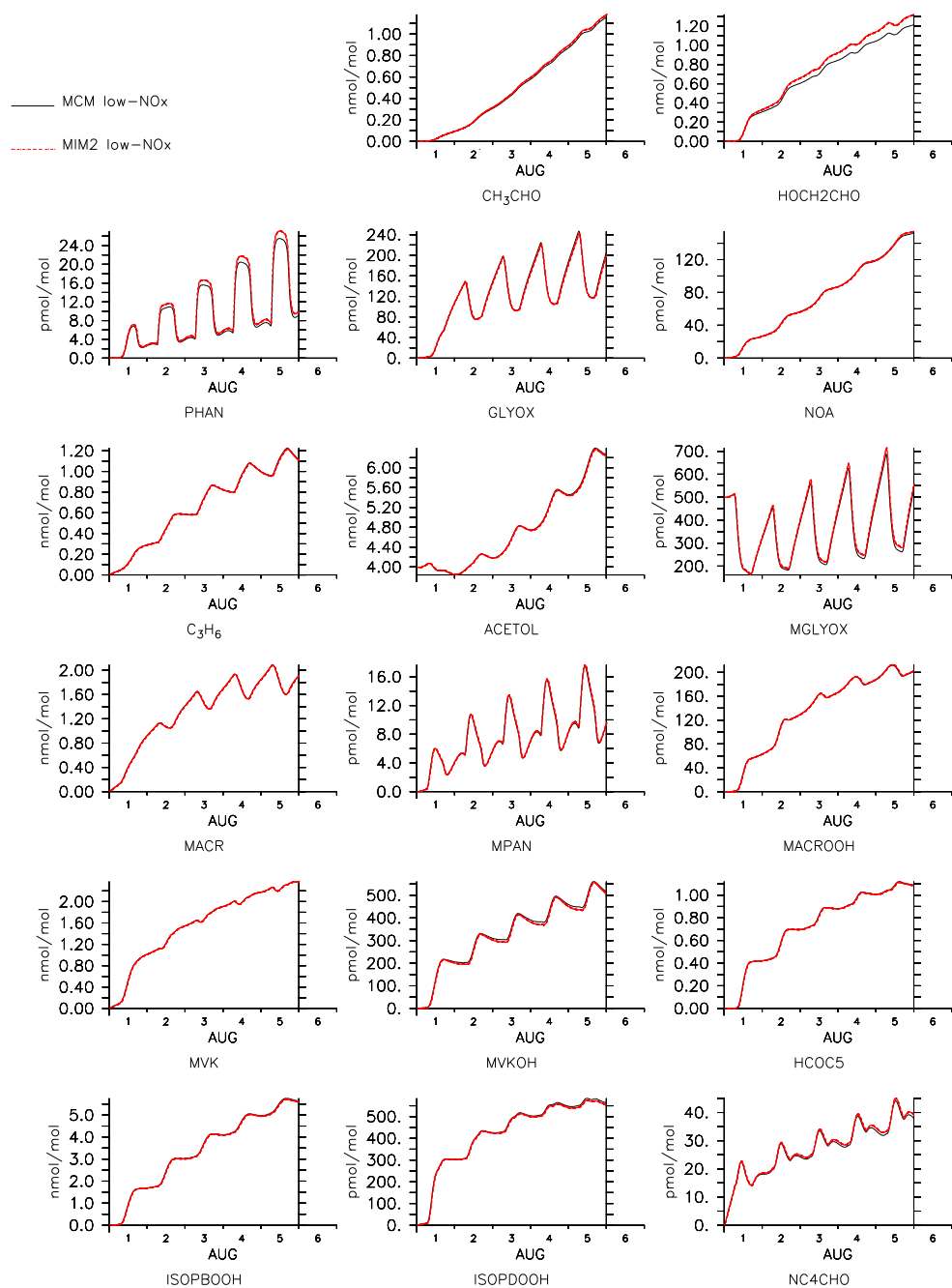
FIGURE A.1: A selection of the most prominent among the news species present now in MIM2. A comparison between MIM2 and MCM in the low-NO$_x$ scenario is shown.
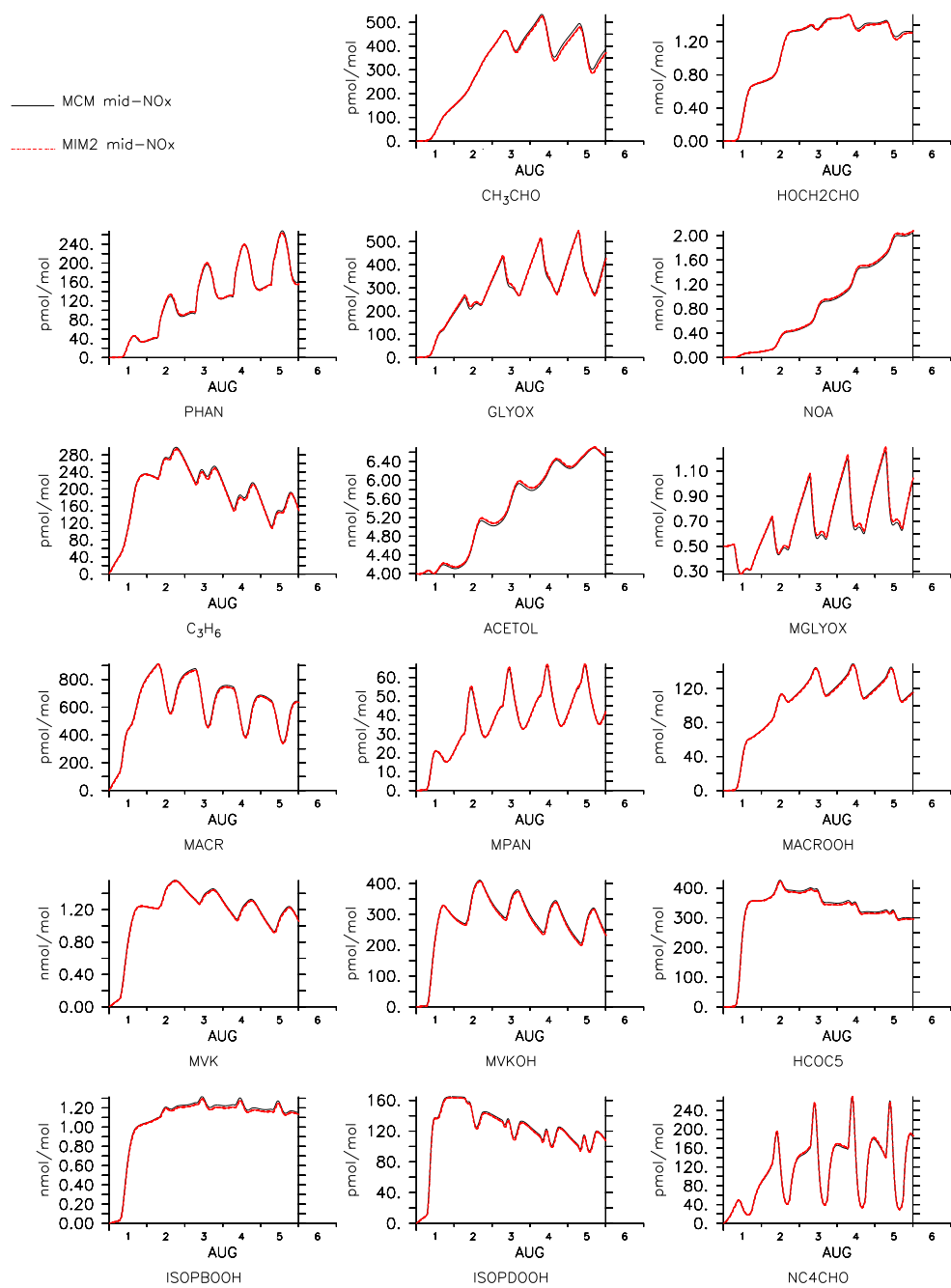
FIGURE A.2: A selection of the most prominent among the news species present now in MIM2. A comparison between MIM2 and MCM in the mid-NO$_x$ scenario is shown.
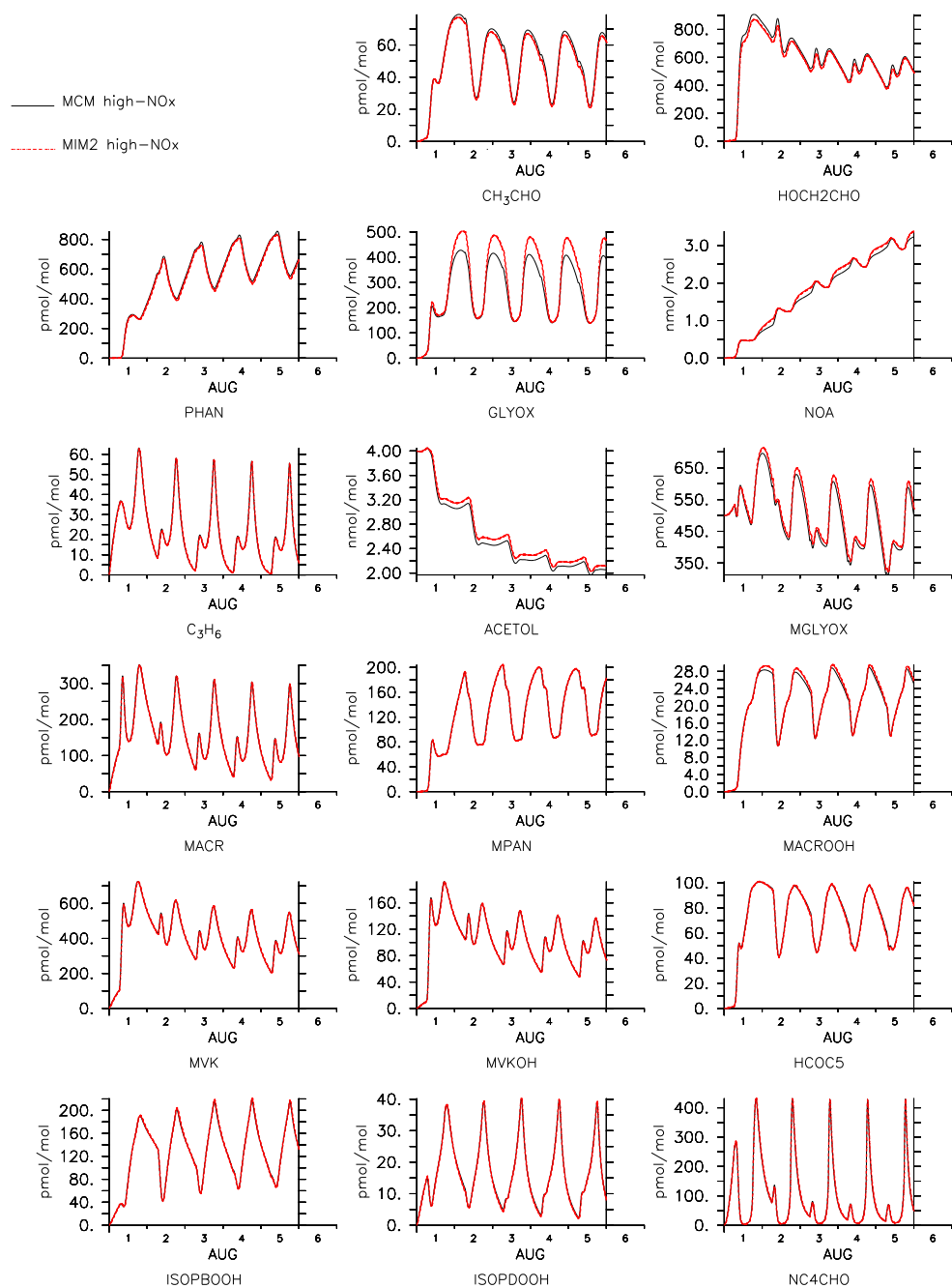
FIGURE A.3: A selection of the most prominent among the news species present now in MIM2. A comparison between MIM2 and MCM in the high-NO$_x$ scenario is shown.

TABLE A.1: MIM2 species. For the lumped species based on isomers in MCM only the condensed formulae are shown. For lumped species representing non-isomeric species the condensed formulae are not shown.

MIM2 name	Formula	Description	Transported
C_5 Stable species			
C5H8	$CH_2=C(CH_3)CH=CH_2$	2-methyl-1,3-butadiene (isoprene)	yes
LISOPACOOH	$C_5H_{10}O_3$ lumped	see Tab. A.2	yes
ISOPBOOH	$HOCH_2C(CH_3)(OOH)CH=CH_2$	β-hydroxyperoxide	yes
ISOPDOOH	$CH_2=C(CH_3)CHOOHCH_2OH$	β-hydroxyperoxide	yes
ISOPAOH	$HOCH_2C(CH_3)=CHCH_2OH$	E-2-methyl-2-butene-1,4-diol	yes
ISOPBOH	$HOCH_2C(CH_3)OHCH=CH_2$	2-methyl-3-butene-1,2-diol	yes
ISOPDOH	$CH_2=C(CH_3)CHOHCH_2OH$	3-methyl-3-butene-1,2-diol	yes
LISOPACNO3	$C_5H_{10}NO_4$ lumped	see Tab. A.2	yes
ISOPBNO3	$HOCH_2C(CH_3)ONO_2CH=CH_2$	alkyl nitrate	yes
ISOPDNO3	$CH_2=C(CH_3)CHONO_2CH_2OH$	alkyl nitrate	yes
NISOPOOH	$O_2NOCH_2C(CH_3)=CHCH_2OOH$	nitro-hydro-peroxide	yes
NC4CHO	$O_2NOCH_2C(CH_3)=CHCHO$	nitro-aldehyde	yes
LNISOOH	$C_5H_7NO_{6.5}$ lumped	see Tab. A.2	yes
LHC4ACCHO	$C_5H_8O_2$ lumped	see Tab. A.2	yes
LC578OOH	$C_5H_{10}O_5$ lumped	see Tab. A.2	yes
LHC4ACCO2H	$C_5H_8O_3$ lumped	see Tab. A.2	yes
LHC4ACCO3H	$C_5H_8O_4$ lumped	see Tab. A.2	yes
LC5PAN1719	$C_5H_7NO_6$ lumped	see Tab. A.2	yes
HCOC5	$CH_2=C(CH_3)COCH_2OH$		yes
C59OOH	$HOCH_2C(CH3)(OOH)COCH_2OH$		yes
C_5-peroxy radicals			
LISOPACO2	$C_5H_9O_3$ lumped	δ-hydroxyperoxy radical see Tab. A.2	no
ISOPBO2	$HOCH_2CO_2(CH_3)CH=CH2$	β-hydroxyperoxy radical	no
ISOPDO2	$CH_2=C(CH_3)CO_2CH_2OH$	β-hydroxyperoxy radical	no
NISOPO2	$O_2NOCH_2C(CH_3)=CHCH_2O_2$	nitro-peroxy radical	no
LNISO3	$C_5H_7NO_{6.5}$ lumped	nitro-peroxy radical see Tab. A.2	no
LHC4ACCO3	$C_5H_7O_4$ lumped	δ-hydroxyperoxyacyl radical see Tab. A.2	no
LC578O2	$C_5H_9O_5$ lumped	see Tab. A.2	no
C59O2	$C_5H_9O_5$	alkyl peroxy radicals from the C_5-hydroxy ketone (HCOC5)	no
C_4 Stable species			
MACR	$CH_2=C(CH_3)CHO$	methacrolein	yes
MACROOH	$HOCH_2C(CH_3)(OOH)CHO$	methacrolein peroxide	yes
MACROH	$HOCH_2C(CH_3)(OH)CHO$	1,2-dihydroxy-2-methyl-propanaldehyde	yes
MACO2H	$CH_2=C(CH_3)CO_2H$	methacroleic acid	yes
MACO3H	$CH_2=C(CH_3)CO_3H$	methacroleic peroxyacid	yes
MPAN	$CH_2=C(CH_3)C(O)OONO_2$	peroxy methacroleil nitrate	yes

TABLE A.1: MIM2 species (continued)

MIM2 name	Formula	Description	Transported
C$_4$ **Stable species**			
MVK	CH$_2$=CHC(O)CH$_3$	butenone (methyl vinyl ketone)	yes
LHMVKABOOH	C$_4$H$_8$O$_4$ lumped	see Tab. A.2	yes
MVKOH	CH$_2$=CHC(O)CH$_2$OH	β-hydroxy methyl vinyl ketone	yes
LMVKOHABOOH	C$_4$H$_8$O$_5$ lumped	see Tab. A.2	yes
CO2H3CHO	CH$_3$COCH$_2$(OH)CHO		yes
CO2H3CO3H	CH$_3$COCH$_2$(OH)CO$_3$H		yes
BIACETOH	CH$_3$C(O)C(O)CH$_2$OH		yes
HO12CO3C4	CH$_3$C(O)CH(OH)CH$_2$OH		yes
C$_4$ **Peroxy radicals**			
MACRO2	HOCH$_2$C(CH$_3$)(O$_2$)CHO		no
MACO3	CH$_2$=C(CH$_3$)CO$_3$		no
LHMVKABO2	C$_4$H$_7$O$_4$ lumped	see Tab. A.2	no
LMVKOHABO2	C$_4$H$_7$O$_5$ lumped	see Tab. A.2	no
CO2H3CO3	CH$_3$COCH$_2$(OH)CO$_3$		no
C$_3$ **Stable species**			
C3H6	C$_3$H$_6$	propene	yes
HYPROPO2H	CH$_3$CH(OOH)CH$_2$OH	β-hydroxyhydroperoxides	yes
PR2O2HNO3	CH$_3$CH(OOH)CH$_2$ONO$_2$		yes
ACETOL	CH$_3$C(O)CH$_2$OH	hydroxyacetone	yes
MGLYOX	CH$_3$C(O)CHO	methylglyoxal	yes
NOA	CH$_3$C(O)CH$_2$ONO$_2$	α-nitrooxy acetone	yes
HOCH2COCHO	HOCH$_2$C(O)CHO		yes
HOCH2COCO2H	HOCH$_2$C(O)CO$_2$H		yes
C$_3$ **Peroxy radicals**			
HYPROPO2	CH$_3$CH(O$_2$)CH$_2$OH	β-hydroxy peroxy radical	no
PRONO3BO2	CH$_3$CH(O$_2$)CH$_2$ONO$_2$	nitro peroxy radical from C3H6	no
C$_2$ **compounds**			
CH3CHO	CH$_3$CHO	acetaldehyde	yes
CH3CO2H	CH$_3$CO$_2$H	acetic acid	yes
CH3CO3H	CH$_3$CO$_3$H	peroxy acetic acid	yes
PAN	CH$_3$C(O)OONO$_2$	peroxy acetyl nitrate	yes
HOCH2CHO	HOCH$_2$CHO	glycolaldehyde	yes
HOCH2CO2H	HOCH$_2$CO$_2$H	carboxilic acid from HOCH2CHO	yes
HOCH2CO3H	HOCH$_2$CO$_3$H	peroxy carboxilic acid from HOCH2CHO	yes
PHAN	HOCH$_2$C(O)OONO$_2$	homologues of PAN for HOCH2CHO	yes
GLYOX	CHOCHO	glyoxal	yes
HCOCO2H	HCOCO$_2$H	carboxilic acid from GLYOX	yes
HCOCO3H	HCOCO$_3$H	peroxy carboxilic acid from GLYOX	yes
C$_2$ **Peroxy radicals**			
CH3CO3	CH$_3$CO$_3$	peroxy acetyl radical	no
HOCH2CO3	HOCH$_2$CO$_3$	peroxy acyl radical from HOCH2CHO	no
HCOCO3	HCOCO$_3$	peroxy acyl radical from GLYOX	no

TABLE A.2: Composition of lumped species in MIM2 is given in terms of MCM species.

Lumped species	Compositions	Kind
LISOPACO2	0.5 ISOPAO2 + 0.5 ISOPCO2	δ-hydroxyperoxy radical (internal double bond)
LISOPACOOH	0.5 ISOPAOOH + 0.5 ISOPCOOH	δ-hydroxyperoxides (internal double bond)
LISOPACNO3	0.5 ISOPANO3 + 0.5 ISOPCNO3	alky nitrates (internal double bond)
LNISO3	0.5 C510O2 + 0.5 NC4CO3	nitro-peroxy radicals from NC4CHO
LNISOOH	0.5 C510OOH + 0.5 NC4CO3H	nitro-peroxides from LNISO3
LHC4ACCO3	0.5 HC4ACO3 + 0.5 HC4CCO3	acyl peroxy radicals from C_5-hydroxy aldehydes
LHC4ACCHO	0.5 HC4ACHO + 0.5 HC4CCHO	carbonyls (internal double bond)
LHC4ACCO2H	0.5 HC4ACO2H + 0.5 HC4CCO2H	carboxylic acids (internal double bond)
LHC4ACCO3H	0.5 HC4ACO3H + 0.5 HC4CCO3H	percarboxylic acids (internal double bond)
LC5PAN1719	0.5 C5PAN17 + 0.5 C5PAN19	homologues of PAN from LHC4ACCO3
LC578O2	0.5 C57O2 + 0.5 C58O2	peroxy radicals from C_5-hydroxy aldehydes
LC578OOH	0.5 C57OOH + 0.5 C58OOH	hydroperoxides from LC578O2
LHMVKABO2	0.3 HMVKAO2 + 0.7 HMVKBO2	peroxy radicals from MVK
LHMVKABOOH	0.3 HMVKAOOH + 0.7 HMVKBOOH	hydroperoxides from LHMVKABO2
LMVKOHABO2	0.3 MVKOHAO2 + 0.7 MVKOHBO2	peroxy radicals from MVKOH
LMVKOHABOOH	0.3 MVKOHAOOH + 0.7 MVKOHBOOH	hydroperoxides from LMVKOHABO2

TABLE A.3: List of MIM2 reactions. The expressions for the simple MCM rate coefficients (KRO2NO, KRO2HO2, KAPHO2, KAPNO, KRO2NO3, KNO3AL) are shown in Tab. A.4. The expressions for the complex MCM rate coefficients (KFPAN, KBPAN and KMT16) are shown in Tab. A.5. M is the concentration of air in $molec\,cm^{-3}$ and T is the temperature in K.

Chemical reaction			Rate coefficient
C_5 compounds			
C5H8 + OH	$\rightarrow$	0.25 LISOPACO2 + 0.491 ISOPBO2 + 0.259 ISOPDO2	2.54E-11$\times$ exp(410/T)
C5H8 + O3	$\rightarrow$	0.051 CH3O2 + 0.1575 CH3CO3 + 0.054 LH-MVKABO2 + 0.522 CO + 0.06875 HCOOH + 0.11 H2O2 + 0.32475 MACR + 0.1275 C3H6 + 0.2625 HO2 + 0.255 CO2 + 0.74975 HCHO + 0.04125 MACO2H + 0.27 OH + 0.244 MVK	7.86E-15$\times$ exp(-1913/T)
C5H8 + NO3	$\rightarrow$	NISOPO2	3.03E-12$\times$ exp(-446/T)
LISOPACO2 + HO2	$\rightarrow$	LISOPACOOH	0.706$\times$KRO2HO2
LISOPACO2 + NO	$\rightarrow$	0.892 LHC4ACCHO + 0.892 HO2 + 0.892 NO2 + 0.108 LISOPACNO3	KRO2NO
LISOPACO2 + NO3	$\rightarrow$	LHC4ACCHO + HO2 + NO2	KRO2NO3
LISOPACO2	$\rightarrow$	0.9 LHC4ACCHO + 0.8 HO2 + 0.1 ISOPAOH	2.4E-12$\times$RO2
LISOPACOOH + OH	$\rightarrow$	LHC4ACCHO + OH	1.07E-10
LISOPACOOH + hν	$\rightarrow$	LHC4ACCHO + HO2 + OH	J(41)
ISOPAOH + OH	$\rightarrow$	LHC4ACCHO + HO2	9.30E-11
LISOPACNO3 + OH	$\rightarrow$	LHC4ACCHO + NO2	8.91E-11
LISOPACNO3 + hν	$\rightarrow$	LHC4ACCHO + HO2 + NO2	J(53)
ISOPBO2 + HO2	$\rightarrow$	ISOPBOOH	0.706$\times$KRO2HO2
ISOPBO2 + NO	$\rightarrow$	0.696 MVK + 0.232 MVKOH + 0.696 HCHO + 0.696 HO2 + 0.232 CH3O2 + 0.928 NO2 + 0.072 ISOPBNO3	KRO2NO
ISOPBO2 + NO3	$\rightarrow$	0.75 MVK + 0.25 MVKOH + 0.75 HCHO + 0.75 HO2 + 0.25 CH3O2 + NO2	KRO2NO3
ISOPBO2	$\rightarrow$	0.6 MVK + 0.2 MVKOH + 0.6 HCHO + 0.6 HO2 + 0.2 CH3O2 + 0.2 ISOPBOH	8.E-13$\times$RO2
ISOPBOOH + OH	$\rightarrow$	ISOPBO2	4.2E-11
ISOPBOOH + hν	$\rightarrow$	0.75 MVK + 0.25 MVKOH + 0.75 HCHO + 0.75 HO2 + 0.25 CH3O2 + OH	J(41)
ISOPBOH + OH	$\rightarrow$	0.75 MVK + 0.25 MVKOH + 0.75 HCHO + 0.75 HO2 + 0.25 CH3O2	3.85E-11
ISOPBNO3 + OH	$\rightarrow$	MVK + HCHO + NO2	3.55E-11
ISOPBNO3 + hν	$\rightarrow$	0.75 MVK + 0.25 MVKOH + 0.75 HCHO + 0.75 HO2 + 0.25 CH3O2 + NO2	J(55)
ISOPDO2 + HO2	$\rightarrow$	ISOPDOOH	0.706$\times$KRO2HO2
ISOPDO2 + NO	$\rightarrow$	0.855 MACR + 0.855 HCHO + 0.855 HO2 + 0.855 NO2 + 0.145 ISOPDNO3	KRO2NO
ISOPDO2 + NO3	$\rightarrow$	MACR + HCHO + HO2 + NO2	KRO2NO3
ISOPDO2	$\rightarrow$	0.8 MACR + 0.8 HCHO + 0.8 HO2 + 0.1 HCOC5 + 0.1 ISOPDOH	2.9E-12$\times$RO2
ISOPDOOH + OH	$\rightarrow$	HCOC5 + OH	1.07E-10
ISOPDOOH + hν	$\rightarrow$	MACR + HCHO + HO2 + OH	J(41)
ISOPDOH + OH	$\rightarrow$	HCOC5 + HO2	7.38E-11
ISOPDNO3 + OH	$\rightarrow$	HCOC5 + NO2	6.1E-11
ISOPDNO3 + hν	$\rightarrow$	MACR + HCHO + HO2 + NO2	J(54)

TABLE A.3: MIM2 reactions (continued)

Chemical reaction			Rate coefficient
C₅ compounds			
NISOPO2	→	0.8 NC4CHO + 0.6 HO2 + 0.2 LISOPACNO3	1.3E-12×RO2
NISOPO2 + NO	→	NC4CHO + HO2 + NO2	KRO2NO
NISOPO2 + NO3	→	NC4CHO + HO2 + NO2	KRO2NO3
NISOPO2 + HO2	→	NISOPOOH	.706×KRO2HO2
NISOPOOH + OH	→	NC4CHO + OH	1.03E-10
NISOPOOH + hν	→	NC4CHO + HO2 + OH	J(41)
NC4CHO + OH	→	LNISO3	4.16E-11
NC4CHO + O3	→	0.445 NO2 + 0.89 CO + 0.075625 H2O2 + 0.034375 HCOCO2H + 0.555 NOA + 0.445 HO2 + 0.520625 GLYOX + 0.89 OH + 0.445 MG-LYOX	2.40E-17
NC4CHO + NO3	→	LNISO3 + HNO3	KNO3AL×4.25
NC4CHO + hν	→	NOA + 2 CO + 2 HO2	J(18)
LNISO3 + NO	→	NOA + 0.5 GLYOX + 0.5 CO + HO2 + NO2 + 0.5 CO2	(KAPNO + KRO2NO)/2
LNISO3 + NO3	→	NOA + 0.5 GLYOX + 0.5 CO + HO2 + NO2 + 0.5 CO2	1.3×KRO2NO
LNISO3 + HO2	→	LNISOOH	(0.706×KRO2HO2 + KAPHO2)/2
LNISOOH + OH	→	LNISO3	2.65E-11
LNISOOH + hν	→	NOA + OH + 0.5 GLYOX + 0.5 CO + HO2 + 0.5 CO2	J(41)
LHC4ACCHO + OH	→	0.52 LC578O2 + 0.48 LHC4ACCO3	4.52E-11
LHC4ACCHO + O3	→	0.2225 CH3CO3 + 0.89 CO + 0.0171875 HOCH2CO2H + 0.075625 H2O2 + 0.0171875 HCOCO2H + 0.2775 ACETOL + 0.6675 HO2 + 0.2603125 GLYOX + 0.2225 HCHO + 0.89 OH + 0.2603125 HOCH2CHO + 0.5 MGLYOX	2.40E-17
LHC4ACCHO + NO3	→	LHC4ACCO3 + HNO3	KNO3AL×4.25
LHC4ACCHO + hν	→	0.5 LHC4ACCO3 + 0.25 ACETOL + 0.25 HOCH2CHO + 0.25 CH3CO3 + 0.75 CO + 1.25 HO2	2×J(19)
LC578O2	→	0.5 ACETOL + 0.5 MGLYOX + 0.5 GLYOX + 0.5 HOCH2CHO + HO2	9.20E-14×RO2
LC578O2 + HO2	→	LC578OOH	KRO2HO2×0.706
LC578O2 + NO	→	0.5 ACETOL + 0.5 MGLYOX + 0.5 GLYOX + 0.5 HOCH2CHO + HO2 + NO2	KRO2NO
LC578O2 + NO3	→	0.5 ACETOL + 0.5 MGLYOX + 0.5 GLYOX + 0.5 HOCH2CHO + HO2 + NO2	KRO2NO3
LC578OOH + OH	→	LC578O2	3.16E-11
LC578OOH + hν	→	0.5 ACETOL + 0.5 MGLYOX + 0.5 GLYOX + 0.5 HOCH2CHO + HO2 + OH	J(41)

TABLE A.3: MIM2 reactions (continued)

Chemical reaction			Rate coefficient
C$_5$ compounds			
LHC4ACCO3	$\rightarrow$	0.3 LHC4ACCO2H + 0.35 ACETOL + 0.35 HOCH2CHO + 0.35 CH3CO3 + 0.35 CO + 0.35 HO2 + 0.7 CO2	1.00E-11× RO2
LHC4ACCO3 + HO2	$\rightarrow$	0.71 LHC4ACCO3H + 0.29 LHC4ACCO2H + 0.29 O3	KAPHO2
LHC4ACCO3 + NO	$\rightarrow$	0.5 ACETOL + 0.5 HOCH2CHO + 0.5 CH3CO3 + 0.5 CO + 0.5 HO2 + NO2 + CO2	KAPNO
LHC4ACCO3 + NO3	$\rightarrow$	0.5 ACETOL + 0.5 HOCH2CHO + 0.5 CH3CO3 + 0.5 CO + 0.5 HO2 + NO2 + CO2	1.6×KRO2NO3
LHC4ACCO3 + NO2	$\rightarrow$	LC5PAN1719	KFPAN(T,M)
LHC4ACCO2H + OH	$\rightarrow$	0.5 ACETOL + 0.5 HOCH2CHO + 0.5 CH3CO3 + 0.5 CO + 0.5 HO2 + CO2	2.52E-11
LHC4ACCO3H + OH	$\rightarrow$	LHC4ACCO3	2.88E-11
LHC4ACCO3H + hν	$\rightarrow$	0.5 ACETOL + 0.5 HOCH2CHO + 0.5 CH3CO3 + 0.5 CO + 0.5 HO2 + OH + CO2	J(41)
LC5PAN1719	$\rightarrow$	LHC4ACCO3 + NO2	KBPAN(T,M)
LC5PAN1719 + OH	$\rightarrow$	0.5 MACROH + 0.5 HO12CO3C4 + CO + NO2	2.52E-11
HCOC5 + OH	$\rightarrow$	C59O2	3.81E-11
HCOC5 + hν	$\rightarrow$	CH3CO3 + HCHO + HOCH2CO3	J(24)
C59O2	$\rightarrow$	ACETOL + HOCH2CO3	9.20E-14×RO2
C59O2 + NO	$\rightarrow$	ACETOL + HOCH2CO3 + NO2	KRO2NO
C59O2 + NO3	$\rightarrow$	ACETOL + HOCH2CO3 + NO2	KRO2NO3
C59O2 + HO2	$\rightarrow$	C59OOH	KRO2HO2×0.706
C59OOH + OH	$\rightarrow$	C59O2	9.7E-12
C59OOH + hν	$\rightarrow$	ACETOL + HOCH2CO3 + OH	J(22)+J(41)
C$_4$ compounds			
MACR + OH	$\rightarrow$	0.57 MACO3 + 0.43 MACRO2	1.86E-11× exp(175/T)
MACR + O3	$\rightarrow$	0.59 MGLYOX + 0.41 CH3CO3 + 0.03375 HCOOH + 0.55625 HCHO + 0.82 CO + 0.12375 H2O2 + 0.41 HO2 + 0.82 OH	1.36E-15× exp(-2112/T)
MACR + NO3	$\rightarrow$	MACO3 + HNO3	KNO3AL×2.0
MACR + hν	$\rightarrow$	0.5 MACO3 + 0.5 CH3CO3 + 0.5 HCHO + 0.5 CO + HO2	J(18)+J(19)
MACO3	$\rightarrow$	0.7 CH3CO3 + 0.7 HCHO + 0.7 CO2 + 0.3 MACO2H	1.00E-11×RO2
MACO3 + HO2	$\rightarrow$	0.71 MACO3H + 0.29 MACO2H + 0.29 O3	KAPHO2
MACO3 + NO	$\rightarrow$	CH3CO3 + HCHO + NO2 + CO2	8.70E-12× exp(290/T)
MACO3 + NO3	$\rightarrow$	CH3CO3 + HCHO + NO2 + CO2	1.6×KRO2NO3
MACO3 + NO2	$\rightarrow$	MPAN	KFPAN(T,M)
MACRO2	$\rightarrow$	0.7 ACETOL + 0.7 HCHO + 0.7 HO2 + 0.3 MACROH	9.20E-14×RO2
MACRO2 + NO	$\rightarrow$	ACETOL + HCHO + HO2 + NO2	KRO2NO
MACRO2 + NO3	$\rightarrow$	ACETOL + HCHO + HO2 + NO2	KRO2NO3
MACRO2 + HO2	$\rightarrow$	MACROOH	KRO2HO2×0.625

TABLE A.3: MIM2 reactions (continued)

Chemical reaction			Rate coefficient
C₄ compounds			
MACROOH + OH	→	MACRO2	2.82E-11
MACROOH + hν	→	ACETOL + HCHO + HO2 + OH	J(41)
MACROOH + hν	→	ACETOL + CO + HO2 + OH	J(17)
MACROH + OH	→	ACETOL + HCHO + HO2	2.46E-11
MACROH + hν	→	ACETOL + CO + HO2 + HO2	J(17)
MPAN	→	MACO3 + NO2	KBPAN(T,M)
MPAN + OH	→	ACETOL + CO + NO2	3.60E-12
MACO2H + OH	→	CH3CO3 + HCHO + CO2	1.51E-11
MACO3H + OH	→	MACO3	1.87E-11
MACO3H + hν	→	CH3CO3 + HCHO + OH + CO2	J(41)
MVK + OH	→	LHMVKABO2	4.13E-12× exp(452/T)
MVK + O3	→	0.28 CH3CO3 + 0.56 CO + 0.225 LCARBON + 0.075 HCOOH + 0.09 H2O2 + 0.28 HO2 + 0.1 CO2 + 0.1 CH3CHO + 0.645 HCHO + 0.36 OH + 0.545 MGLYOX	7.51E-16× exp(-1521/T)
MVK + hν	→	0.5 C3H6 + 0.5 CH3CO3 + 0.5 HCHO + CO + 0.5 HO2	2×J(23)
LHMVKABO2	→	0.06 CO2H3CHO + 0.18 HO2 + 0.18 HCHO + 0.18 MGLYOX + 0.42 CH3CO3 + 0.42 HOCH2CHO+ 0.2 HO12CO3C4 + 0.14 BIACE-TOH	(0.3×2.00E-12 + 0.7×8.80E-13)×RO2
LHMVKABO2 + HO2	→	LHMVKABOOH	KRO2HO2×0.625
LHMVKABO2 + NO	→	0.3 MGLYOX + 0.7 HOCH2CHO + 0.7 CH3CO3 + 0.3 HCHO + 0.3 HO2 + NO2	KRO2NO
LHMVKABO2 + NO3	→	0.3 MGLYOX + 0.7 HOCH2CHO + 0.7 CH3CO3 + 0.3 HCHO + 0.3 HO2 + NO2	KRO2NO3
LHMVKABOOH + OH	→	0.3 CO2H3CHO + 0.7 BIACETOH + OH	0.3×5.77E-11 + 0.7×3.95E-11
LHMVKABOOH + hν	→	0.3 MGLYOX + 0.7 CH3CO3 + 0.7 HOCH2CHO + 0.3 HCHO + 0.3 HO2 + OH	J(41)
MVKOH + OH	→	LMVKOHABO2	4.60E-12× exp(452/T)
MVKOH + O3	→	0.56 CO + 0.545 HOCH2COCHO + 0.075 HOCH2COCO2H + 0.075 HCOOH + 0.09 H2O2 + 0.28 HOCH2CO3 + 0.28 HO2 + 0.2 CO2 + 0.545 HCHO + 0.36 OH + 0.1 HOCH2CHO	7.51E-16× exp(-1521/T)
MVKOH + hν	→	0.5 HCHO + 0.5 HO2 + 0.5 HOCH2CO3 + CO + 1.5 LCARBON	2×J(23)
LMVKOHABO2	→	0.7 HOCH2CHO + 0.7 HOCH2CO3 + 0.3 HOCH2COCHO + 0.3 HCHO + 0.3 HO2	(0.3×2.00E-12+.7× 8.80E-13)×RO2
LMVKOHABO2 + NO	→	0.3 HOCH2COCHO + 0.3 HCHO + 0.3 HO2 + 0.7 HOCH2CHO + 0.7 HOCH2CO3 + NO2	KRO2NO
LMVKOHABO2 + NO3	→	0.3 HOCH2COCHO + 0.3 HCHO + 0.3 HO2 + 0.7 HOCH2CHO + 0.7 HOCH2CO3 + NO2	KRO2NO3
LMVKOHABO2 + HO2	→	LMVKOHABOOH	KRO2HO2×0.625
LMVKOHABOOH + OH	→	0.7 HO12CO3C4 + 0.3 CO2H3CHO + OH	5.98E-11
LMVKOHABOOH + hν	→	0.3 HOCH2COCHO + 0.3 HCHO + 0.3 HO2 + 0.7 HOCH2CHO + 0.7 HOCH2CO3 + OH	J(22)+J(41)

TABLE A.3: MIM2 reactions (continued)

Chemical reaction			Rate coefficient
C$_4$ **compounds**			
CO2H3CHO + OH	$\rightarrow$	CO2H3CO3	2.45E-11
CO2H3CHO + NO3	$\rightarrow$	CO2H3CO3 + HNO3	KNO3AL×4.0
CO2H3CHO + hν	$\rightarrow$	MGLYOX + CO + HO2 + HO2	J(15)
CO2H3CO3	$\rightarrow$	MGLYOX + HO2 + CO2	1.00E-11×RO2
CO2H3CO3 + HO2	$\rightarrow$	CO2H3CO3H	KAPHO2
CO2H3CO3 + NO	$\rightarrow$	MGLYOX + HO2 + NO2 + CO2	KAPNO
CO2H3CO3 + NO3	$\rightarrow$	MGLYOX + HO2 + NO2 + CO2	1.6×KRO2NO3
CO2H3CO3H + OH	$\rightarrow$	CO2H3CO3	7.34E-12
CO2H3CO3H + hν	$\rightarrow$	MGLYOX + HO2 + OH + CO2	J(41)
CO2H3CO3H + hν	$\rightarrow$	CH3CO3 + HO2 + HCOCO3H	J(22)
HO12CO3C4 + OH	$\rightarrow$	BIACETOH + HO2	1.88E-11
HO12CO3C4 + hν	$\rightarrow$	CH3CO3 + HOCH2CHO + HO2	J(22)
BIACETOH + hν	$\rightarrow$	CH3CO3 + HOCH2CO3	J(35)
C$_3$ **compounds**			
C3H6 + OH	$\rightarrow$	HYPROPO2	KMT16(T,M)
C3H6 + O3	$\rightarrow$	0.28 CH3O2 + 0.1 CH4 + 0.075 CH3CO2H + 0.56 CO + 0.075 HCOOH + 0.09 H2O2 + 0.28 HO2 + 0.2 CO2 + 0.545 CH3CHO + 0.545 HCHO + 0.36 OH	5.51E-15× exp(-1878/T)
C3H6 + NO3	$\rightarrow$	PRONO3BO2	9.4E-15
HYPROPO2 + HO2	$\rightarrow$	HYPROPO2H	KRO2HO2×0.520
HYPROPO2 + NO	$\rightarrow$	CH3CHO + HCHO + HO2 + NO2	KRO2NO
HYPROPO2 + NO3	$\rightarrow$	CH3CHO + HCHO + HO2 + NO2	KRO2NO3
HYPROPO2	$\rightarrow$	CH3CHO + HCHO + HO2	8.80E-13×RO2
HYPROPO2H + OH	$\rightarrow$	HYPROPO2	1.90E-12× exp(190/T)
HYPROPO2H + OH	$\rightarrow$	ACETOL + OH	2.44E-11
HYPROPO2H + hν	$\rightarrow$	CH3CHO + HCHO + HO2 + OH	J(41)
PRONO3BO2 + NO	$\rightarrow$	NOA + HO2 + NO2	KRO2NO
PRONO3BO2 + NO3	$\rightarrow$	NOA + HO2 + NO2	KRO2NO3
PRONO3BO2 + HO2	$\rightarrow$	PR2O2HNO3	KRO2HO2×0.520
PR2O2HNO3 + OH	$\rightarrow$	PRONO3BO2	1.90E-12× exp(190/T)
PR2O2HNO3 + OH	$\rightarrow$	NOA + OH	3.47E-12
PR2O2HNO3 + hν	$\rightarrow$	NOA + HO2 + OH	J(41)
ACETOL + OH	$\rightarrow$	MGLYOX + HO2	3.00E-12
ACETOL + hν	$\rightarrow$	CH3CO3 + HCHO + HO2	J(22)
MGLYOX + OH	$\rightarrow$	CH3CO3 + CO	1.72E-11
MGLYOX + NO3	$\rightarrow$	CH3CO3 + CO + HNO3	KNO3AL×2.4
MGLYOX + hν	$\rightarrow$	CH3CO3 + CO + HO2	J(34)
NOA + OH	$\rightarrow$	MGLYOX + NO2	1.30E-13
NOA + hν	$\rightarrow$	CH3CO3 + HCHO + NO2	J(56)+J(57)
HOCH2COCHO + OH	$\rightarrow$	HOCH2CO3 + CO	1.44E-11
HOCH2COCHO + NO3	$\rightarrow$	HOCH2CO3 + CO + HNO3	KNO3AL×2.4
HOCH2COCHO + hν	$\rightarrow$	HOCH2CO3 + CO + HO2	J(34)
HOCH2COCO2H + OH	$\rightarrow$	HOCH2CO3 + CO2	2.89E-12
HOCH2COCO2H + hν	$\rightarrow$	HOCH2CO3 + HO2 + CO2	J(34)

TABLE A.3: MIM2 reactions (continued)

Chemical reaction			Rate coefficient
C$_2$ **compounds**			
CH3CO3	→	0.7 CH3O2 + 0.7 CO2 + 0.3 CH3CO2H	1.00E-11×RO2
CH3CO3 + HO2	→	0.71 CH3CO3H + 0.29 CH3CO2H + 0.29 O3	KAPHO2
CH3CO3 + NO2	→	PAN	KFPAN(T,M)
CH3CO3 + NO	→	NO2 + CH3O2 + CO2	KAPNO
CH3CO3 + NO3	→	NO2 + CH3O2 + CO2	KRO2NO3×1.60
CH3CO2H + OH	→	CH3O2 + CO2	8.00E-13
CH3CO3H + OH	→	CH3CO3	3.70E-12
CH3CO3H + hν	→	CH3O2 + OH + CO2	J(41)
CH3CHO + OH	→	CH3CO3	5.55E-12× exp(311/T)
CH3CHO + NO3	→	CH3CO3 + HNO3	KNO3AL
CH3CHO + hν	→	CH3O2 + HO2 + CO	J(13)
PAN	→	CH3CO3 + NO2	KBPAN(T,M)
PAN + OH	→	HCHO + CO + NO2	9.50E-13× exp(-650/T)
HOCH2CHO + OH	→	0.8 HOCH2CO3 + 0.2 GLYOX + 0.2 HO2	1.00E-11
HOCH2CHO + NO3	→	HOCH2CO3 + HNO3	KNO3AL
HOCH2CHO + hν	→	HO2 + HCHO + HO2 + CO	J(15)
HOCH2CO3 + NO2	→	PHAN	KFPAN(T,M)
HOCH2CO3 + HO2	→	0.71 HOCH2CO3H + 0.29 HOCH2CO2H + 0.29 O3	KAPHO2
HOCH2CO3	→	0.7 HCHO + 0.7 CO2 + 0.7 HO2 + 0.3 HOCH2CO2H	1.00E-11×RO2
HOCH2CO3 + NO	→	NO2 + HO2 + HCHO + CO2	KAPNO
HOCH2CO3 + NO3	→	NO2 + HO2 + HCHO + CO2	1.6×KRO2NO3
HOCH2CO2H + OH	→	HCHO + HO2 + CO2	2.73E-12
HOCH2CO3H + OH	→	HOCH2CO3	6.19E-12
HOCH2CO3H + hν	→	HCHO + HO2 + OH + CO2	J(41)
PHAN	→	HOCH2CO3 + NO2	KBPAN(T,M)
PHAN + OH	→	HCHO + CO + NO2	1.12E-12
GLYOX + OH	→	1.2 CO + 0.6 HO2 + 0.4 HCOCO3	1.14E-11
GLYOX + NO3	→	1.2 CO + 0.6 HO2 + 0.4 HCOCO3 + HNO3	KNO3AL
GLYOX + hν	→	2 CO + H2	J(31)
GLYOX + hν	→	HCHO + CO	J(32)
GLYOX + hν	→	2 CO + 2 HO2	J(33)
HCOCO3	→	0.7 CO + 0.7 HO2 + 0.7 CO2 + 0.3 HCOCO2H	1.00E-11×RO2
HCOCO3 + HO2	→	0.71 HCOCO3H + 0.29 HCOCO2H + 0.29 O3	KAPHO2
HCOCO3 + NO	→	HO2 + CO + NO2 + CO2	KAPNO
HCOCO3 + NO3	→	HO2 + CO + NO2 + CO2	1.6×KRO2NO3
HCOCO2H + OH	→	CO + HO2 + CO2	1.23E-11
HCOCO2H + hν	→	2 HO2 + CO + CO2	J(34)
HCOCO3H + OH	→	HCOCO3	1.58E-11
HCOCO3H + hν	→	HO2 + CO + OH + CO2	J(41)+J(15)

The total peroxy radicals are defined as: RO2 = LISOPACO2 + ISOPBO2 + ISOPDO2 + NISOPO2 + LHC4ACCO3 + LC578O2 + C59O2 + LNISO3 + LHMVK-ABO2 + LMVKOHABO2 + MACO3 + MACRO2 + CO2H3CO3 + HYPROPO2 + PRONO3BO2 + CH3CO3 + HOCH2CO3 + HCOCO3 + CH3O2.

TABLE A.4: MCM simple rate constants. T is the temperature in K.

name	expression
KRO2NO	$2.54\text{E-}12 \times \exp(360/T)$
KRO2HO2	$2.91\text{E-}13 \times \exp(1300/T)$
KAPHO2	$4.30\text{E-}13 \times \exp(1040/T)$
KAPNO	$8.10\text{E-}12 \times \exp(270/T)$
KRO2NO3	$2.50\text{E-}12$
KNO3AL	$1.44\text{E-}12 \times \exp(-1862/T)$

TABLE A.5: Parameters for the MCM complex rate constants used in MIM2. M is the concentration of air in molec cm^{-3} and T is the temperature in K.

rate constant	parameters
KMT16	
K0	$8.00 \times 10^{-27} \times (T/300)^{-3.5} \times M$
KI	3.00×10^{-11}
FC	0.5
KFPAN	
K0	$2.70 \times 10^{-28} \times (T/300)^{-7.1} \times M$
KI	$1.20 \times 10^{-11} \times (T/300)^{-0.9}$
FC	0.3
KBPAN	
K0	$4.90 \times 10^{-03} \times \exp(-12100/T) \times M$
KI	$5.40 \times 10^{+16} \times \exp(-13830/T)$
FC	0.3

The rate constants are then calculated according to the follwing expressions: $k_{comp} = K0 \cdot KI \cdot F/(K0+KI)$, where $F = 10^{\log FC/(1+(\log krd/nu)^2)}$ and $nu = 0.75 - 1.27 \cdot \log FC$
.

TABLE A.6: Photolysis Parameters (l, m and n) from MCM and used in the box model evaluation (Saunders et al., 2003). They J-values (in s^{-1}) are computed with the expression $J = l \times (cos(\theta))^m \times \exp(-n \sec(\theta))$, where θ is the solar zenith angle.

J	l	m	n	structural pattern
$J(1)$	6.073E-05	1.743	0.474	
$J(2)$	4.775E-04	0.298	0.080	
$J(3)$	1.041E-05	0.723	0.279	
$J(4)$	1.165E-02	0.244	0.267	
$J(5)$	2.485E-02	0.168	0.108	
$J(6)$	1.747E-01	0.155	0.125	
$J(7)$	2.644E-03	0.261	0.288	
$J(8)$	9.312E-07	1.230	0.307	
$J(11)$	4.642E-05	0.762	0.353	HCHO
$J(12)$	6.853E-05	0.477	0.323	HCHO
$J(13)$	7.344E-06	1.202	0.417	CH_3CHO
$J(14)$	2.879E-05	1.067	0.358	C_2H_5CHO
$J(15)$	2.792E-05	0.805	0.338	C_3H_7CHO
$J(16)$	1.675E-05	0.805	0.338	$C_5H_{11}CHO$
$J(17)$	7.914E-05	0.764	0.364	RCHOHCHO
$J(18)$	1.140E-05	0.396	0.298	RR'C=CR''CHO
$J(19)$	1.140E-05	0.396	0.298	RR'C=CR''CHO
$J(21)$	7.992E-07	1.578	0.271	CH_3COCH_3
$J(22)$	5.804E-06	1.092	0.377	RCOCHR'OH
$J(23)$	1.836E-05	0.395	0.296	$CH_3COCH=CH2$
$J(24)$	1.836E-05	0.395	0.296	RCOCR'=CH2
$J(31)$	6.845E-05	0.130	0.201	$(HCO)_2$
$J(32)$	1.032E-05	0.130	0.201	$(HCO)_2$
$J(33)$	3.802E-05	0.644	0.312	$(HCO)_2$
$J(34)$	1.537E-04	0.170	0.208	RCOCHO
$J(35)$	3.326E-04	0.148	0.215	RCOCOR'
$J(41)$	7.649E-06	0.682	0.279	ROOH
$J(51)$	1.588E-06	1.154	0.318	CH_3NO_3
$J(52)$	1.907E-06	1.244	0.335	$C_2H_5NO_3$
$J(53)$	2.485E-06	1.196	0.328	$RR'CHNO_3$
$J(54)$	4.095E-06	1.111	0.316	$RR'CHNO_3$
$J(55)$	1.135E-05	0.974	0.309	$RR'R''CNO_3$
$J(56)$	7.549E-06	1.015	0.324	$RCOCHR'NO_3$
$J(57)$	3.363E-06	1.296	0.322	$RCOCHR'NO_3$
$J(61)$	7.537E-04	0.499	0.266	

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