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Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds

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Abstract. Kinetic and mechanistic data relevant to the tropospheric degradation of volatile organic compounds (VOC), and the production of secondary pollutants, have previously been used to define a protocol which underpinned the construction of a near-explicit Master Chemical Mechanism. In this paper, an update to the previous protocol is presented, which has been used to define degradation schemes for 107 non-aromatic VOC as part of version 3 of the Master Chemical Mechanism (MCM v3). The treatment of 18 aromatic VOC is described in a companion paper. The protocol is divided into a series of subsections describing initiation reactions, the reactions of the radical intermediates and the further degradation of first and subsequent generation products. Emphasis is placed on updating the previous information, and outlining the methodology which is specifically applicable to VOC not considered previously (e.g., α - and β -pinene). The present protocol aims to take into consideration work available in the open literature up to the beginning of 2001, and some other studies known by the authors which were under review at the time. Application of MCM v3 in appropriate box models indicates that the representation of isoprene degradation provides a good description of the speciated distribution of oxygenated organic products observed in reported field studies where isoprene was the dominant emitted hydrocarbon, and that the α -pinene degradation chemistry provides a good description of the time dependence of key gas phase species in α -pinene/NO_x photo-oxidation experiments carried out in the European Photoreactor (EU-PHORE). Photochemical Ozone Creation Potentials (POCP) have been calculated for the 106 non-aromatic non-methane VOC in MCM v3 for idealised conditions appropriate to north-west Europe, using a photochemical trajectory model.

The POCP values provide a measure of the relative ozone forming abilities of the VOC. Where applicable, the values are compared with those calculated with previous versions of the MCM.

1 Introduction

Volatile organic compounds (VOC) are emitted in substantial quantities from both biogenic and anthropogenic sources (e.g. Guenther et al., 1995; Olivier et al., 1996), and have a major influence on the chemistry of the lower atmosphere. It is well established that the gas phase degradation of VOC plays a central role in the generation of a variety of secondary pollutants (e.g. Leighton, 1961; Finlayson Pitts and Pitts, 1999; Atkinson, 2000a; Jenkin and Clemitshaw, 2000), which may have a harmful impact on human health and on the environment. The complete gas phase oxidation of VOC into carbon dioxide and water occurs predominantly (but not exclusively) by sunlight-initiated mechanisms, and produces carbon monoxide and a variety of intermediate oxidised organic products, some nitrogen-containing, which may have detrimental health effects (PORC, 1997; IARC, 2002). Furthermore, certain oxidised organic products, particularly those produced from large, unsaturated VOC, are sufficiently involatile to promote aerosol formation and growth (e.g. Asher et al., 2002), and the important contribution of oxygenated organics to secondary aerosols is becoming increasingly recognised (e.g., Rogge et al., 1993; Turpin and Huntzicker, 1995; Saxena and Hildemann, 1996; Pio et al., 2001). Of particular importance, however, is the generation of ozone as a by-product of VOC oxidation in the presence of nitrogen oxides: ozone is known to have adverse effects on health,

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vegetation and materials, it is a greenhouse gas, and it promotes the oxidation of trace gases both directly, and as a free radical precursor (NRC, 1991; PORG, 1997).

The essential features of the chemistry of VOC degradation, particularly in relation to ozone formation, are well documented (e.g., Atkinson, 2000a; Jenkin and Clemitshaw, 2000). However, it is well established that the degradation of each emitted VOC occurs by a unique mechanism (because of differences in reactivity and structure), such that the relative contributions of VOC to the formation of ozone and other secondary pollutants varies from one compound to another (e.g. Carter and Atkinson, 1987; Grosjean and Seinfeld, 1989; Derwent and Jenkin, 1991). Over the past two decades, the availability of kinetic and mechanistic data to help elucidate the degradation mechanisms of VOC has increased significantly, and various aspects of the tropospheric chemistry of organic compounds have been reviewed extensively (e.g. Roberts, 1990; Wayne et al., 1991; Atkinson, 1997a, b; Calvert et al., 2000; Tyndall et al., 2001). Such information has previously been used to define a mechanism development protocol for VOC degradation (Jenkin et al., 1997), which has underpinned the construction of a Master Chemical Mechanism (MCM) describing the degradation of over 100 VOC (Saunders et al., 1997; Derwent et al., 1998). To remain viable, however, mechanisms must be reviewed and maintained in line with the current literature. In this paper, an update to the previous protocol is presented, which has been used to define degradation schemes for 107 non-aromatic VOC as part of version 3 of the Master Chemical Mechanism (MCM v3). The treatment of 18 aromatic VOC is described separately in a companion paper (Jenkin et al., 2003).

2 The Master Chemical Mechanism (MCM)

The MCM is a near-explicit chemical mechanism describing the detailed gas phase degradation of a series of emitted VOC, and the resultant generation of ozone and other secondary pollutants, under conditions appropriate to the planetary boundary layer. The philosophy behind the construction of the MCM is to use available information on the kinetics and products of elementary reactions relevant to VOC oxidation to build up a near-explicit representation of the degradation mechanisms. A fundamental assumption in its construction, therefore, is that the kinetics and products of a large number of unstudied chemical reactions can be defined on the basis of the known reactions of a comparatively small number of similar chemical species, by analogy and with the use of structure-reactivity correlations. The present paper, together with the previous protocol (Jenkin et al., 1997) and the companion paper (Jenkin et al., 2003), summarises how this has been achieved for the 125 VOC in MCM v3.

The resultant mechanism comprises 12 691 reactions of 4351 organic species, and 46 associated inorganic reactions.

It can be accessed from MCM v3 website at, <http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html>, where the full mechanism can be downloaded as a reaction listing (in FACSIMILE format), and embedded in a photochemical trajectory model. A tool for assembling subsets of MCM v3 is also available, which allows the user to select any number of compounds from the primary VOC list, and extract a complete degradation mechanism for that subset. Options for the resultant file storage are also available, including a simple mechanism text listing and FACSIMILE format.

MCM v3 describes the degradation of 22 alkanes, 20 alkenes (including 2 dienes and 2 monoterpenes), 1 alkyne, 18 aromatics, 6 aldehydes, 10 ketones, 17 alcohols and glycols, 10 ethers and glycolethers, 8 esters, 3 carboxylic acids, 2 other oxygenated VOC and 8 chlorinated hydrocarbons, the complete listing of which is available on the website. The VOC were selected on the basis of the speciation determined by the UK National Atmospheric Emissions Inventory (UK NAEI, 2002). Although the inventory currently contains 650 entries, the VOC considered in MCM v3 place emphasis on those with greater emissions such that ca. 70% coverage of the mass emissions of unique chemical species is achieved.

3 Structure and methodology

The protocol, outlined in Sect. 4, is designed to allow the construction of comprehensive, consistent gas phase degradation schemes for a variety of non-aromatic VOC. The structure follows that of the previous protocol (Jenkin et al., 1997). In Sects. 4.1 – 4.3, the initiation reactions of OH radicals with organic compounds are considered, and guidelines are established to indicate for which compounds O₃ and NO₃ initiated chemistry is also likely to be important, and therefore treated. Photolysis reactions, which are significant for some classes of VOC, are identified in Sect. 4.4 and photolysis rates are assigned to a series of generic reactions. In Sects. 4.5 – 4.8, the reactions of the reactive intermediates generated as a result of the initiation chemistry are identified, and various generic parameters and criteria are summarised. In Sect. 4.9, the further degradation of first, and subsequent generation products is discussed. To minimise duplication of information, the previous protocol (Jenkin et al., 1997) is frequently cited and may need to be consulted for full details of the methodology employed for a given class of reaction. Emphasis is placed, therefore, on updating the previous information, and outlining the methodology which is specifically applicable to VOC not considered previously (e.g., α - and β -pinene).

The general methodology is illustrated by the flow chart in Fig. 1, which summarises the main types of reaction considered and classes of organic intermediate and product which are potentially generated. The chemistry of a given VOC is thus developed within this framework, based on a predefined set of rules (i.e. the protocol). The flow chart essentially

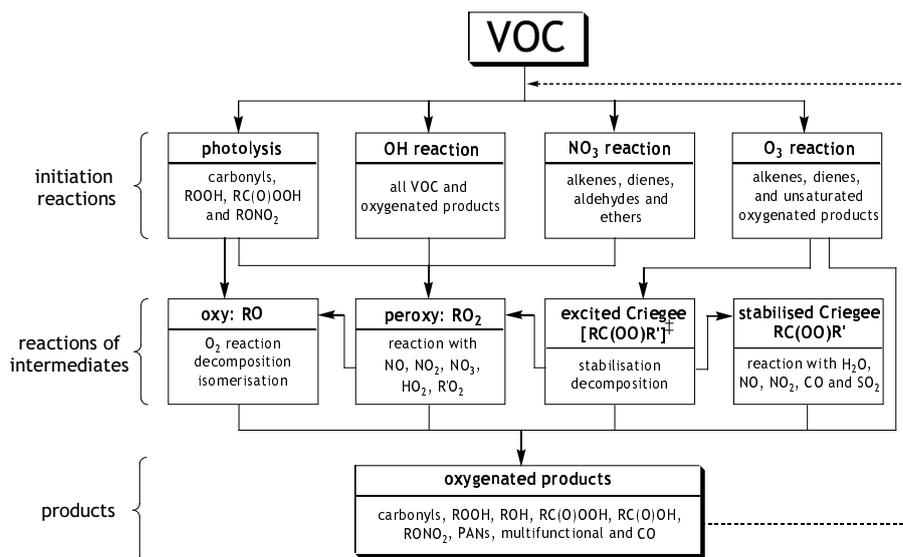


Fig. 1. Flow chart indicating the major reactions, intermediate classes and product classes considered in the MCM protocol (see text).

represents the degradation of the given VOC into a set of ‘first generation products’, which are themselves further degraded within the same general framework. This process is continued until the chemistry either yields CO₂, or until an organic product or radical is generated for which the subsequent chemistry is already represented in the mechanism.

It is recognised that the rigorous application of a series of rules can lead to an unmanageably large number of reactions, particularly for larger VOC. The ideal of a fully explicit mechanism is therefore impractical, and a degree of simplification is required even for so called explicit mechanisms. The protocol is designed to incorporate some strategic simplification in the degradation schemes generated. As discussed previously (Jenkin et al., 1997), this is partially achieved by limiting the proliferation of the chemistry related to minor reaction pathways through disregarding OH reaction channels of low probability (Sect. 4.1), and simplifying the treatment of the degradation of a number of product classes deemed to be ‘minor’ (Sect. 4.9). In addition a substantial reduction is achieved through parameterising the representation of the permutation (i.e. self and cross) reactions of organic peroxy radicals. A fully explicit inclusion of these reactions alone for the 902 peroxy radicals generated in MCM v3 would require approximately 400 000 reactions (assuming a single channel in each case). The parameterisation used in the MCM (described in Sect. 4.6.5 and by Jenkin et al., 1997) requires only one reaction for each peroxy radical, with up to three channels in each case.

In Sect. 5, the testing and validation of selected MCM v3 degradation schemes is described. The degradation scheme for isoprene is tested by comparing the distribution of oxygenated products simulated in a boundary layer box model with product ratios measured in the field as part of the US

Southern Oxidants Studies (Lee et al., 1995, 1998; Williams et al., 1997). In addition, the time dependences of α -pinene, NO_x and ozone, observed in photo-oxidation experiments in the European Photoreactor (EUPHORE) as part of the EU OSOA project, are used to test the performance of the MCM v3 α -pinene degradation scheme.

Finally, ‘Photochemical Ozone Creation Potentials’ (POCP) calculated with MCM v3, implemented in a photochemical trajectory model, are presented in Sect. 6. The POCP values provide a measure of the relative ozone forming abilities of the 106 non-aromatic, non-methane VOC for idealised conditions appropriate to north-west Europe. Where applicable, the values are compared with those reported previously as calculated with MCM v1 (Derwent et al., 1998) and MCM v2 (Jenkin and Hayman, 1999).

4 Protocol for mechanism development

4.1 OH radical initiation reactions

4.1.1 Rates of initiation reactions

Rate coefficients for the reactions of OH with organic compounds have been reviewed extensively by Atkinson (1989; 1994; 1997a), Atkinson et al. (1999) and Calvert et al. (2000), with recommendations made in a large number of cases. These recommendations are used unless superseded by more recent evaluations. If recent laboratory determinations are available, which are likely to influence, or form the basis of future recommendations, these are also taken into account. Where no experimental data exist, rate coefficients appropriate to 298 K are estimated by a number of reported methods. For alkanes, carbonyls and chlorinated hy-

drocarbons, the structure-activity relationship (SAR) method devised by Atkinson (1987), and subsequently updated by Kwok and Atkinson (1995) and Atkinson (2000b), is employed. The SAR method of Peeters et al. (1994) is used for alkenes and dienes, and the group reactivity (GR) method developed by Dagaut et al. (1989), and updated by Porter et al. (1997), is used for alcohols, glycols, ethers and glycol ethers, as described previously by Jenkin and Hayman (1999).

4.1.2 Initial radical products

Where the relative importance of product channels for reaction of OH with a given VOC has been determined by laboratory investigation, the data are used accordingly. This information is generally available in the kinetics evaluations. In the majority of cases, such data are not available, however, and the initial distribution of radical products is estimated from partial rate coefficients calculated using the SAR and GR methods referred to above. In some cases, the chemistry is simplified by limiting the number of product channels, as described in detail in the previous protocol (Jenkin et al., 1997).

4.2 O₃ initiation reactions

O₃ initiated degradation chemistry is included for those VOC for which both the following relations apply:

$$k(\text{O}_3 + \text{VOC}) > 10^{-8} k(\text{OH} + \text{VOC})$$

$$k(\text{O}_3 + \text{VOC}) > 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These relations were formulated on the basis that typical ambient concentrations of OH and O₃ in the boundary layer are 10⁶ and 10¹² molecule cm⁻³, respectively. Thus, the first criterion applies when the removal rate by reaction with O₃ exceeds 1% of the removal rate by reaction with OH, and the second when the lifetime of the VOC with respect to reaction with O₃ is less than 10⁷ s (ie. ca. 100 days). O₃ initiated degradation is expected to be important only for alkenes, dienes, monoterpenes and some unsaturated oxygenated products.

4.2.1 Rates of initiation reactions

Rate coefficients for the reactions of O₃ with alkenes, dienes and monoterpenes have been reviewed by Atkinson (1994; 1997a), Atkinson et al. (1999) and Calvert et al. (2000), with recommendations made in many cases. These recommendations are used unless superseded by more recent evaluations. If recent laboratory determinations are available, which are likely to influence, or form the basis of future recommendations, these are also taken into account. Where no experimental data exist for monoalkenes, an appropriate generic rate coefficient defined by analogy is used, as reported previously (Jenkin et al., 1997).

4.2.2 Initial products

The reaction mechanisms follow the general pattern described by Atkinson (1997a) and Calvert et al. (2000), with addition of ozone to the double bond leading initially to the formation of an energy rich primary ozonide. This ozonide decomposes rapidly by the two possible channels, each forming a carbonyl compound and a 'Criegee' biradical, which also possesses excess energy (denoted ‡):



Available data on primary carbonyl product yields indicate that both channels typically make an important contribution to the reaction (e.g. Calvert et al., 2000), although formation of the more alkyl substituted Criegee biradical tends to be favoured. As described previously (Jenkin et al., 1997), the two channels are currently assumed to compete equally in the majority of cases in the MCM. For α - and β -pinene, however, the route forming the more substituted Criegee biradical is assigned a higher probability of 60%. Note that in the case of α -pinene (and other endocyclic alkenes) the product of either reaction (1a) or (1b) is a Criegee biradical of the same carbon number as the parent VOC, which also contains a carbonyl substitution (i.e. separate carbonyl and biradical products are not formed).

In the case of the unsymmetric diene, isoprene (the only such compound currently considered in the MCM), addition of ozone to the less substituted double bond is assumed to be favoured relative to the more substituted double bond by a factor of 1.5, which is in accordance with the results of Grosjean et al. (1993) and Aschmann and Atkinson (1994).

4.3 NO₃ radical initiation reactions

NO₃ initiated degradation chemistry is included for those VOC for which both the following relations apply:

$$k(\text{NO}_3 + \text{VOC}) > 10^{-5} k(\text{OH} + \text{VOC})$$

$$k(\text{NO}_3 + \text{VOC}) > 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These relations were formulated on the basis that typical boundary layer concentrations of OH and NO₃ are 10⁶ and 10⁹ molecule cm⁻³, respectively. Thus, the first criterion applies when the removal rate by reaction with NO₃ exceeds 1% of the removal rate by reaction with OH, and the second when the lifetime of the VOC with respect to reaction with NO₃ is less than 10⁷ s (ie. ca. 100 days). NO₃ initiated degradation is therefore believed to be important for alkenes, dienes, aldehydes and ethers.

4.3.1 Rates of initiation reactions

Rate coefficients for the reactions of NO₃ with organic compounds have been reviewed by Atkinson (1991; 1994;

Table 1. Generic rate coefficients used for the reactions of NO₃ with aldehydes

	k (298 K) ^a	Comment
C ₂ aldehyde	2.8	b
C ₃ aldehyde	6.7	c
C ₄ aldehyde	11.0	d
≥ C ₅ linear aldehyde	15.0	e
≥ C ₅ branched aldehyde	24.0	f

Notes:

^a units: 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹; T-dependence of $E/R = -1862$ K applied to all reactions, based on recommendation of Atkinson (1991) for acetaldehyde;^b recommendation of Atkinson (1991);^c based on data of Papagni et al. (2000) and D'Anna et al. (2001) for propanal;^d based on data of Papagni et al. (2000), Ullerstam et al. (2001) and D'Anna et al. (2001) for butanal and 2-methylpropanal;^e based on data of Papagni et al. (2000) and D'Anna et al. (2001) for pentanal and hexanal;^f based on data of D'Anna et al. (2001) for branched C₅ and C₆ aldehydes;

1997a), Wayne et al. (1991), Atkinson et al. (1999) and Calvert et al. (2000). The reviews of Atkinson and Calvert also make recommendations in many cases. These recommendations are used unless superseded by more recent evaluations. If recent laboratory determinations are available, which are likely to influence, or form the basis of future recommendations, these are also taken into account. The reactions of NO₃ with aldehydes for which no experimental data exist, are assigned an appropriate generic rate coefficient based on the data presented in Table 1, which makes use of a substantial new body of kinetic data on this class of reaction (Papagni et al., 2000; Ullerstam et al., 2000; D'Anna et al., 2001). The generic coefficients allow for the observed significant increase in the rate coefficient with increasing carbon number and branching for the series of aldehydes considered in these studies. Appropriate generic rate coefficients are also assigned to reactions of NO₃ with ethers and alkenes for which no experimental data exist, as described in detail in the previous protocol (Jenkin et al., 1997).

4.3.2 Initial radical products

The reactions of NO₃ with aldehydes are assumed to proceed via abstraction of the aldehydic H-atom, leading to the production of acyl radicals. The reactions with ethers and glycol ethers are also assumed to result in H-atom abstraction. The attack of NO₃ on alkenes, dienes and monoterpenes is assumed to proceed by an addition mechanism, leading to the formation of nitroxy-substituted alkyl radicals. The initial distribution of radical products is assigned as described previously (Jenkin et al., 1997).

4.4 Initiation by photolysis

Photolysis reactions are considered for simple carbonyl compounds, such as aldehydes and ketones which are both emitted into the troposphere and formed as degradation products, and also for many other complex carbonyl compounds, hydroperoxides and organic nitrates which are generated as degradation products. Certain classes of compound containing carbonyl groups (e.g. carboxylic acids and esters) do not absorb significantly at wavelengths above 290 nm (Calvert and Pitts, 1966), and photolysis reactions are therefore not considered for these species.

As described previously (Jenkin et al., 1997), the methodology used in the MCM involves assigning photolysis parameters to a core number of reactions (shown in Table 2) for which absorption cross section and quantum yield data are available. Some of these parameters are also used to define the photolysis rates of a much larger number of related species, for which the required information is not available (e.g. C₂H₅C(O)CH₃ is used as a surrogate for aliphatic ketones). This procedure is described fully in the previous protocol (Jenkin et al., 1997).

For much of the work performed with the MCM by the authors, photolysis rates as a function of solar zenith angle have been determined from the available data for the core reactions using a two stream isotropic scattering model described previously (Hayman, 1997). Calculations were performed for clear sky conditions at an altitude of 0.5 km on 1 July at a latitude of 45° N. In each case, variation of photolysis rate with solar zenith angle can be described well by an expression of the following form,

$$J = l(\cos \chi)^m \exp(-n \cdot \sec \chi) \quad (i)$$

by optimising the values of the three parameters, l , m and n (see discussion in Jenkin et al., 1997). The optimised parameters for all the core photolysis reactions are presented in Table 2.

4.5 Reactions of organic radicals

The large majority of organic radicals (R) react rapidly and exclusively with oxygen under tropospheric conditions, to form stabilised peroxy radicals, RO₂:



This is assumed in almost all cases in the MCM. In a small number of exceptions, decomposition of either the organic radical itself, or the intermediate peroxy radical is believed to occur, leading to the overall chemistry shown, under tropospheric conditions:

Specific cases:

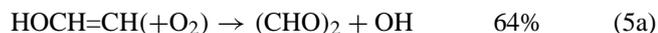


Table 2. Photolysis reactions and parameters assigned as a function of solar zenith angle (χ)

reaction		$J = I(\cos \chi)^m \exp(-n \cdot \sec \chi)$			
Inorganic reactions		l	m	n	
O ₃	→ O(¹ D) + O ₂	(J ₁) ^a	6.073×10^{-5}	1.743	0.474
	→ O(³ P) + O ₂	(J ₂)	4.775×10^{-4}	0.298	0.080
H ₂ O ₂	→ OH + OH	(J ₃)	1.041×10^{-5}	0.723	0.279
NO ₂	→ NO + O(³ P)	(J ₄)	1.165×10^{-2}	0.244	0.267
NO ₃	→ NO + O ₂	(J ₅)	2.485×10^{-2}	0.168	0.108
	→ NO ₂ + O(³ P)	(J ₆)	1.747×10^{-1}	0.155	0.125
HONO	→ OH + NO	(J ₇)	2.644×10^{-3}	0.261	0.288
HNO ₃	→ OH + NO ₂	(J ₈)	9.312×10^{-7}	1.230	0.307
Carbonyls					
HCHO	→ HCO + H	(J ₁₁)	4.642×10^{-5}	0.762	0.353
	→ CO + H ₂	(J ₁₂)	6.853×10^{-5}	0.477	0.323
CH ₃ CHO	→ HCO + CH ₃	(J ₁₃)	7.344×10^{-6}	1.202	0.417
C ₂ H ₅ CHO	→ HCO + C ₂ H ₅	(J ₁₄)	2.879×10^{-5}	1.067	0.358
n-C ₃ H ₇ CHO	→ HCO + n-C ₃ H ₇	(J ₁₅) ^b	2.792×10^{-5}	0.805	0.338
	→ CH ₃ CHO + C ₂ H ₄	(J ₁₆)	1.675×10^{-5}	0.805	0.338
i-C ₃ H ₇ CHO	→ HCO + i-C ₃ H ₇	(J ₁₇) ^b	7.914×10^{-5}	0.764	0.364
CH ₂ =C(CH ₃)CHO	→ CH ₃ C=CH ₂ + HCO	(J ₁₈) ^b	1.140×10^{-5}	0.396	0.298
	→ CH ₂ =C(CH ₃)CO + H	(J ₁₉) ^b	1.140×10^{-5}	0.396	0.298
CH ₃ C(O)CH ₃	→ CH ₃ CO + CH ₃	(J ₂₁)	7.992×10^{-7}	1.578	0.271
CH ₃ C(O)C ₂ H ₅	→ CH ₃ CO + C ₂ H ₅	(J ₂₂) ^b	5.804×10^{-6}	1.092	0.377
CH ₃ C(O)CH=CH ₂	→ CH ₃ CH=CH ₂ + CO	(J ₂₃)	1.836×10^{-5}	0.395	0.296
	→ CH ₃ CO + CH=CH ₂	(J ₂₄) ^b	1.836×10^{-5}	0.395	0.296
α -Dicarbonyls					
(CHO) ₂	→ CO + CO + H ₂	(J ₃₁)	6.845×10^{-5}	0.130	0.201
	→ CO + HCHO	(J ₃₂)	1.032×10^{-5}	0.130	0.201
	→ HCO + HCO	(J ₃₃)	3.802×10^{-5}	0.644	0.312
CH ₃ C(O)CHO	→ CH ₃ CO + HCO	(J ₃₄) ^b	1.537×10^{-4}	0.170	0.208
CH ₃ C(O)C(O)CH ₃	→ CH ₃ CO + CH ₃ CO	(J ₃₅) ^b	3.326×10^{-4}	0.148	0.215
Hydroperoxides					
CH ₃ OOH	→ CH ₃ O + OH	(J ₄₁) ^b	7.649×10^{-6}	0.682	0.279
Organic nitrates					
CH ₃ ONO ₂	→ CH ₃ O + NO ₂	(J ₅₁)	1.588×10^{-6}	1.154	0.318
C ₂ H ₅ ONO ₂	→ C ₂ H ₅ O + NO ₂	(J ₅₂)	1.907×10^{-6}	1.244	0.335
n-C ₃ H ₇ ONO ₂	→ n-C ₃ H ₇ O + NO ₂	(J ₅₃) ^b	2.485×10^{-6}	1.196	0.328
i-C ₃ H ₇ ONO ₂	→ i-C ₃ H ₇ O + NO ₂	(J ₅₄) ^b	4.095×10^{-6}	1.111	0.316
t-C ₄ H ₉ ONO ₂	→ t-C ₄ H ₉ O + NO ₂	(J ₅₅) ^b	1.135×10^{-5}	0.974	0.309
CH ₃ C(O)CH ₂ ONO ₂	→ CH ₃ C(O)CH ₂ O + NO ₂	(J ₅₆) ^b	7.549×10^{-6}	1.015	0.324
	→ CH ₃ CO + HCHO + NO ₂	(J ₅₇) ^b	3.363×10^{-6}	1.296	0.322

Notes:

^a Parameter numbers are consistent with those applied in the MCM;^b these parameters are also used to define the photolysis rates of a much larger number of related species (see text and Jenkin et al., 1997)



General cases:

α -hydroxy radicals:



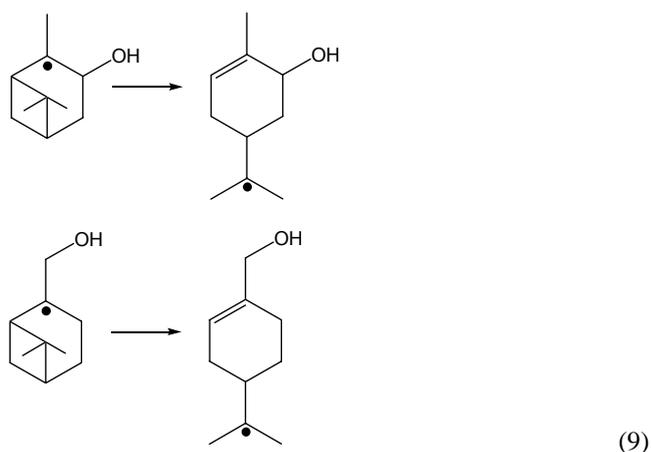
vinyl-type radicals:



α -carbonyl acyl radicals:



In a number of other cases, the organic radical can isomerise prior to addition of O_2 . For example, the terminal addition of OH or NO_3 to the conjugated dienes considered in the MCM (1,3-butadiene and isoprene) leads to the production of hydroxy or nitro-oxy substituted organic radicals containing an allyl resonance. Consequently, the addition of O_2 in these cases can lead to the production of two isomeric RO_2 radicals, for which the assigned relative formation probabilities have been discussed fully previously (Jenkin et al., 1997). In the cases of α - and β -pinene, the hydroxy-substituted tertiary organic radicals generated from OH addition are assumed to isomerise partially prior to O_2 addition under tropospheric conditions, following the mechanism suggested by Noziere et al. (1999) and Vereecken and Peeters (2000) for α -pinene:



The importance of the isomerisation mechanism is set such that the primary yield of the isomerised radical from the reaction of the terpene with OH is 7.5%. On the basis of this figure, the subsequent chemistry leads to formation of acetone as a first generation product in each case with a yield of ca. 6.5%, which is consistent with the reported range (Aschmann et al., 1998; Noziere et al., 1999; Orlando et al., 2000)

4.6 Reactions of peroxy radical intermediates

There are several reactions of a given peroxy radical (RO_2) which are treated, namely the reactions with NO , NO_2 , NO_3 , HO_2 and with itself and other peroxy radicals ($\text{R}'\text{O}_2$).

4.6.1 The reactions of RO_2 with NO

Available rate coefficients for the reactions of RO_2 with NO have been reviewed by Lightfoot et al. (1992), Wallington et al. (1992; 1997), Atkinson et al. (1999) and Tyndall et al. (2001), with recommendations made in a number of cases. Where applicable, the kinetic data applied to these reactions in the MCM are consistent with these recommendations. For the vast majority of the ca. 900 RO_2 radicals, however, kinetic data are unavailable, and the assigned rate coefficients are based on two generic expressions. For acyl peroxy radicals a value of

$$k_{11} = 8.1 \times 10^{-12} \exp(270/T) \quad (\text{ii})$$

is used, based on the temperature-dependent rate coefficient reported for $\text{CH}_3\text{C(O)O}_2$ by Villalta and Howard (1996). For other classes of peroxy radical, rate coefficients are defined by the expression

$$k_{11} = 2.54 \times 10^{-12} \exp(360/T) \cdot f \quad (\text{iii})$$

which is the product of the rate coefficient and an efficiency factor, ' f '. The rate coefficient is based on recommended values for CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ (Atkinson et al., 1999), and the observations of Eberhard et al. (1996) and Eberhard and Howard (1996; 1997) for $\text{C}_3 - \text{C}_5$ alkyl peroxy radicals. A unity value of ' f ' is thus applied to alkyl peroxy radicals in general. In contrast to the treatment of alkyl peroxy radicals in our previous protocol (Jenkin et al., 1997), therefore, there is no dependence of the rate coefficient on peroxy radical size. A unity value of ' f ' is also applied to the majority of other peroxy radicals, with the exception of α -chlorinated peroxy radicals and β -chlorinated peroxy radicals, for which respective values of 2.2 and 1.6 are used, to account for the consistently larger reported rate coefficients for a number of C_1 and C_2 halogenated RO_2 , as described previously (Jenkin et al., 1997).

The following two channels are considered for the reactions of RO_2 with NO :



The methodology for assigning branching ratios to the nitrate-forming channels, $k_{11b}/(k_{11a} + k_{11b})$, has been described in detail previously (Jenkin et al., 1997).

4.6.2 The reactions of RO₂ with NO₂

These reactions are only treated in the MCM for acyl peroxy radicals, for which the product peroxy nitrates (ROONO₂) are comparatively stable, and for the most abundant peroxy radical, CH₃O₂:



Available rate coefficients for the forward and reverse reactions have been reviewed by Lightfoot et al. (1992), Wallington et al. (1992; 1997), Atkinson et al. (1999) and Tyndall et al. (2001). The treatment in the MCM is largely unchanged from that reported previously (Jenkin et al., 1997), except that relevant rate coefficients have been updated on the basis of the more recent recommendations.

4.6.3 The reactions of RO₂ with NO₃

On the basis of reported information, these reactions are assumed to proceed via a single channel, as follows:



Based on the data of Biggs et al. (1994), Daele et al. (1995) and Helleis et al. (1996), a value of $k_{13} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is assigned to the reaction involving CH₃O₂. A value of $2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is used for C₂H₅O₂, (based on the reported coefficients of Biggs et al., 1995 and Ray et al., 1996), and this value is also used for the reactions of non-acyl peroxy radicals with NO₃ in general. The rate coefficients for reactions of acyl peroxy radicals are assigned a value of $k_{13} = 4.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on the reported value for CH₃C(O)O₂ (Canosa-Mas et al., 1996).

4.6.4 The reactions of RO₂ with HO₂

Available rate coefficients for the reactions of RO₂ with HO₂ have been reviewed by Lightfoot et al. (1992), Wallington et al. (1992; 1997), Atkinson et al. (1999) and Tyndall et al. (2001), with recommendations made in a number of cases. Where applicable, the kinetic data applied to these reactions in the MCM are consistent with these recommendations. Where no experimental data are available, generic rate coefficients are defined by analogy. For acyl peroxy radicals and α -chlorinated peroxy radicals, the rate coefficients are assumed equivalent to those recommended by Atkinson et al. (1999) for CH₃C(O)O₂ and CH₂ClO₂, respectively. In all other cases, the rate coefficients are given by the expression,

$$k_{14} = 2.91 \times 10^{-13} \exp(1300/T) \cdot [1 - \exp(-0.245n)] \quad (\text{iv})$$

where n is the carbon number. This expression was defined on the basis of room temperature data for the available series of reactions of alkyl and β -hydroxy RO₂ radicals with HO₂, as shown in Fig. 2. The temperature dependence is based on

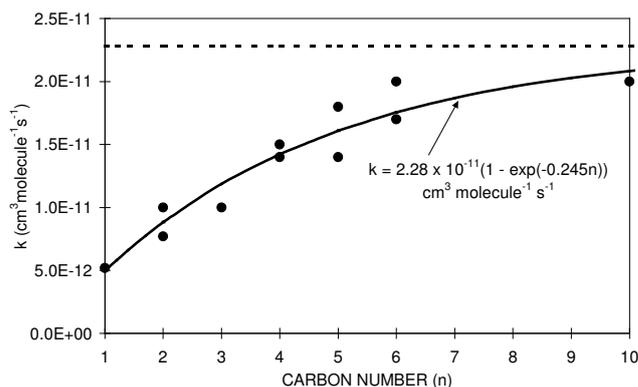
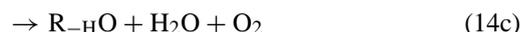


Fig. 2. Room temperature data for reactions of alkyl and β -hydroxyalkyl peroxy radicals with HO₂ as a function of carbon number. Line is the best fit to the data on the basis of the assumed function $k = a(1 - \exp(-bn))$ used previously by Jenkin et al. (1997). Presented data are recommendations of Atkinson et al. (1999) for reactions involving CH₃O₂, C₂H₅O₂ and HOCH₂CH₂O₂, and additional data from Rowley et al. (1992), Jenkin and Hayman (1995), Boyd et al. (1996) and Lesclaux et al. (1998) for a variety of RO₂ radicals.

reported values for > C₂ alkyl and β -hydroxy RO₂ radicals (Rowley et al., 1992; Boyd et al., 1996).

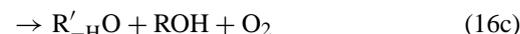
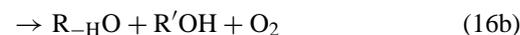
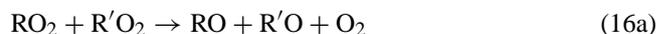
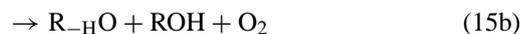
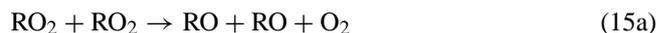
The following channels are considered for the reactions of RO₂ with HO₂:



The methodology for assigning branching ratios to these channels, has been described in detail previously (Jenkin et al., 1997).

4.6.5 The permutation reactions of RO₂

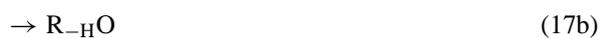
The “permutation” reactions of a given RO₂ radical are its self reaction (15), and its cross reactions (16) with other peroxy radicals, R’O₂, for which a number of product channels may occur:



Available rate coefficients for the permutation reactions of RO₂ have been reviewed by Lightfoot et al. (1992), Wallington et al. (1992), Lesclaux (1997), Atkinson et al. (1999) and

Tyndall et al. (2001), with recommendations made in a number of cases.

In view of the large number of RO₂ radicals generated in a detailed chemical mechanism, however, it is unrealistic to represent these reactions explicitly, and the use of a simplified parameterisation is essential (Madronich and Calvert, 1990). As described in detail previously (Jenkin et al., 1997), a very simplified approach is adopted in the MCM, in which each peroxy radical is assumed to react with all other peroxy radicals (i.e. the peroxy radical ‘pool’) at a single, collective rate. This is achieved by defining a parameter “ΣRO₂” which is the sum of the concentrations of all peroxy radicals, excluding HO₂. The collective rate of all the permutation reactions of a particular peroxy radical is then represented by a pseudo-unimolecular reaction, which has an assigned rate coefficient equal to $k_{17} \cdot \Sigma \text{RO}_2$:



Each reaction has up to three product channels, the branching ratios of which depend on the structure of the radical. The assigned values of k_{17} for various classes of peroxy radical also depend on the structure of the organic group, and are based on trends of reactivity of peroxy radical self reactions. The majority of values remain unchanged from those reported in the previous protocol (Jenkin et al., 1997), which should be consulted for full details. However, on the basis of more recent information on the rates of peroxy radical cross reactions, the following updates have been made. The value of k_{17} for acyl peroxy radicals has been increased to $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on the data of Villenave et al. (1998) for reactions of CH₃C(O)O₂ with a series of other RO₂ radicals, and those for the peroxy radicals generated during the oxidation of isoprene and 1,3-butadiene (which contain combinations of allyl, β-hydroxy and β-hydroxy groups) have been increased to the values given in Table 3. These are based on data summarised by Jenkin et al. (1998) for RO₂ radicals generated in these systems.

4.7 Reactions of Criegee biradicals

4.7.1 The reactions of the excited Criegee biradicals

The energy rich Criegee biradicals, [RC(OO)R'][‡], formed from the reactions of ozone with alkenes and dienes (Sect. 4.2) are either collisionally stabilised, or decompose to yield a variety of radical and molecular products (e.g. Atkinson, 1997a). As described previously (Jenkin et al., 1997), three possible fates of the excited Criegee biradicals are considered in the MCM, namely (i) collisional stabilisation to produce a stabilised Criegee biradical, (ii) decomposition to

generate OH (and other) radicals, and (iii) decomposition not generating OH radicals. In the majority of cases, the treatment of the reactions of the excited Criegee biradicals in MCM v3 currently remains unchanged from that described in detail previously (Jenkin et al., 1997), in that the relative importance of the available reactions for a given biradical is dependent on the degree of alkyl substitution in the parent alkene, rather than by the identity of the biradical itself.

In the cases of α- and β-pinene, however, an alternative approach has been adopted which is based on Criegee biradical structure. On the basis of the structure-reactivity relationship proposed by Rickard et al. (1999), excited Criegee biradicals of generic formula [RC(OO)H][‡] are assumed to decompose to generate OH with 50% probability (with the remaining 50% being stabilised), whilst those of generic formula [RC(OO)R'][‡] are assumed to decompose exclusively to generate OH. In the exceptional latter case when one of the organic groups is attached to the carbonyl oxide group via a bridgehead carbon (as in β-pinene), a decomposition probability of 50% is assumed because the H atom on the bridgehead carbon is difficult to abstract and cannot easily participate in the ‘hydroperoxide mechanism’ (see below). [HC(OO)H][‡] is assumed to decompose with a probability of 12%, as in the case of ethene ozonolysis (Atkinson, 1997a). In conjunction with the primary yields assigned to the Criegee biradicals in the α- and β-pinene systems above (Sect. 4.2.2), this approach leads to overall OH radical yields of 80% and 35% for α- and β-pinene ozonolysis, respectively. These values are fully consistent with available studies (Atkinson, 1997a; Rickard et al., 1999, and references therein).

OH generation from excited Criegee biradicals is mainly assumed to occur by the ‘hydroperoxide mechanism’, involving isomerisation by a 1,4 H atom shift followed by decomposition of the resultant α, β-unsaturated hydroperoxide intermediate, as first proposed by Niki et al. (1987):



This leads to simultaneous formation of an α-carbonyl organic radical, which is assumed to add O₂ to generate a peroxy radical.

4.7.2 The reactions of the stabilised Criegee biradicals

The stabilised Criegee biradicals, formed from the reactions of O₃ with alkenes, are assumed to react with SO₂, CO, NO, NO₂ and H₂O as described previously (Jenkin et al., 1997). The rate coefficients assigned to these reactions remain unchanged from the previous appraisal, and are consistent with reaction with water vapour being the dominant fate under tropospheric conditions.

Table 3. Self reaction rate coefficients (k_{15}) and rate coefficients assigned to the parameterized permutation reactions (k_{17}) of complex RO₂ formed from 1,3-butadiene and isoprene (see text)

Radical	k_{15}^a	k_{17}^b	Comment
HOCH ₂ CH=CHCH ₂ O ₂	2.8×10^{-12}	2.0×10^{-12}	c
CH ₂ =CHCH(O ₂)CH ₂ OH	5.7×10^{-12}	2.9×10^{-12}	c
CH ₂ =CHCH(OH)CH ₂ O ₂	4.8×10^{-12}	2.7×10^{-12}	d
HOCH ₂ C(CH ₃)=CHCH ₂ O ₂	2.8×10^{-12}	2.0×10^{-12}	c, e
CH ₂ =CHC(CH ₃)(O ₂)CH ₂ OH	6.9×10^{-14}	8.0×10^{-13}	c, f, g
HOCH ₂ CH=C(CH ₃)CH ₂ O ₂	3.9×10^{-12}	2.4×10^{-12}	c, h
CH ₂ =C(CH ₃)CH(O ₂)CH ₂ OH	4.8×10^{-12}	2.9×10^{-12}	d

Notes:

^a self reaction rate coefficients at 298 K;

^b $k_{17} = 2\sqrt{(k_{15} \cdot k_{\text{CH}_3\text{O}_2} + k_{\text{CH}_3\text{O}_2})}$, unless otherwise stated;

^c based on rate coefficient reported by Jenkin et al. (1998);

^d based on k_{15} for HOC(CH₃)₂CH₂O₂ reported by Boyd et al. (1996);

^e based of k_{15} for HOCH₂CH=CHCH₂O₂;

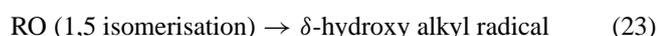
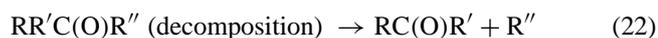
^f based on k_{15} for CH₂=C(CH₃)C(CH₃)(O₂)CH₂OH;

^g $k_{17} = 5\sqrt{(k_{15} \cdot k_{\text{CH}_3\text{O}_2} + k_{\text{CH}_3\text{O}_2})}$; elevated scaling factor is based on observation of Jenkin et al. (1998) for complex tertiary RO₂ cross reactions;

^h based of k_{15} for HOCH₂C(CH₃)=C(CH₃)CH₂O₂

4.8 Reactions of oxy radical intermediates

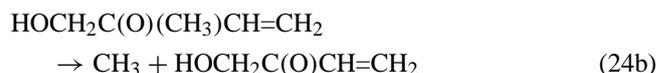
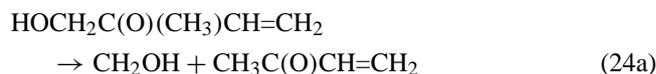
The behaviour of the oxy radicals, RO, under conditions relevant to the present work, is generally dominated by three modes of reaction, namely reaction with O₂, thermal decomposition and isomerisation by a 1,5 H atom shift:



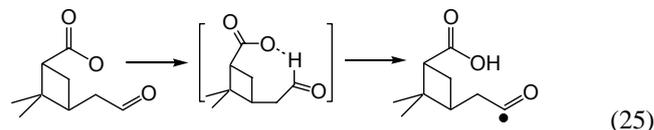
Available experimental information for alkoxy and β -hydroxyalkoxy radicals (which have particular relevance to VOC degradation) has been reviewed by Atkinson (1997b), and experimental studies for a number other classes of substituted oxy radical have been reported. In the absence of such data, the fates of oxy radicals in the MCM are generally defined by analogy, as described previously (Jenkin et al., 1997) and updated below.

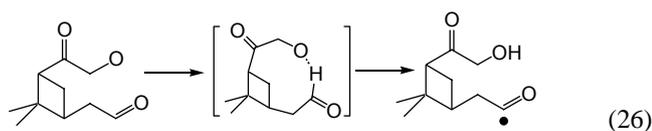
Atkinson (1997b) described an approach for estimating rate coefficients for atmospheric reactions of alkoxy and β -hydroxyalkoxy radicals. The expressions recommended for the reactions of primary and secondary alkoxy radicals with O₂ (reaction type 21) are used as generic rate coefficients for all oxy radical types in MCM v3. The methodology for estimating decomposition and isomerisation rate coefficients has been applied to reactions of RO radicals generated in the MCM v3 degradation schemes for alkanes, alkenes and alcohols.

A series of alternative rules for oxy radicals containing certain functional groups was described in detail in the previous protocol (Jenkin et al., 1997), and the treatment of these RO radicals remains virtually unchanged. In the specific cases of three structurally complex RO radicals generated from the degradation of isoprene, α -pinene and β -pinene, additional reaction channels are included in competition with those defined by the previous rules. On the basis of observations of the formation of hydroxymethyl vinyl ketone (Yu et al., 1995), and of CH₃OH and CH₃OOH (Ruppert and Becker, 2000) from the OH-initiated oxidation of isoprene, a second decomposition channel (24b) is included for the tertiary oxy radical, HOCH₂C(O)(CH₃)CH=CH₂, in which CH₃ is eliminated:



with a branching ratio, $k_{24b}/(k_{24a} + k_{24b}) = 0.25$. In the α - and β -pinene schemes, the following isomerisation reactions are included in competition with alternative decomposition routes:





These reactions were included to allow the formation of the identified products pinic acid from α - and β -pinene degradation and 10-hydroxypinonic acid from α -pinene degradation (e.g. Christoffersen et al., 1998; Hoffmann et al., 1998; Jang and Kamens, 1999; Glasius et al., 2000), as described by Jenkin et al. (2000). Reaction (25) for the complex acyl-oxy radical is assigned a probability of 80%, with the remaining 20% decomposing to eliminate CO_2 and an organic radical (in accordance with the reaction assumed for acyl-oxy radicals in general). Reaction (26) for the complex α -carbonyl oxy radical is assigned a probability of 20%, with the remaining 80% decomposing to generate HCHO and an acyl radical (in accordance with the reaction assumed for α -carbonyl oxy radicals in general).

4.9 Reactions of degradation products

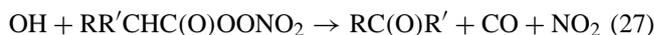
The degradation of VOC by the reactions summarised in the preceding subsections, and the previous protocol (Jenkin et al., 1997), leads to a wide variety of ‘first generation’ oxygenated products of varying complexity, which are themselves further degraded in the MCM. These products are a variety of carbonyl compounds, organic nitrates (RONO_2), acyl peroxy nitrates (RC(O)OONO_2), hydroperoxides (ROOH), percarboxylic acids (RC(O)OOH), carboxylic acids (RC(O)OH), alcohols (ROH), and multifunctional compounds containing two or more of these functionalities. Some of the product carbonyls, carboxylic acids and alcohols have significant tropospheric emissions and are necessarily treated as primary VOC by the procedures outlined in Sects. 4.1 – 4.8, and the previous protocol (Jenkin et al., 1997). The rigorous treatment of the other products would also require these procedures to be applied. However, as indicated in Sect. 3, this would lead to chemical schemes of unrealistic complexity, since the degradation of minor products is often disproportionately complex.

As described in detail previously (Jenkin et al., 1997), the further degradation of first and subsequent generation products in the MCM is simplified in comparison with the parent VOC, so that a limit can be placed on the size of the degradation scheme. The carbonyl compounds formed from the NO_x catalysed chemistry (i.e. resulting from the reactions of RO_2 with NO) are the major products under most conditions. These species are therefore degraded following the above general procedure, but with some degree of simplification achieved by limiting the number of product channels resulting from the attack of OH. The organic nitrates, acyl peroxy nitrates, hydroperoxides, percarboxylic acids, carboxylic acids and alcohols are regarded as minor products, and the chemistry of their degradation is therefore significantly simplified. This simplified chemistry aims to give the correct

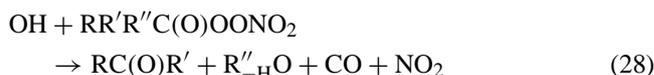
lifetimes of the products, to maintain the carbon and nitrogen balance and to represent radical propagation and termination processes adequately. As a result some of the reactions are unbalanced in terms of hydrogen and oxygen, usually because the production of O_2 or H_2O has not been included in the representation of the simplified or composite reaction.

The methodology applied to degradation of these products is largely unchanged from that described in the previous protocol (which should be consulted for full details), although changes to parameters consistent with those described in Sects. 4.1 to 4.8 have been made, where appropriate. However, some changes have been made to the treatment of the reactions of OH with acyl peroxy nitrates and hydroperoxides in MCM v3.

In the absence of mechanistic information on the reactions of OH with acyl peroxy nitrates, these reactions are currently assumed to release NO_x by the following generic mechanism for primary and secondary species,



and for tertiary species:



In the majority of cases, kinetic data are unavailable for this class of reaction, and overall rate coefficients are estimated using SAR methods (see Sect. 4.1). For this purpose, a neighbouring group activation parameter of 0.3 is currently assigned to ‘ $-\text{C(O)OONO}_2$ ’, which leads to an estimated parameter for the reaction involving $\text{CH}_3\text{C(O)OONO}_2$ (PAN) which is consistent with the recommended upper limit value of Sander et al. (2000).

The representation of the reactions of OH with hydroperoxides remains unchanged from that described previously (Jenkin et al., 1997). However, the neighbouring group activation parameter used for ‘ $-\text{OOH}$ ’, for the purposes of rate parameter estimation using SAR methods, has been reduced to 8.4. This parameter thus accounts for the substantial activating influence implied by the comparison of the reactivity of the CH_3- group in CH_3OOH (Atkinson et al., 1999) with the reference reactivity of the CH_3- group applied in the SAR method of Kwok and Atkinson (1995) and Atkinson (2000b), but also allows for the fact that the same procedure applied to CH_3OH alone generates an activation parameter for ‘ $-\text{OH}$ ’ which is greater by a factor of ca. 1.7, than that derived from a larger database of reactions involving alcohols.

5 Mechanism testing and validation

The MCM construction methodology relies on knowledge of the kinetics and products of elementary reactions relevant to VOC oxidation to build up a near-explicit representation of

the degradation chemistry. Unlike other mechanisms used in ozone policy models (e.g. Carbon Bond IV: Simonaitis et al., 1997), it is not primarily developed in conjunction with environmental chamber datasets, and does not therefore have the associated in-built validation. As a result, testing of the MCM has generally been achieved through its application in simulations of the atmospheric boundary layer, either by intercomparison with the results of chamber-validated mechanisms (e.g. Derwent et al., 1998), or through its ability to reproduce speciated distributions of organic products and radicals observed in the field (e.g. Jenkin, 2001). No extensive testing using environmental chamber data has been carried out, although the use of the MCM in a number of ongoing projects involving the European Photoreactor (EUPHORE) in Valencia (EUPHORE, 2002) is providing the basis for validation of selected VOC within the mechanism. In this section examples of testing MCM v3 chemistry are presented, using both reported data for isoprene oxidation products observed in the field, and chamber data from EUPHORE for the photo-oxidation of α -pinene/NO_x mixtures.

5.1 Isoprene oxidation products

5.1.1 Introduction

The degradation of isoprene leads to the generation of a series of carbonyl compounds as major first generation products (Tuazon and Atkinson, 1990; Paulson et al., 1992; Miyoshi et al., 1994; Kwok et al., 1995; Ruppert and Becker, 2000). These include formaldehyde (HCHO), the C₄ unsaturated carbonyls methacrolein (MACR, CH₂=C(CH₃)CHO) and methyl vinyl ketone (MVK, CH₃C(O)CH=CH₂), and the isomeric C₅ unsaturated hydroxy aldehydes, HOCH₂C(CH₃)=CHCHO and HOCH₂CH=C(CH₃)CHO. As represented in MCM v3, the further degradation of the C₄ and C₅ compounds leads ultimately to the generation of CO and CO₂ via intermediate products such as methyl glyoxal (CH₃C(O)CHO), glycolaldehyde (HOCH₂CHO) and glyoxal (CH(O)CHO). During the 1992 and 1995 US Southern Oxidants Studies, many of these products were identified in the field at locations where isoprene was believed to represent the dominant local primary hydrocarbon emission (e.g. Lee et al., 1995, 1998). Another important isoprene degradation product is PAN, which is generated because the precursor acetyl radical is eliminated from many of the intermediate products (e.g. methyl glyoxal) during their breakdown. In addition, the degradation of the aldehydic products leads to the probable formation of other PAN-type compounds in lower yields. Of these, peroxy methacryloyl nitrate (MPAN: CH₂=C(CH₃)C(O)O₂NO₂), formed from methacrolein, has received the most attention and has been detected commonly in field studies (e.g. Bertman and Roberts, 1991; Williams et al., 1997). MPAN is believed to provide a unique marker for isoprene chemistry.

5.1.2 Methodology

A boundary layer box model has been used to test the MCM v3 isoprene scheme against field observations of PAN, MPAN, methyl glyoxal, glyoxal, glycolaldehyde and formaldehyde. The model is designed to represent a well-mixed boundary layer of 1000 m depth which receives emissions of isoprene and NO_x, and includes a background concentration of 1.8 ppmv methane. The boundary layer air parcel is continuously exchanged with the free troposphere on a timescale of 3 days, thus representing a loss process for long-lived products. The free troposphere is assumed to contain the following trace species which are mixed into the boundary layer on the same timescale: NO_x (100 pptv), O₃ (30 ppbv), H₂ (500 ppbv), CO (100 ppbv), HCHO (200 pptv). The model includes a full diurnal photolysis code, and is initialised for 10 days such that exchange processes reach steady state.

The applied conditions are intended to be representative of the 1995 Southern Oxidants Study (Latitude 36° N, 10 July), as reported by Williams et al. (1997) and Lee et al. (1998). The isoprene emission rate was varied to allow for diurnal variation in light intensity and temperature, with a diurnal average isoprene emission rate of 3×10^{15} molecule m⁻² s⁻¹ (i.e. in the middle of the reported range). NO_x emission rates over a range of two orders of magnitude were considered ($10^{14} - 10^{16}$ molecule m⁻²). This led to diurnally-averaged NO_x concentrations which varied approximately proportionately with emission rate, leading to values lying in the approximate range 0.1–7 ppbv. The level of NO_x typically observed in the 1995 Southern Oxidants Study was of the order of 1 ppbv (Lee et al., 1998), and therefore towards the centre of the simulated range.

5.1.3 Results and discussion

The simulated concentrations of isoprene and the series of oxygenated products were determined for a series of NO_x emissions rates in the range stated above. At an emissions rate of 10^{15} molecule m⁻² (corresponding to ca. 1 ppbv NO_x), simulated diurnally-averaged concentrations were found to be 0.36 ppbv isoprene, 0.81 ppbv glycolaldehyde, 0.17 ppbv glyoxal, 0.35 ppbv methylglyoxal, 4.5 ppbv formaldehyde, 1.6 ppbv PAN and 0.15 ppbv MPAN. These levels are close to the means of the values reported by Lee et al. (1998) and Williams et al. (1997) for the entire 1995 campaign, demonstrating that the model provides an acceptable representation. The corresponding product ratios were also found to be in good agreement with those reported, as shown in Table 4. These results clearly indicate that the near-explicit representation of isoprene degradation in MCM v3, based on the protocol described above, provides an acceptable description of the speciated product distribution observed in the reported field studies of Lee et al. (1995, 1998) and Williams et al. (1997).

Table 4. Ratios of concentrations of isoprene degradation products observed in the field, and calculated using a boundary layer box model with MCM v3 (see text)

Ratio	Observed	Calculated (MCM v3) ^d
[glycolaldehyde]/[HCHO]	0.23 ^a 0.23 ^b	0.18
[methyl glyoxal]/[HCHO]	0.067 ^a 0.067 ^b	0.078
[glyoxal]/[methyl glyoxal]	0.70 ^a 0.29 ^b	0.48
[PAN]/[MPAN]	10.4 ^c	10.5

^a Lee et al. (1995);

^b Lee et al. (1998);

^c Williams et al. (1997);

^d Modelling studies indicate variations of ratios with conditions. Displayed values are based on diurnally averaged concentrations for conditions closely resembling the mean conditions of the reported field studies (see discussion in text).

The simulated product ratios were found to vary with level of NO_x. This arises because the mechanism of the OH-initiated chemistry is NO_x-dependent, and also because the ozone-initiated chemistry makes a contribution at the low end of the NO_x range, when the simulated levels of OH are substantially lower. It is well established that the yield ratio of the primary products MACR/MVK is greater from the ozone initiated chemistry than from the OH-initiated chemistry (Grosjean et al., 1993; Aschmann and Atkinson, 1994), and also that the MACR/MVK ratio increases at low NO_x during OH-initiated oxidation (Jenkin et al., 1998; Ruppert and Becker, 2000). Because MPAN is derived exclusively from MACR, this has a particular influence on the simulated PAN/MPAN ratio, which was found to vary from 7.8 at the low end of the NO_x range to 11.8 close to the high end of the range.

5.2 Photo-oxidation of α -pinene

5.2.1 Introduction

Experiments to investigate the photo-oxidation of mixtures of α -pinene and NO_x in air have been carried out in EUPHORE, as part of the EU project 'Origin and Formation of Secondary Organic Aerosol, OSOA'. The time evolution of α -pinene, NO, NO₂ and ozone, measured during the course of three experiments, is shown in Figs. 3–5. The profiles are typical of the general pattern observed in photo-oxidation experiments (e.g. Carter et al., 1995). The oxidation of the hydrocarbon is catalysed by the presence of free radicals, with the chemistry also leading to the simultaneous oxidation of NO to NO₂, and therefore generation of ozone. Free rad-

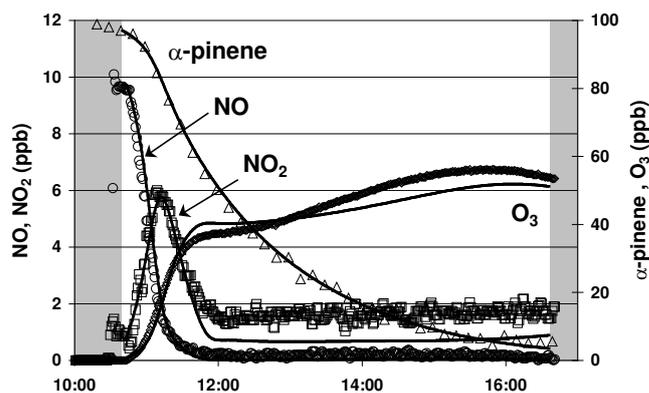


Fig. 3. Comparison of observed time dependences of α -pinene, NO, NO₂ and O₃ in a photo-oxidation experiment in EUPHORE on 27 September 2000 (symbols), and those simulated using MCM v3 (lines). Unshaded area indicates when chamber was open to sunlight. Reagent concentrations at start of photo-oxidation: α -pinene = 97.0 ppb; NO = 9.7 ppbv; NO₂ = 0.85 ppbv. Experimental data kindly supplied by the collaborating partners in the EU OSOA project.

icals may be generated as a result of the photodissociation of stable molecules (e.g. carbonyl compounds). However, in the case of α -pinene (and other reactive alkenes/terpenes), the reaction with ozone also represents an important source of free radicals. Under the conditions of the chamber experiments, the chemistry is then driven predominantly by oxidation initiated by reaction with the OH radical, and α -pinene is oxidised to carbonyl (and other) products, which may then photolyse to generate further free radicals. Consequently, after an induction period, the chemistry accelerates and the removal of α -pinene and the production rate of NO₂ increase. Although the observed behaviour is understood qualitatively, the precise time dependence provides a stringent test for mechanisms designed to represent degradation chemistry in the boundary layer. The MCM v3 α -pinene scheme, embedded in a box model, has therefore been used to simulate the time dependence of α -pinene, NO, NO₂ and ozone for the conditions of the experiments shown in Figs. 3–5.

5.2.2 Methodology

The box model is based on that used previously for simulations of EUPHORE experiments by Hayman et al. (1998). Photolysis rate coefficients were calculated for all reference reactions, J₁ – J₅₇ (Table 2), by the method described in Sect. 4.4 for the location of EUPHORE and the appropriate day of the year. Photolysis rates for NO₂ and HCHO were determined experimentally from in situ solar radiometer measurements, and these values were applied accordingly in the simulations. In all other cases, the calculated photolysis rates were scaled by the factor J₄(observed)/J₄(calculated), where J₄ is the photolysis rate of NO₂. In addition to the

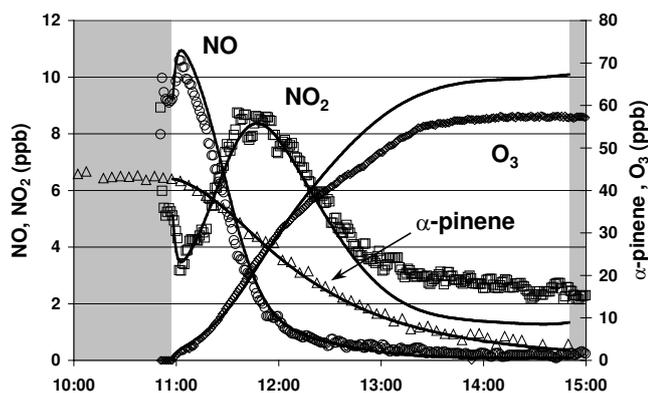


Fig. 4. Comparison of observed time dependences of α -pinene, NO, NO₂ and O₃ in a photo-oxidation experiment in EUPHORE on 26 September 2000 (symbols), and those simulated using MCM v3 (lines). Unshaded area indicates when chamber was open to sunlight. Reagent concentrations at start of photo-oxidation: α -pinene = 42.7 ppb; NO = 9.2 ppbv; NO₂ = 5.1 ppbv. Experimental data kindly supplied by the collaborating partners in the EU OSOA project.

MCM v3 α -pinene chemistry, a chamber-dependent auxiliary mechanism was also included, providing a description of background radical and NO_x sources based on independent experiments (e.g., Hayman et al., 1998). Simulations were performed for the conditions of the three α -pinene/NO_x photo-oxidation experiments (Figs. 3–5), with temperature and relative humidity constrained to measured values.

5.2.3 Results and discussion

The comparisons in Figs. 3–5 indicate that the near-explicit representation of α -pinene degradation in MCM v3, based on the protocol described above, provides an acceptable description of the time dependences of the key gas phase species under the conditions of the EUPHORE photo-oxidation experiments. In each case, the mechanism provides a precise description of the observations for the first hour of the experiment. At longer times, the observed levels of NO₂ lie consistently higher than those simulated, although the time dependences of the other species remain in adequate agreement. However, the NO_x measurements in these experiments were made using a chemiluminescence analyser (with measurement of NO₂ by photolytic conversion to NO), such that contributions to the apparent NO₂ signal from other oxidised nitrogen species (e.g. HONO, oxidised organic nitrogen compounds) are likely in the latter stages of the experiment.

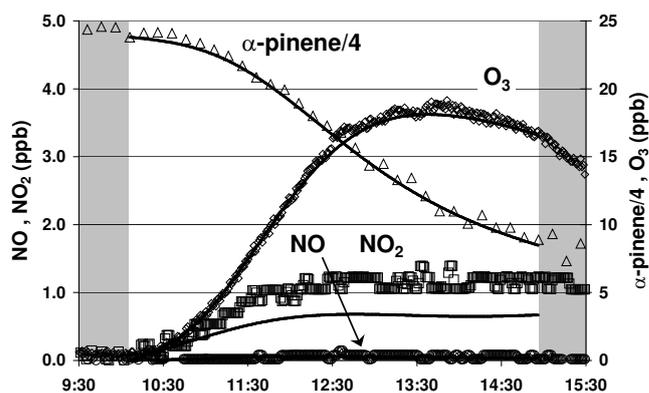


Fig. 5. Comparison of observed time dependences of α -pinene, NO, NO₂ and O₃ in a photo-oxidation experiment in EUPHORE on 28 September 2000 (symbols), and those simulated using MCM v3 (lines). Unshaded area indicates when chamber was open to sunlight. Reagent concentrations at start of photo-oxidation: α -pinene = 95.2 ppb; HCHO = 882 ppbv (not shown); background NO_x (ca. 0.5 ppb h⁻¹). Experimental data kindly supplied by the collaborating partners in the EU OSOA project.

6 Photochemical Ozone Creation Potentials (POCP)

6.1 Introduction

It is well documented that the contributions of VOC to ozone formation can vary from one compound to another by virtue of differences in their reactivity and structure, since these factors influence the rate of oxidation and the degradation mechanism. This has led to the development of scales of so called ‘reactivity’ or ‘ozone formation potential’ for VOC (e.g. Carter, 1994; Derwent et al., 1998). The Photochemical Ozone Creation Potential (POCP) scale was initially developed to describe the relative contributions of VOC to ozone formation of a regional scale over north-west Europe (Derwent and Jenkin, 1991), and previous versions of the MCM have been applied to calculation of POCP values (Derwent et al., 1998; Jenkin and Hayman, 1999).

6.2 Method of calculation

POCP values are calculated using a Photochemical Trajectory Model (PTM), which has been widely applied to the simulation of photochemical ozone formation in north-west Europe (e.g. Derwent et al., 1996, 1998). The PTM simulates the chemical development in a boundary layer air parcel travelling along pre-selected trajectories over Europe. The air parcel thus picks up emissions of NO_x, CO, SO₂, methane, non-methane VOC and biogenic isoprene (based on available inventories), which are processed using an appropriate description of the chemical and photochemical transformations leading to ozone formation. As described in detail previously (Derwent et al., 1996), diurnal variations in atmospheric boundary layer depth, windspeeds, temperatures

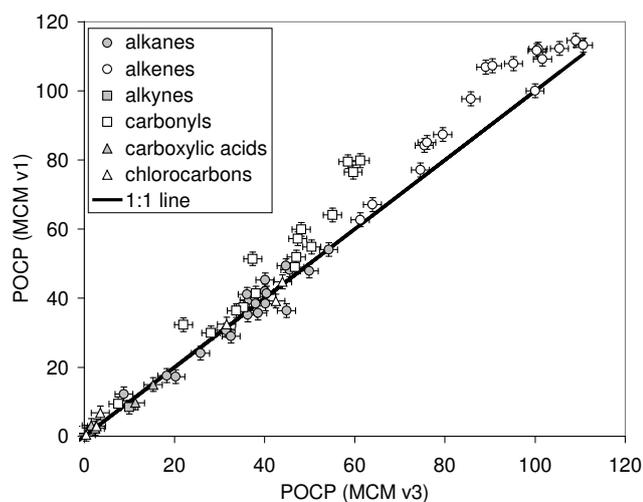


Fig. 6. Comparison of POCP values calculated for alkanes, alkenes, alkynes, carbonyls, carboxylic acids and chlorocarbons/hydrochlorocarbons using MCM v3, and those reported previously using MCM v1 (Derwent et al., 1998).

and humidities are represented as climatological means over a number of photochemical episodes.

POCP values were determined from the calculated formation of ozone over a period of almost five days along an idealised linear trajectory. The boundary layer air parcel was followed from its release point in Austria with subsequent passage over Germany and Belgium prior to arriving in the southern UK on the fifth day. This trajectory describes a highly idealised anticyclonic meteorological situation of easterly winds, leading to a broad air flow carrying photochemically-aged polluted air masses out of mainland Europe towards the UK, and is broadly representative of trajectory paths which are frequently associated with elevated ozone concentrations in the southern UK (Jenkin et al., 2002). The production of ozone on this (and similar) trajectories has previously been shown to display some sensitivity to the availability of VOC (Derwent et al., 1998; Jenkin et al., 2002). Consequently, the chosen trajectory is appropriate for the definition of a comparative ozone formation index for VOC.

The POCP for a particular VOC is determined by quantifying the effect of a small incremental increase in its emission on ozone formation along the trajectory, relative to that resulting from an identical increase in the emission (on a mass basis) of a reference VOC, which is taken to be ethene. Thus, the POCP for the given VOC ‘*i*’ is defined by Eq. (v),

$$\text{POCP}_i = \frac{\text{ozone increment with the } i\text{th VOC}}{\text{ozone increment with ethene}} \times 100 \quad (\text{v})$$

with the value for ethene being 100 by definition. The POCP is calculated from the results of separate model experiments. A base case scenario is initially run, followed by model runs

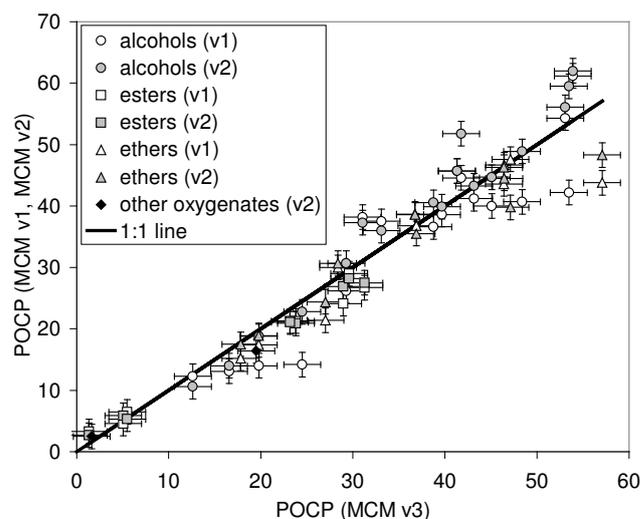


Fig. 7. Comparison of POCP values calculated for alcohols/glycols, esters, ethers/glycoethers and other oxygenates using MCM v3, and those reported previously using MCM v1 (Derwent et al., 1998) and/or MCM v2 (Jenkin and Hayman, 1999).

in which the emission term of the selected VOC and of ethene are, in turn, incremented by ca. $1 \text{ kg km}^{-2} \text{ day}^{-1}$ across the entire model domain. The extra VOC emission stimulates additional ozone formation over the base case, and this incremental quantity of ozone can be defined for a particular point along the trajectory or integrated over the entire trajectory length. POCP values published previously using MCM v1 (Derwent et al., 1998) and MCM v2 (Jenkin and Hayman, 1999), and those reported below and in the companion paper (Jenkin et al., 2003), are based on the integrated incremental ozone formation.

6.3 Results and discussion

POCP values were calculated for all 124 non-methane VOC using MCM v3. The results for the 18 aromatic VOC are presented and discussed in the companion paper (Jenkin et al., 2003). The POCP values calculated for the 106 non-aromatic, non-methane VOC are presented in Table 5. Where possible, the values are compared with those calculated with MCM v1 and MCM v2 in Figs. 6 and 7. The comparison indicates the same general trend in POCP values calculated with MCM v3, such that overall conclusions concerning the comparative ozone formation propensities of the various non-aromatic VOC classes are unchanged from those discussed in previous publications (e.g. Derwent et al., 1998). Figure 6 shows some modest differences between POCP values calculated with MCM v1 and MCM v3. The largest percentage discrepancies are observed for the carbonyl compounds, in particular the longer chain aldehydes and some ketones. This results from the thermal decomposition rate of peroxyacyl nitrates being updated subse-

Table 5. Photochemical Ozone Creation Potentials (POCP) calculated for 106 non-aromatic, non-methane VOC in MCM v3 ^a

VOC	POCP	VOC	POCP	VOC	POCP
alkanes		α -pinene	57.5	ethan-1,2-diol	31.0
ethane	8.8	β -pinene	62.1	propan-1,2-diol	41.3
propane	18.3	buta-1,3-diene	76.0	4-hydroxy-4-methylpentan-2-one	29.3
butane	36.3	2-methylbuta-1,3-diene(isoprene)	101.6	ethers / glycoethers	
2-methylpropane	31.4	alkynes		dimethyl ether	19.8
pentane	36.6	ethyne	9.9	diethyl ether	46.4
2-methylbutane	37.7	aldehydes		methyl-t-butyl ether	17.8
2,2-dimethylpropane	20.3	methanal (formaldehyde)	47.1	di-i-propyl ether	47.1
hexane	45.6	ethanal (acetaldehyde)	55.0	ethyl-t-butyl ether	27.0
2-methylpentane	40.0	propanal	61.2	2-methoxyethanol	28.4
3-methylpentane	49.9	butanal	58.5	2-ethoxyethanol	36.8
2,2-dimethylbutane	25.8	2-methylpropanal	37.4	1-methoxypropan-2-ol	36.9
2,3-dimethylbutane	54.2	pentanal	59.7	2-butoxyethanol	57.1
cyclohexane	32.5	ketones		1-butoxypropan-2-ol	46.4
heptane	44.8	propanone (acetone)	7.5	esters	
2-methylhexane	36.1	butanone (methyl ethyl ketone)	35.3	methyl formate	1.3
3-methylhexane	44.9	pentan-2-one	50.4	methyl acetate	5.1
octane	40.1	pentan-3-one	38.0	ethyl acetate	23.8
nonane	40.4	3-methylbutan-2-one	33.7	n-propyl acetate	29.6
decane	40.2	hexan-2-one	47.4	i-propyl acetate	23.2
undecane	38.0	hexan-3-one	48.1	n-butyl acetate	28.9
dodecane	38.5	4-methylpentan-2-one	46.7	s-butyl acetate	31.3
alkenes / dienes		3,3-dimethylbutan-2-one	22.0	t-butyl acetate	5.5
ethene	100.0	cyclohexanone	28.1	carboxylic acids	
propene	105.4	alcohols / glycols		formic acid	1.5
but-1-ene	95.2	methanol	16.5	acetic acid	11.3
cis-but-2-ene	109.1	ethanol	39.7	propanoic acid	15.3
trans-but-2-ene	110.7	propan-1-ol	53.1	other oxygenates	
2-methylpropene	61.2	propan-2-ol	19.8	dimethoxymethane	19.5
cis-pent-2-ene	100.7	butan-1-ol	53.9	dimethoxycarbonate	1.6
trans-pent-2-ene	100.4	butan-2-ol	45.1	chloro- / hydrochlorocarbons	
pent-1-ene	85.7	2-methylpropan-1-ol	33.1	trichloromethane	2.4
2-methylbut-1-ene	74.6	2-methylpropan-2-ol	12.6	dichloromethane	3.5
3-methylbut-1-ene	63.9	pentan-3-ol	53.5	1,1,1-trichloroethane	-1.6
2-methylbut-2-ene	75.4	2-methylbutan-1-ol	48.4	tetrachloroethene	2.7
hex-1-ene	79.5	3-methylbutan-1-ol	43.2	trichloroethene	31.6
cis-hex-2-ene	89.0	2-methylbutan-2-ol	24.5	chloromethane	0.4
trans-hex-2-ene	90.6	3-methylbutan-2-ol	38.7	cis-1,2-dichloroethene	44.0
2,3-dimethylbut-2-ene	56.4	cyclohexanol	41.8	trans-1,2-dichloroethene	42.5

Notes

^a POCP values are quoted to one decimal place, not as an indication of inherent precision, but to facilitate comparisons. The precision in an individual POCP value is estimated to be ± 2 POCP units.

quently to MCM v1, such that these species are more stable in MCM v3. Since peroxyacyl nitrates are formed in the primary oxidation step from the OH-initiated oxidation of aldehydes $\geq C_2$ (and to a lesser extent from ketone photolysis), this has a resultant increased inhibiting influence on ozone formation in MCM v3, through the increased sequestering of free radicals and NO_x in an inactive form. As a result, POCP values for longer chain carbonyl compounds

are now up to 25% lower than previously reported (Derwent et al., 1998). Those for small carbonyls (e.g. formaldehyde) remain almost unchanged. The POCP values calculated for some larger alkenes in MCM v3 are also notably lower than those calculated with MCM v1 by virtue of updates in the chemistry for β -hydroxyalkoxy radicals, and the influence this has on the carbonyl product distribution. Despite this, however, alkenes remain the class of non-aromatic VOC with

the greatest propensity to form ozone.

Figure 7 shows the results for several oxygenated VOC classes where POCP data have previously been published with both MCM v1 and MCM v2. For the most part, the POCP values calculated with MCM v3 are similar to those calculated with MCM v2. Notable differences between the values for alcohols and some ethers, calculated with MCM v1, and those calculated with the later mechanisms result from a previous significant revision to the treatment of these compounds, as described by Jenkin and Hayman (1999). However there are also some modest differences in the values calculated for alcohols with MCM v2 and MCM v3, which result from updates in the chemistry for β -hydroxyalkoxy radicals, as also indicated above for the alkenes.

POCP values have not previously been reported for the monoterpenes, α - and β -pinene, and for the branched alkene, 2,3-dimethyl-2-butene. The values for all three VOC calculated with MCM v3 are comparable (57.5, 62.1 and 56.4, respectively), and lie at the low end of the range of POCP values calculated for alkenes. The values are therefore comparatively high by virtue of all these VOC being very reactive, but are substantially lower than those for smaller reactive alkenes (e.g. the 2-butene isomers have $\text{POCP} \approx 110$) because of significant generation of acetone and organic nitrates during the degradation. Acetone is very unreactive, and previous work has shown that its formation significantly inhibits the ability of the precursor VOC to generate ozone on the timescale of the trajectory calculation (Jenkin and Hayman, 1999). Organic nitrates also appear to have a notable influence on calculated POCP values, since they can act as comparatively unreactive reservoirs for free radicals and NO_x .

7 Conclusions

The mechanism construction protocol described above in Sect. 4 has allowed consistent degradation schemes to be defined for 107 non-aromatic compounds as part of MCM v3. The methodology is based on reported information on elementary reactions, and aims to take account of work which was in the public domain at the beginning of 2001. Although the performance of the mechanism has not been extensively tested and validated, the degradation schemes for two of the most structurally complex species considered (isoprene and α -pinene) provide acceptable descriptions of available field and chamber data. Since this requires not only a reasonable representation of chemistry of the parent hydrocarbons, but also of a variety of complex and simple oxygenated products formed during the degradation, this allows some confidence to be placed in the general mechanism construction methodology.

As described in the companion paper (Jenkin et al., 2003), a main focus of ongoing MCM development work is the further improvement of the representation of the degradation of

aromatic VOC. However, attention is also being given to expanding the coverage of biogenic VOC to include additional terpenes and oxygenates, and a representation of gas-aerosol partitioning of the oxidised products of monoterpene degradation is being developed to assist interpretation of the formation of secondary organic aerosol observed in chamber studies (e.g. Hoffmann et al., 1997; BIOVOC, 1998; Yu et al., 1999; Jang and Kamens, 1999; Cocker et al., 2001).

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