



## THE TROPOSPHERIC DEGRADATION OF VOLATILE ORGANIC COMPOUNDS: A PROTOCOL FOR MECHANISM DEVELOPMENT

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**Abstract**—Kinetic and mechanistic data relevant to the tropospheric oxidation of volatile organic compounds (VOCs) are used to define a series of rules for the construction of detailed degradation schemes for use in numerical models. These rules are intended to apply to the treatment of a wide range of non-aromatic hydrocarbons and oxygenated and chlorinated VOCs, and are currently being used to provide an up-to-date mechanism describing the degradation of a range of VOCs, and the production of secondary oxidants, for use in a model of the boundary layer over Europe. The schemes constructed using this protocol are applicable, however, to a wide range of ambient conditions, and may be employed in models of urban, rural or remote tropospheric environments, or for the simulation of secondary pollutant formation for a range of  $\text{NO}_x$  or VOC emission scenarios. These schemes are believed to be particularly appropriate for comparative assessments of the formation of oxidants, such as ozone, from the degradation of organic compounds. The protocol is divided into a series of subsections dealing with initiation reactions, the reactions of the radical intermediates and the further degradation of first and subsequent generation products. The present work draws heavily on previous reviews and evaluations of data relevant to tropospheric chemistry. Where necessary, however, existing recommendations are adapted, or new rules are defined, to reflect recent improvements in the database, particularly with regard to the treatment of peroxy radical ( $\text{RO}_2$ ) reactions for which there have been major advances, even since comparatively recent reviews. The present protocol aims to take into consideration work available in the open literature up to the end of 1994, and some further studies known by the authors, which were under review at that time. A major disadvantage of explicit chemical mechanisms is the very large number of reactions potentially generated, if a series of rules is rigorously applied. The protocol aims to limit the number of reactions in a degradation scheme by applying a degree of strategic simplification, whilst maintaining the essential features of the chemistry. These simplification measures are described, and their influence is demonstrated and discussed. The resultant mechanisms are believed to provide a suitable starting point for the generation of reduced chemical mechanisms. Copyright © AEA Technology. Published by Elsevier Science Ltd

**Key word index:** VOC oxidation, tropospheric chemistry, secondary pollutants, oxidants, ozone, free radical reactions, mechanisms, modelling.

### 1. INTRODUCTION

It is well established that the degradation of volatile organic compounds (VOCs) in the troposphere leads to the production of a range of secondary pollutants which may have a harmful impact on human health and on the environment (Leighton, 1961; Finlayson-Pitts and Pitts, 1986; Wayne, 1991). The complete gas-phase oxidation of VOCs 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, for example as carcinogens or mutagens (PORG, 1993). Furthermore, certain oxidised organic products, particularly those produced from larger or more complex VOCs, are sufficiently involatile to promote aerosol formation and growth (e.g. Finlayson-Pitts and Pitts, 1986; Grosjean and Seinfeld, 1989; Pandis *et al.*, 1992). 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, vegetation and materials, it

is a greenhouse gas, and it promotes the oxidation of trace gases both directly, and as a free radical precursor (e.g. WMO, 1986; PORG, 1993; IPCC, 1995).

The relative contributions of VOCs to the formation of specific secondary pollutants vary from one compound to another by virtue of differences in reactivity and structure, since these factors influence the rate of oxidation and the precise oxidation pathway (i.e. the degradation mechanism). Some published studies which have ranked VOCs by their ability to generate ozone have therefore involved the use of trajectory models of the planetary boundary layer, incorporating detailed chemical schemes describing the degradation of the range of organic compounds considered (Derwent and Jenkin, 1991; Andersson-Skold *et al.*, 1992; Derwent *et al.*, 1996). The production of certain oxidised organic products is often even more sensitive to the structure of the parent compound, and therefore the ability of a chemical scheme to represent accurately the production of secondary pollutants depends strongly on the assumptions made in defining the scheme.

In recent years, the availability of kinetic and mechanistic data relevant to the oxidation of VOCs has increased significantly, and various aspects of the tropospheric chemistry of organic compounds have been reviewed extensively (e.g. Atkinson, 1990, 1994; Roberts, 1990; Wayne *et al.*, 1991; Lightfoot *et al.*, 1992). In this paper, the available information is used to define a series of rules which can be used to construct detailed degradation schemes for a range of organic compounds, for use in numerical models. These rules are intended to apply to the treatment of many hydrocarbons and oxygenated and chlorinated VOCs, with the notable exception of aromatic species, for which there are still major uncertainties in our understanding of the detailed chemistry. The compounds which are currently being addressed using this protocol (listed in the Appendix) were taken mainly from the U.K. speciated emissions inventories (PORG, 1993; Rudd, 1995). The original objective of this work was the provision of an up-to-date mechanism which could be used to describe the degradation of a range of VOCs, and the production of secondary photochemical pollutants in the boundary layer over the U.K. and continental Europe, and a preliminary version of the mechanism has recently been assembled (Jenkin *et al.*, 1996). The present work draws heavily on previous reviews and evaluations, in particular the numerous, excellent publications of Atkinson and co-workers (e.g. Carter and Atkinson, 1985; Atkinson, 1990, 1991, 1994; Atkinson and Carter, 1991). Where necessary, existing recommendations are adapted, or new rules are defined, to reflect recent improvements in the database, particularly with regard to the treatment of peroxy radical ( $\text{RO}_2$ ) reactions for which there have been major advances, even since the comparatively recent reviews of Lightfoot *et al.* (1992) and Wallington *et al.* (1992). The present protocol aims to take into consideration work

available in the open literature up to the end of 1994, and some further studies known by the authors, which were under review at that time.

The major disadvantage of explicit chemical mechanisms is the very large number of reactions potentially generated, if a series of rules is rigorously applied. A practical protocol for mechanism development must therefore aim to limit the number of reactions in a degradation scheme, whilst maintaining the essential features of the chemistry and minimising significant *a priori* assumptions. In the present work, a degree of strategic simplification is applied which substantially reduces the total number of reactions describing the degradation of a given VOC. This is illustrated using the OH-initiated degradation of isoprene to first generation products as an example.

## 2. STRUCTURE AND METHODOLOGY

The protocol, outlined in Section 3, is designed to allow the construction of comprehensive and consistent degradation schemes for a range of VOCs. It is divided into ten subsections. In Sections 3.1–3.3, the initiation reactions of OH radicals with organic compounds are considered, and guidelines are established to indicate for which compounds  $\text{O}_3$  and  $\text{NO}_3$  initiated chemistry is also likely to be important, and should also be treated. Photolysis reactions, which are significant for some classes of VOCs, are identified in Section 3.4 and photolysis rates are assigned to a series of generic reactions. In Sections 3.5–3.9, the reactions of the reactive intermediates (organic radicals, peroxy radicals, Criegee biradicals, oxy radicals and chlorine atoms) generated as a result of the initiation chemistry are identified, and various generic parameters and criteria are summarised. In Section 3.10, the further degradation of first, and subsequent generation products is discussed.

As an example, the degradation chemistry of butane defined by the protocol is displayed schematically in Fig. 1. This illustrates some of the types of reaction of the peroxy ( $\text{RO}_2$ ) and oxy ( $\text{RO}$ ) radical intermediates which are considered, and also a range of carbonyl, hydroperoxide, carboxylic acid, percarboxylic acid, nitrate and peroxy nitrate products which are generated. The chemistry along a given degradation pathway is developed until butane is broken down into  $\text{CO}_2$ , CO or an organic product (or radical) which is treated independently. Thus, in the present case, the first generation carbonyl products, butanone ( $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ ) and n-butanal ( $n\text{-C}_4\text{H}_9\text{CHO}$ ), are degraded no further, as they are primary emitted compounds which are treated independently (see the Appendix). In contrast, the hydroxy aldehyde,  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO}$ , is further degraded via a second generation product,  $\text{HOCH}_2\text{CH}_2\text{CHO}$ , before yielding  $\text{CO}_2$  and the radicals, HCO and  $\text{HOCH}_2\text{CH}_2\text{O}_2$ , which are formed from the degradation of HCHO and  $\text{C}_2\text{H}_4$ , respectively, and therefore treated in the schemes for those compounds.



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 the structure-activity relationship (SAR) method devised by Atkinson (1987), and recently updated by Kwok and Atkinson (1995), for alkanes, carbonyls, alcohols, ethers and chlorinated hydrocarbons, and the method of Peeters *et al.* (1994) for alkenes and dienes.

**3.1.2. Initial radical products.** Where the relative importance of product channels for the 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 method (Atkinson, 1987; Peeters *et al.*, 1994).

In some cases, the chemistry is simplified by limiting the number of product channels. As a general rule, only a maximum of four product channels is considered. For comparatively small molecules for which  $\leq 4$  product channels exist, they may all be treated. If a channel represents  $< 5\%$  of the reaction, however, it is disregarded, and the remaining channels scaled proportionately to maintain the same overall rate coefficient. Where more than four channels exist, simplification is achieved as follows:

(a) For relatively small molecules ( $\leq C_6$ ), minor channels collectively representing up to 10% of the reaction are disregarded, and the importance of the remaining channels scaled proportionately to maintain the overall rate coefficient.

(b) For larger molecules, it is usual for many "minor" product channels to exist. In these cases, radical products possessing similarities in their subsequent degradation chemistry are represented by a single radical species (e.g. secondary alkyl radicals formed from long-chain hydrocarbons, for which the alkoxy radicals formed subsequently all have 1, 5 isomerisation as their dominant fate).

### 3.2. $O_3$ initiation reactions

$O_3$ -initiated degradation chemistry is included for those VOCs for which both the following relations apply:

$$k(O_3 + \text{VOC}) > 10^{-8} k(\text{OH} + \text{VOC})$$

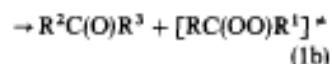
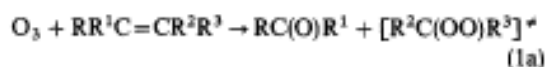
$$k(O_3 + \text{VOC}) > 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

These relations were formulated on the basis that typical ambient concentrations of OH and  $O_3$  in the boundary layer are  $10^6$  and  $10^{12}$  molecule  $\text{cm}^{-3}$ , respectively. Thus, the first criterion applies when the removal rate by reaction with  $O_3$  exceeds 1% of the removal rate by reaction with OH, and the second when the lifetime of the VOC with respect to reaction with  $O_3$  is less than  $10^3$  s (i.e. ca. 100 d).  $O_3$ -initiated degradation is expected to be important only for

alkenes, dienes and some unsaturated oxygenated products.

**3.2.1. Rates of initiation reactions.** Rate coefficients for the reactions of  $O_3$  with alkenes, dienes have been reviewed by Atkinson and Carter (1984) and recently by Atkinson (1994), 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 indicated in Table 1.

**3.2.2. Initial products.** The reaction mechanisms follow the general pattern described by Atkinson (1994), with addition of ozone to the double bond leading initially to the formation of an energy-rich ozonide. In the present work, this ozonide is assumed to decompose equally by the two possible channels, each forming a carbonyl compound and an energy-rich "Criegee" biradical:



In the case of the unsymmetric diene, isoprene (the only such compound considered in the present work), 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 recent studies (Grosjean *et al.*, 1993a; Aschmann and Atkinson, 1994).

### 3.3. $NO_3$ radical initiation reactions

$NO_3$ -initiated degradation chemistry is included for those VOCs for which both the following relations apply:

$$k(NO_3 + \text{VOC}) > 10^{-5} k(\text{OH} + \text{VOC})$$

$$k(NO_3 + \text{VOC}) > 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Table 1. Generic rate coefficients used for the reactions of  $O_3$  with alkenes

Generic alkene	$k(298)^a$	Comment
$CH_2=CHR$	1.0	b
$CH_2=CRR^1$	1.3	c
$CHR=CHR^1$	16.0	d
$CHR=CR^1R^2$	40.0	e
$CRR^1=CR^2R^3$	110.0	f

<sup>a</sup> Units  $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; <sup>b</sup> the mean of recommended values for propene, 1-butene, 1-pentene and 1-hexene (Atkinson, 1994); <sup>c</sup> the mean of recommended values for methyl propene and  $\beta$ -pinene (Atkinson, 1994); <sup>d</sup> the mean of recommended values for *cis*- and *trans*-2-butene (Atkinson, 1994); <sup>e</sup> based on 2-methyl 2-butene (Atkinson, 1994); <sup>f</sup> based on 2,3-dimethyl 2-butene (Atkinson, 1994).

These relations were formulated on the basis that typical boundary layer concentrations of OH and NO<sub>3</sub> are 10<sup>6</sup> and 10<sup>9</sup> molecule cm<sup>-3</sup>, respectively. Thus, the first criterion applies when the removal rate by reaction with NO<sub>3</sub> exceeds 1% of the removal rate by reaction with OH, and the second when the lifetime of the VOC with respect to reaction with NO<sub>3</sub> is less than 10<sup>7</sup> s (i.e. ca. 100 d). NO<sub>3</sub>-initiated degradation is therefore believed to be important for alkenes, dienes, aldehydes and ethers (also for some aromatics, although not considered in the present protocol).

**3.3.1. Rates of initiation reactions.** Rate coefficients for the reactions of NO<sub>3</sub> with organic compounds have been reviewed by Atkinson (1991, 1994) and by Wayne *et al.* (1991). The reviews of Atkinson 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 NO<sub>3</sub> with aldehydes for which no experimental data exist are all assumed to proceed at a rate equal to the reaction involving acetaldehyde (rate coefficient recommended by Atkinson, 1991, 1994):



$$k_2 = 1.44 \times 10^{-12} \exp(-1862/T).$$

The kinetics of the reactions of NO<sub>3</sub> with dimethyl ether, diethyl ether, di-*n*-propyl ether and methyl *t*-butyl ether have been studied by Langer and Ljungström (1994), and the reported rate coefficients are used accordingly. Partial rate coefficients for methyl, ethyl, *n*-propyl and *t*-butyl groups of 0.13, 1.40, 3.25 and 0.51 (in units of 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) may be inferred from these data, and were used for these groups and related hydroxy substituted groups in the ethers and glycol ethers considered in the present work. In the absence of experimental data, the partial rate coefficient for the *n*-butyl group is assumed equivalent to that for the *n*-propyl group.

Rate coefficients for the reactions of NO<sub>3</sub> with monoalkenes increase dramatically with alkyl substitution (Atkinson, 1991, 1994; Wayne *et al.*, 1991). Table 2 lists a series of generic rate coefficients, which

were estimated by analogy. These are used in the absence of available experimental data.

**3.3.2. Initial radical products.** The reactions of NO<sub>3</sub> with aldehydes are assumed to proceed via abstraction of the aldehydic H-atom, leading to the production of acyl radicals, as shown in reaction (2). The reactions with ethers and glycol ethers are also assumed to result in H atom abstraction, although there are insufficient data to assign the distribution of the initial radical products with any certainty. In the present study, therefore, the relative attack rates at the two organic groups are determined from the partial rate coefficients inferred above. With the exception of the *t*-butyl group, abstraction is assumed to occur exclusively at the carbon atom adjacent to the oxygen linkage.

The attack of NO<sub>3</sub> on alkenes is assumed to proceed by an addition mechanism, leading to the formation of  $\beta$ -nitro-oxy alkyl radicals, which is consistent with available product studies (e.g. Shepson *et al.*, 1985; Barnes *et al.*, 1990; Hjorth *et al.*, 1990). In the present work, the addition of NO<sub>3</sub> to alkenes of generic formulae CH<sub>2</sub>=CHR, CH<sub>2</sub>=CRR<sup>1</sup> and CHR=CR<sup>1</sup>R<sup>2</sup> is assumed to occur on the less alkyl substituted carbon 65, 80 and 65% of the time, respectively. Thus, in the case of CH<sub>2</sub>=CHR:



For unsymmetric alkenes of generic formula CHR=CHR<sup>1</sup> or CRR<sup>1</sup>=CR<sup>2</sup>R<sup>3</sup>, NO<sub>3</sub> is assumed to add equally at both sites.

On the basis of the data of Skov *et al.* (1992), the addition of NO<sub>3</sub> to 1,3-butadiene is assumed to occur only at the terminal carbon atoms, and in the case of isoprene, entirely at the terminal carbon adjacent to the methyl substitution.

### 3.4. 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 carbonyl compound (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.

Relevant species for which available absorption cross-section and quantum yield data allow the determination of photolysis parameters are given in Table 3. Photolysis rates as a function of solar zenith angle were determined from these data using a two stream isotropic scattering model as described previously (Hough, 1988), for clear sky conditions at an altitude of 0.5 km. The results are plotted in Fig. 2 for acetaldehyde and acetone. In each case, variation of

Table 2. Generic rate coefficients used for the reactions of NO<sub>3</sub> with alkenes

Generic alkene	<i>k</i> (298) <sup>a</sup>	Reference alkene
CH <sub>2</sub> =CHR	1.2	CH <sub>2</sub> =CHC <sub>2</sub> H <sub>5</sub>
CH <sub>2</sub> =CRR <sup>1</sup>	33.0	CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub>
CHR=CHR <sup>1</sup>	37.0	CH <sub>3</sub> CH=CHCH <sub>3</sub>
CHR=CR <sup>1</sup> R <sup>2</sup>	940.0	CH <sub>3</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>
CRR <sup>1</sup> =CR <sup>2</sup> R <sup>3</sup>	5700.0	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>

<sup>a</sup> Units 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; rate coefficients taken from Atkinson (1994).

Table 3. Photolysis reactions and parameters assigned as a function of solar zenith angle ( $\chi$ )

Reaction	$J = I(\cos \chi)^n \exp(-n \sec \chi)$			Sources of data	
	$I$	$m$	$n$	Absorption cross-sections	Quantum yields
<b>Aldehydes</b>					
$\text{HCHO} \rightarrow \text{HCO} + \text{H}$	$4.866 \times 10^{-5}$	0.781	0.349	DeMore <i>et al.</i> (1994)	DeMore <i>et al.</i> (1994)
$\rightarrow \text{CO} + \text{H}_2$	$6.790 \times 10^{-5}$	0.565	0.275		DeMore <i>et al.</i> (1994)
$\text{CH}_3\text{CHO} \rightarrow \text{HCO} + \text{CH}_3$	$8.443 \times 10^{-6}$	1.177	0.437	Martinez <i>et al.</i> (1992)	Atkinson <i>et al.</i> (1992)
$\text{C}_2\text{H}_5\text{CHO} \rightarrow \text{HCO} + \text{C}_2\text{H}_5$	$3.169 \times 10^{-5}$	1.059	0.373	Martinez <i>et al.</i> (1992)	Atkinson <i>et al.</i> (1992)
$n\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{HCO} + n\text{-C}_3\text{H}_7$	$2.964 \times 10^{-5}$	0.812	0.341	Martinez <i>et al.</i> (1992)	Foreteig <i>et al.</i> (1978)
$\rightarrow \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5$	$1.779 \times 10^{-5}$	0.812	0.341		Foreteig <i>et al.</i> (1978)
$i\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{HCO} + i\text{-C}_3\text{H}_7$	$8.304 \times 10^{-5}$	0.788	0.367	Martinez <i>et al.</i> (1992)	Derais <i>et al.</i> (1986)
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO} \rightarrow \text{CH}_3\text{C}=\text{CH}_2 + \text{HCO}$	$1.096 \times 10^{-5}$	0.526	0.227	Raber and Moortgat (1996)	Raber and Moortgat (1996)
$\rightarrow \text{CH}_2=\text{C}(\text{CH}_3)\text{CO} + \text{H}$	$1.096 \times 10^{-5}$	0.526	0.227		Raber and Moortgat (1996)
<b>Ketones</b>					
$\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CO} + \text{CH}_3$	$9.269 \times 10^{-7}$	1.563	0.301	Martinez <i>et al.</i> (1992)	Atkinson <i>et al.</i> (1992)
$\text{CH}_3\text{COCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CO} + \text{C}_2\text{H}_5$	$6.591 \times 10^{-6}$	1.070	0.399	Martinez <i>et al.</i> (1992)	Raber and Moortgat (1996)
$\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CO}$	$1.769 \times 10^{-5}$	0.522	0.226	Raber and Moortgat (1996)	Raber and Moortgat (1996)
$\rightarrow \text{CH}_3\text{CO} + \text{CH}=\text{CH}_2$	$1.769 \times 10^{-5}$	0.522	0.226		Raber and Moortgat (1996)
<b><math>\alpha</math>-Dicarbonyls</b>					
$(\text{CHO})_2 \rightarrow \text{CO} + \text{CO} + \text{H}_2$	$6.828 \times 10^{-3}$	0.222	0.154	Plum <i>et al.</i> (1983)	Atkinson <i>et al.</i> (1992) <sup>a</sup>
$\rightarrow \text{CO} + \text{HCHO}$	$1.030 \times 10^{-5}$	0.222	0.154		Atkinson <i>et al.</i> (1992) <sup>a</sup>
$\rightarrow \text{HCO} + \text{HCO}$	$3.887 \times 10^{-5}$	0.695	0.289		Atkinson <i>et al.</i> (1992) <sup>a</sup>
$\text{CH}_3\text{C}(\text{O})\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{HCO}$	$1.524 \times 10^{-4}$	0.270	0.156	Atkinson <i>et al.</i> (1992)	Raber and Moortgat (1996)
$\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_3 \rightarrow \text{CH}_3\text{CO} + \text{CH}_3\text{CO}$	$3.276 \times 10^{-4}$	0.256	0.159	Plum <i>et al.</i> (1983)	Plum <i>et al.</i> (1983)
<b>Hydroperoxides</b>					
$\text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O} + \text{OH}$	$5.797 \times 10^{-6}$	0.764	0.249	Atkinson <i>et al.</i> (1992)	Atkinson <i>et al.</i> (1992)
<b>Organic nitrates</b>					
$\text{CH}_3\text{ONO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	$1.748 \times 10^{-6}$	1.166	0.324	Taylor <i>et al.</i> (1980), Roberts and Fajer (1989)	Atkinson <i>et al.</i> (1992) <sup>a</sup>
$\text{C}_2\text{H}_5\text{ONO}_2 \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$	$2.113 \times 10^{-6}$	1.255	0.342	Roberts and Fajer (1989), Turberg <i>et al.</i> (1990)	Atkinson <i>et al.</i> (1992) <sup>a</sup>
$n\text{-C}_3\text{H}_7\text{ONO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{O} + \text{NO}_2$	$2.772 \times 10^{-6}$	1.183	0.348	Roberts and Fajer (1989), Turberg <i>et al.</i> (1990)	Atkinson <i>et al.</i> (1992) <sup>a</sup>
$i\text{-C}_3\text{H}_7\text{ONO}_2 \rightarrow i\text{-C}_3\text{H}_7\text{O} + \text{NO}_2$	$4.518 \times 10^{-6}$	1.104	0.331	Roberts and Fajer (1989), Turberg <i>et al.</i> (1990)	Atkinson <i>et al.</i> (1992) <sup>a</sup>
$i\text{-C}_4\text{H}_9\text{ONO}_2 \rightarrow i\text{-C}_4\text{H}_9\text{O} + \text{NO}_2$	$1.221 \times 10^{-5}$	0.988	0.312	Roberts and Fajer (1989)	Roberts and Fajer (1989)
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O} + \text{NO}_2$	$8.198 \times 10^{-6}$	1.020	0.331	Roberts and Fajer (1989), Barnes <i>et al.</i> (1993)	Estimated <sup>b</sup>
$\rightarrow \text{CH}_3\text{CO} + \text{HCHO} + \text{NO}_2$	$3.797 \times 10^{-6}$	1.278	0.346		Estimated <sup>b</sup>

<sup>a</sup> Based on comments made in this reference; <sup>b</sup> estimated by analogy with  $n\text{-C}_3\text{H}_7\text{ONO}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ .



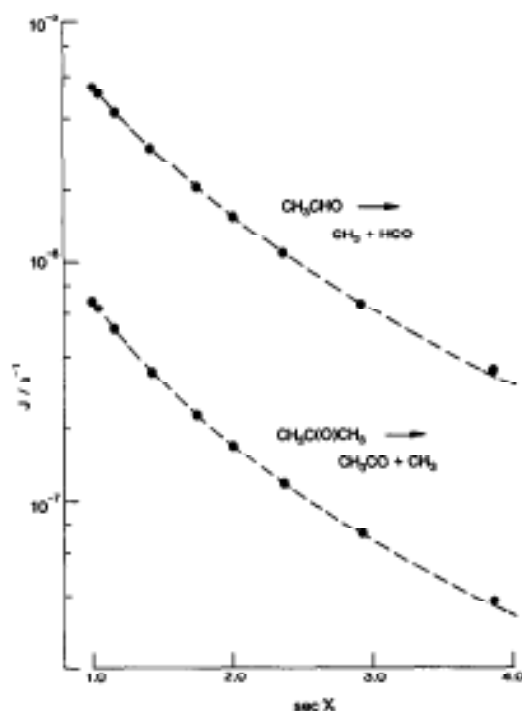


Fig. 2. (●) Calculated photolysis rates of acetaldehyde and acetone as a function of solar zenith angle (clear sky, 0.5 km altitude; see text); (---) variation of photolysis rates with solar zenith angle defined by parameterisation given in Table 3.

photolysis rate with solar zenith angle can be described well by an expression of the following form,

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

by optimising the values of the three parameters,  $I$ ,  $m$  and  $n$ . The results of this procedure are shown in Fig. 2 for acetaldehyde and acetone, and the optimised parameters for all the species considered are also given in Table 3. In some cases, the parameters determined for these photolysis reactions are also used to describe the rates and products of photolysis of a series of related compounds for which the required information is not available, e.g.  $n$ -C<sub>3</sub>H<sub>7</sub>CHO for straight-chain aldehydes. These generic reactions and the adopted photolysis rates are given in Table 4.

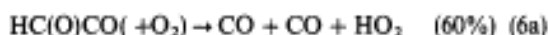
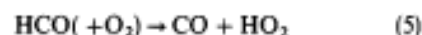
### 3.5. Reactions of organic radicals

The large majority of organic radicals (R) react rapidly and exclusively with oxygen under tropospheric conditions, to form stabilised peroxy radicals, RO<sub>2</sub>:



This is assumed in all cases except for those shown below, where 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:



General cases:

$\alpha$ -hydroxy radicals:



vinyl-type radicals:



$\alpha$ -carbonyl acyl radicals:



The terminal addition of OH or NO<sub>3</sub> to the conjugated dienes considered in the present work (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<sub>2</sub> in these cases can lead to the production of two possible peroxy radicals. In the hydroxy substituted cases, the peroxy radical is assumed to be produced at the more substituted site with 75% probability, since this assumption has been shown to lead to a reasonable description of the observed products of the OH-initiated degradation of isoprene (Jenkin and Hayman, 1995). In the nitro-oxy substituted cases, the formation of the peroxy radical exclusively at the other terminal carbon (i.e. 1,4 addition) is assumed for isoprene, whereas 1,4 addition and 1,2 addition are assumed to compete equally for 1,3-butadiene. These assumptions are based on the data of Skov *et al.* (1992).

### 3.6. Reactions of peroxy radical intermediates

There are several reactions of the peroxy radicals (RO<sub>2</sub>) which are treated, namely the reactions with NO, NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub> and with itself and other peroxy radicals (R'O<sub>2</sub>).

3.6.1. The reactions of RO<sub>2</sub> with NO. Where applicable, the kinetic data applied to these reactions are the recommendations made by Lightfoot *et al.* (1992), and the more recent series of measurements made by Sehested *et al.* (1993) and Langer *et al.* (1994, 1995). In all cases other than CH<sub>3</sub>O<sub>2</sub>, only a value at 298 K is available, and the temperature dependence is assumed equivalent to that for the reaction of CH<sub>3</sub>O<sub>2</sub> with NO ( $E/R = -180$  K). Where no experimental data are available, generic rate coefficients are defined by the expression

$$k_{10} = 4.1 \times 10^{-12} \exp(180/T) \quad (ii)$$

which is the product of the rate coefficient recommended by Lightfoot *et al.* (1992) for the reaction of

Table 4. Generic photolysis reactions and adopted parameters

Reaction	Photolysis parameter
<i>Aldehydes</i>	
$RCH_2CHO \rightarrow HCO + RCH_2$	$J_1$
$RR'CHCHO \rightarrow HCO + RCHR'$	$J_{II}$
$RR'R''CHO \rightarrow HCO + RCR'R''$	$J_{II}$
$RR'C-C(R'')CHO \rightarrow RR'C-CR'' + HCO$	$J_{III}$
$\rightarrow RR'C=C(R'')CO + H$	$J_{IV}$
<i>Ketones</i>	
$RC(O)R' \rightarrow RCO + R'$	$J_V$
$RC(O)C(R')=CR''R''' \rightarrow RCO + R'C=CR''R'''$	$J_{VI}$
<i><math>\alpha</math>-dicarbonyls</i>	
$RC(O)CHO \rightarrow RCO + HCO$	$J_{VII}$
$RC(O)C(O)R' \rightarrow RCO + R'CO$	$J_{VIII}$
<i>Hydroperoxides and percarboxylic acids</i>	
$ROOH \rightarrow RO + OH$	$J_{IX}$
<i>Organic nitrates</i>	
$RCH_2ONO_2 \rightarrow RCH_2O + NO_2$	$J_X$
$RR'CHONO_2 \rightarrow RR'CHO + NO_2$	$J_{XI}$
$RR'R''CONO_2 \rightarrow RR'R''CO + NO_2$	$J_{XII}$
$RC(O)CR'R''ONO_2 \rightarrow RC(O)CR'R''O + NO_2$	$J_{XIII}$
$\rightarrow RCO + R'C(O)R' + NO_2$	$J_{XIV}$

\* Where there is a choice of organic radical eliminated, tertiary is favoured over secondary over primary, and within these categories, larger over smaller.

Table 5. Generic rate coefficients for reactions of  $RO_2$  radicals with NO ( $k_{11} = 4.1 \times 10^{-12} \exp(180/T)f$ )

Organic group	$f$
$C_1$ and $C_2$ (except chlorinated) <sup>a</sup>	1.0
$C_n$ ( $n \geq 3$ ; except $\alpha,\beta$ -chlorinated) <sup>b</sup>	$\exp(-0.17(n-1))$
$C_1$ and $C_2$ ( $\alpha$ -chlorinated) <sup>c</sup>	2.2
$C_1$ and $C_2$ ( $\beta$ -chlorinated) <sup>d</sup>	1.6
$C_n$ ( $n \geq 3$ ; $\alpha,\beta$ -chlorinated) <sup>e</sup>	1.0
Acyl <sup>f</sup>	2.7

<sup>a</sup> Based on data for  $CH_3O_2$ ,  $HOCH_2O_2$ ,  $C_2H_5O_2$  and  $HOCH_2CH_2O_2$  (Lightfoot *et al.*, 1992); <sup>b</sup> based on data presented in Fig. 3 (see text); <sup>c</sup> based on data for  $CH_2ClO_2$ ,  $CF_2ClO_2$ ,  $CFCl_2O_2$  and  $CCl_2O_2$  (summarised by Sehested *et al.*, 1993); <sup>d</sup> based on data for  $CFCl_2CH_2O_2$  and  $CF_2ClCH_2O_2$  (summarised by Sehested *et al.*, 1993); <sup>e</sup> assumed unity in the absence of available data; <sup>f</sup> based on data for  $CH_3C(O)O_2$  (Lightfoot *et al.*, 1992).

$CH_3O_2$  with NO, and an efficiency factor,  $f$ . The values of  $f$  representative of different classes of peroxy radical are given in Table 5. These were assigned on the basis of available room temperature data for the range of reactions of  $RO_2$  with NO (Lightfoot *et al.*, 1992; Sehested *et al.*, 1993; Langer *et al.*, 1994, 1995). For example, the most extensive set of data for alkyl and  $\beta$ -oxygenated radicals (shown in Fig. 3) indicates a progressive decrease in reactivity as the size of the organic group becomes larger, which is reasonably well described by values of  $f = \exp(-0.17 \times (n-1))$ , where  $n$  is the carbon number, for  $\geq C_3$  peroxy radicals. Consequently, corresponding values of  $f$  are applied to all alkyl,  $\beta$ -oxygenated and remotely substituted peroxy radicals containing three or

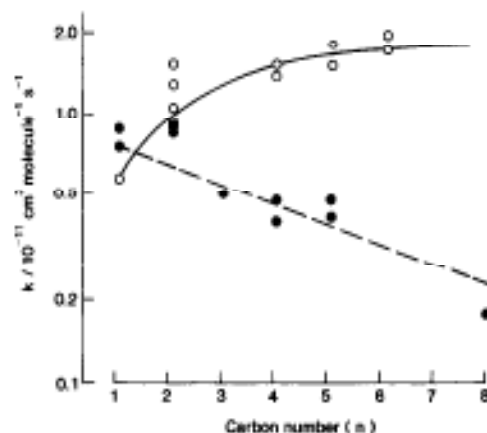
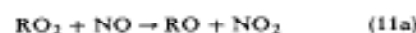


Fig. 3. Room temperature kinetic data for reactions of alkyl and  $\beta$ -hydroxy alkyl peroxy radicals with  $HO_2$  (open symbols) and NO (closed symbols) as a function of carbon number. Lines are recommended expressions for these types of reaction given in Section 3.6.

more carbon atoms. These values of  $f$  are also used for the reactions of the  $\beta$ -nitro-oxy peroxy radicals formed from the addition of  $NO_3$  to alkenes.

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



The assigned branching ratios for the nitrate-forming channels,  $k_{11b}/(k_{11a} + k_{11b})$ , are based on experimental measurements, where possible (Carter and Atkinson, 1989; Lightfoot *et al.*, 1992).



Where data are not available, ratios for other primary, secondary and tertiary alkyl peroxy radicals are calculated using the expression recommended originally by Carter and Atkinson (1989) and subsequently by Atkinson (1990, 1994). On the basis of available data for peroxy radicals formed from propene, methyl propene and *cis*-2-butene (Shepson *et al.*, 1985; Lightfoot *et al.*, 1992; Muthuramu *et al.*, 1993), ratios for  $\beta$ -hydroxy RO<sub>2</sub>, for which experimental data are not available, are taken to be 0.5 of the values for the corresponding unsubstituted alkyl RO<sub>2</sub>.

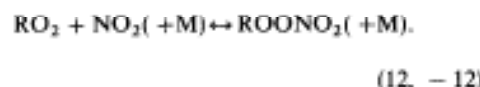
With the exception of  $\delta$ -hydroxy RO<sub>2</sub> radicals, branching ratios for other RO<sub>2</sub> possessing functional groups remote from the peroxy radical centre are also calculated using the expression of Carter and Atkinson (1989) for alkyl peroxy radicals of the same carbon number. Ratios for  $\delta$ -hydroxy RO<sub>2</sub> (i.e. formed following 1,5 isomerisation reactions of oxy radicals as described below) have long been suspected to be somewhat lower than for the unsubstituted counterparts (Carter and Atkinson, 1985; Carter, 1995), and nitrate formation has often been assumed not to occur in these cases. However,  $\delta$ -hydroxy alkyl nitrates have recently been detected as products of the oxidation of hexane (Eberhard *et al.*, 1995). The tentative yields in that study, and the recently observed chain formation of NO<sub>2</sub> during the oxidation of a series of C<sub>1</sub>–C<sub>8</sub> alkanes (Hoffmann *et al.*, 1995) may be interpreted in terms of the formation of the organic nitrate being ca. 40% as efficient for  $\delta$ -hydroxy RO<sub>2</sub> compared with the corresponding alkyl peroxy radicals (i.e. the same carbon skeleton), and this is assumed in the present work.

For acyl and  $\alpha$ -carbonyl RO<sub>2</sub> radicals, the ratio is taken as zero, on the basis of observations for CH<sub>3</sub>C(O)O<sub>2</sub> and CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> (Lightfoot *et al.*, 1992). For simplicity, and in the absence of definitive product data, the ratios for the  $\beta$ -nitro-oxy peroxy radicals are assumed to be zero.

On the basis of data presented by Lightfoot *et al.* (1992), values of  $k_{11b}/(k_{11a} + k_{11b})$  for the C<sub>5</sub> allyl-type peroxy radicals derived from the OH-initiated oxidation of isoprene are all taken to be 0.10. Ratios for the similar C<sub>4</sub> peroxy radicals formed from 1,3-butadiene are assumed to be 0.065, on the basis of the relative ratios calculated for C<sub>4</sub> and C<sub>3</sub> alkyl peroxy radicals (Carter and Atkinson, 1989).

The degradation of the organic nitrates (RONO<sub>2</sub>) formed from channel (11b) is treated in a simplified manner, as described in Section 3.10.2 below.

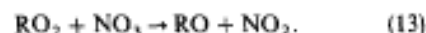
**3.6.2. The reactions of RO<sub>2</sub> with NO<sub>2</sub>.** These reactions are only considered for acyl peroxy radicals, for which the product peroxy nitrates (ROONO<sub>2</sub>) are comparatively stable, and for the most abundant peroxy radical, CH<sub>3</sub>O<sub>2</sub>:



Rate parameters for the forward and reverse reactions involving CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub> are taken as those recommended by Lightfoot *et al.* (1992). In the absence of rate data for the forward reaction (12) for other acyl peroxy radicals, the rates are assumed equivalent to that for CH<sub>3</sub>C(O)O<sub>2</sub>. Limited available information on the thermal decomposition rates of C<sub>2</sub>H<sub>5</sub>C(O)OONO<sub>2</sub>, *n*-C<sub>3</sub>H<sub>7</sub>C(O)OONO<sub>2</sub>, *n*-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> and *i*-C<sub>4</sub>H<sub>9</sub>C(O)OONO<sub>2</sub> indicate values of  $k_{-12}$  ca. 110, 77, 60 and 80%, respectively, of that for CH<sub>3</sub>C(O)OONO<sub>2</sub> at 298 K and atmospheric pressure (Lightfoot *et al.*, 1992; Grosjean *et al.*, 1994a,b), and these values are used accordingly. For other acyl peroxy nitrates, the decomposition rates are assumed equivalent to that for CH<sub>3</sub>C(O)OONO<sub>2</sub>.

The degradation of the peroxy nitrates is treated in a simplified manner, as described in Section 3.10.3 below.

**3.6.3. The reactions of RO<sub>2</sub> with NO<sub>3</sub>.** On the basis of available information (Lightfoot *et al.*, 1992; Biggs *et al.*, 1994, 1995; Daele *et al.*, 1995), these reactions are assumed to proceed via a single channel, as follows:



Recent data provide a mean value of  $k_{13} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction involving CH<sub>3</sub>O<sub>2</sub> (Biggs *et al.*, 1994; Daele *et al.*, 1995), and a value of  $2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction involving C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> (Biggs *et al.*, 1995), which is also assigned to the reactions of RO<sub>2</sub> with NO<sub>3</sub> in general.

**3.6.4. The reactions of RO<sub>2</sub> with HO<sub>2</sub>.** The kinetic data applied to those reactions for which experimental data are available, are given in Table 6. In cases for which only a value at 298 K has been measured, the temperature dependence is assumed to be  $E/R = -1250 \text{ K}$ , on the basis of observed temperature dependences for this type of reaction. Where no experimental data are available, generic rate coefficients are defined by analogy. For acyl peroxy radicals and  $\alpha$ -chlorinated peroxy radicals, the rate coefficients are assumed equivalent to those for CH<sub>3</sub>C(O)O<sub>2</sub> and CH<sub>2</sub>ClO<sub>2</sub>, respectively. In all other cases, the rate coefficients are given by the expression

$$k_{14} = 3.0 \times 10^{-12} \exp(1250/T) [1 - \exp(-0.34n)] \quad (\text{iii})$$

where  $n$  is the carbon number. This expression was defined on the basis of available room temperature data for the range of reactions of alkyl and  $\beta$ -hydroxy RO<sub>2</sub> radicals with HO<sub>2</sub> (Lightfoot *et al.*, 1992; Rowley *et al.*, 1992; DeMore *et al.*, 1994; Jenkin and Hayman, 1995; Boyd *et al.*, 1996), as shown in Fig. 3.

The following channels are considered for the reactions of RO<sub>2</sub> with HO<sub>2</sub>:



Table 6. Reported rate coefficients for reactions of RO<sub>2</sub> radicals with H<sub>2</sub>O<sub>2</sub> used in the present work

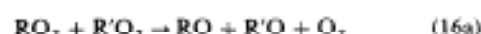
Peroxy radical	10 <sup>13</sup> k(298 K) <sup>a,b</sup>	E/R <sup>c</sup>	10 <sup>13</sup> A <sup>d</sup>	Comment
<i>Alkyl</i>				
CH <sub>3</sub> O <sub>2</sub>	5.8	-700	4.1	d
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	7.9	-700	7.5	e
neo-C <sub>3</sub> H <sub>7</sub> O <sub>2</sub>	14.4	-1380	1.4	f
c-C <sub>3</sub> H <sub>7</sub> O <sub>2</sub>	17.6	-1320	2.1	d
c-C <sub>4</sub> H <sub>9</sub> O <sub>2</sub>	17.2	-1250	2.6	d
<i>β-Hydroxy</i>				
HOCH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>	13.5	-1250	2.03	g,h
(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> O <sub>2</sub>	14.2	-1650	0.56	i
CH <sub>3</sub> CH(OH)CH(O <sub>2</sub> )CH <sub>3</sub>	15.0	-1250	2.26	g,j
(CH <sub>3</sub> ) <sub>2</sub> C(OH)C(O <sub>2</sub> )CH <sub>3</sub>	20.0	-1250	3.01	g,j
<i>α-Carbonyl</i>				
CH <sub>3</sub> C(O)CH <sub>2</sub> O <sub>2</sub>	9.0	-1250	1.36	g,k
<i>Acyl</i>				
CH <sub>3</sub> C(O)O <sub>2</sub>	14.1	-1040	4.3	d
<i>Chlorinated</i>				
CH <sub>2</sub> ClO <sub>2</sub>	5.2	-820	3.3	l

<sup>a</sup> Units, cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; <sup>b</sup> value calculated from reported Arrhenius parameters, and not necessarily the 298 K value quoted in reference; <sup>c</sup> units, K; <sup>d</sup> recommended by Lightfoot *et al.* (1992); <sup>e</sup> recommended by DeMore *et al.* (1994); <sup>f</sup> Rowley *et al.* (1992); <sup>g</sup> "A" calculated from assumed E/R and reported k(298 K); <sup>h</sup> mean of Murrells *et al.* (1991) and Jenkin and Hayman (1995); <sup>i</sup> Boyd *et al.* (1996); <sup>j</sup> Jenkin and Hayman (1995); <sup>k</sup> Bridier *et al.* (1993); <sup>l</sup> Catoire *et al.* (1994).

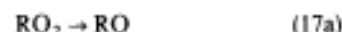
For the majority of peroxy radicals, the reaction is assumed to proceed exclusively by channel (14a), which is consistent with published data (Lightfoot *et al.*, 1992; Wallington *et al.*, 1992). For acyl peroxy radicals (RC(O)O<sub>2</sub>), branching ratios  $k_{14a}/k_{14} = 0.71$  and  $k_{14b}/k_{14} = 0.29$  are assumed, on the basis of the available data for CH<sub>3</sub>C(O)O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>C(O)O<sub>2</sub> (Lightfoot *et al.*, 1992). In the case of peroxy radicals of general formula ROCH<sub>2</sub>O<sub>2</sub>, branching ratios  $k_{14a}/k_{14} = 0.6$  and  $k_{14b}/k_{14} = 0.4$  are assigned on the basis of data reported for HOCH<sub>2</sub>O<sub>2</sub> (Burrows *et al.*, 1989) and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> (Wallington *et al.*, 1993).

The degradation of the hydroperoxides (ROOH), percarboxylic acids (ROOH, R = acyl), carboxylic acids (ROH, R = acyl) and esters (R-HO, R = alkoxy alkyl) formed from these reactions is treated in a simplified manner, as described below in Sections 3.10.1 and 3.10.4–3.10.6.

3.6.5. *The permutation reactions of RO<sub>2</sub>.* The "permutation" reactions of a given RO<sub>2</sub> radical are its self-reaction (15), and its cross-reactions (16) with other peroxy radicals, R'O<sub>2</sub>, for which a number of product channels may occur:



In view of the large number of RO<sub>2</sub> radicals generated in a detailed chemical mechanism, it is unrealistic to represent these reactions explicitly, and the use of a simplified parameterisation is essential, as discussed previously by Madronich and Calvert (1990). In the present work, a very simplified approach is adopted 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 "RO<sub>2</sub>" which is the sum of the concentrations of all peroxy radicals, excluding HO<sub>2</sub>. The collective rate of all the permutation reactions of a particular peroxy radical (RO<sub>2</sub>) is then represented by a pseudo-unimolecular reaction, which has an assigned rate coefficient equal to  $k_{17}\text{RO}_2$ :



Each reaction has up to three product channels, the branching ratios of which depend on the structure of the radical, as shown in Table 7. The assigned values of  $k_{17}$  for various classes of peroxy radical (given in Table 8) also depend on the structure of the organic group, and are based on trends of reactivity of peroxy radical self-reactions. The parameters are twice the geometric mean of an estimated self-reaction rate coefficient,  $k_{15}$ , for that class of peroxy radical and the self-reaction rate coefficient for CH<sub>3</sub>O<sub>2</sub> (i.e. it is assumed that CH<sub>3</sub>O<sub>2</sub> is the major reaction partner). Accordingly, the representation of the reaction for

CH<sub>3</sub>O<sub>2</sub> itself reduces to its self-reaction with recommended rate coefficient and branching ratios, when it is the dominant radical. The rate coefficients for alkyl peroxy radicals are also taken to apply to remotely substituted (i.e. not  $\alpha$  or  $\beta$ ) oxygen- and chlorine-containing radicals, radicals containing unsaturated linkages, and  $\beta$ -nitro-oxy peroxy radicals.

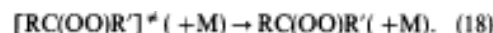
If not already considered, the degradation of the alcohols (ROH), carboxylic acids (ROH, R = acyl) and carbonyl compounds (R<sub>2</sub>C=O) formed from the

permutation reactions is treated in a simplified manner, as described in Sections 3.10.1, 3.10.6 and 3.10.7 below.

### 3.7. Reactions of Criegee biradicals

3.7.1. *The reactions of the excited Criegee biradicals.* The energy-rich Criegee biradicals, [RC(OO)R']<sup>\*</sup>, formed from the reactions of ozone with alkenes and dienes (Section 3.2) are either collisionally stabilised, or decompose to yield a range of radical and molecular products (e.g. Atkinson and Aschmann, 1993; Atkinson, 1994; Grosjean *et al.*, 1994c). It appears, however, that the relative importance of the available reactions for a given energy-rich biradical may be dependent on the system in which it is generated (Atkinson, 1994), and this is intrinsic to the approach adopted in the present work. Three possible fates of the excited Criegee biradicals are considered, the relative importance of which is governed by the degree of alkyl substitution in the parent alkene, rather than by the identity of the biradical itself:

- (i) Collisional stabilisation to produce a stabilised Criegee biradical:



- (ii) Decomposition to generate OH radicals by one of the following two reactions:

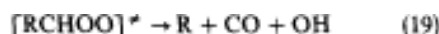


Table 7. Branching ratios assigned to parameterised permutation reactions of RO<sub>2</sub> (see text)

Class of radical	Reaction	Branching ratio
CH <sub>3</sub> O <sub>2</sub> <sup>a</sup>	CH <sub>3</sub> O <sub>2</sub> → CH <sub>3</sub> O	0.330
	→ HCHO	0.335
	→ CH <sub>3</sub> OH	0.335
Primary and secondary RO <sub>2</sub> <sup>b</sup>	RO <sub>2</sub> → RO	0.6
	→ R <sub>2</sub> HO	0.2
	→ ROH	0.2
Tertiary and acyl RO <sub>2</sub> <sup>c</sup>	RO <sub>2</sub> → RO	0.7
	→ ROH	0.3

<sup>a</sup> Branching ratios equivalent to those for the self-reaction of CH<sub>3</sub>O<sub>2</sub> at 298 K (Lightfoot *et al.*, 1992); <sup>b</sup> Branching ratios based on the mean of the values for the self-reactions of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, *i*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>, *neo*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>, *c*-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>O<sub>2</sub>, HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> and ClCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> (Lightfoot *et al.*, 1992; Barnes *et al.*, 1992; Jenkin *et al.*, 1993a, b; Bridier *et al.*, 1993); <sup>c</sup> assumed value.

Table 8. Self-reaction rate coefficients (*k*<sub>15</sub>) and rate coefficients assigned to the parameterised permutation reactions of RO<sub>2</sub> (*k*<sub>17</sub>) as described in the text

R	<i>k</i> <sub>15</sub> <sup>a</sup>	<i>k</i> <sub>17</sub> <sup>c</sup>	Comment
<i>Primary peroxy radicals</i>			
CH <sub>3</sub>	9.1 × 10 <sup>-14</sup> exp(416/T)	1.82 × 10 <sup>-13</sup> exp(416/T)	d
C <sub>2</sub> H <sub>5</sub>	6.6 × 10 <sup>-14</sup>	3.1 × 10 <sup>-13</sup>	d
Alkyl (< C <sub>3</sub> ) <sup>a</sup>	2.4 × 10 <sup>-13</sup>	6.0 × 10 <sup>-13</sup>	d, e
Alkyl (> C <sub>3</sub> ) <sup>a</sup>	1.2 × 10 <sup>-12</sup>	1.3 × 10 <sup>-12</sup>	d, f
Containing $\alpha$ or $\beta$ O or Cl	2.7 × 10 <sup>-12</sup>	2.0 × 10 <sup>-12</sup>	g
<i>Secondary peroxy radicals</i>			
CH <sub>3</sub> CHCH <sub>3</sub>	1.1 × 10 <sup>-13</sup>	4.0 × 10 <sup>-14</sup>	d
Alkyl (> C <sub>3</sub> ) <sup>a</sup>	4.4 × 10 <sup>-14</sup>	2.5 × 10 <sup>-13</sup>	d, h
Containing $\alpha$ or $\beta$ O or Cl	5.3 × 10 <sup>-13</sup>	8.8 × 10 <sup>-13</sup>	i
Containing allyl and $\beta$ -hydroxy	1.4 × 10 <sup>-12</sup>	1.4 × 10 <sup>-12</sup>	j
<i>Tertiary peroxy radicals</i>			
Alkyl <sup>a</sup>	3.0 × 10 <sup>-17</sup>	6.7 × 10 <sup>-15</sup>	d, k
Containing $\alpha$ or $\beta$ O or Cl	5.7 × 10 <sup>-15</sup>	9.2 × 10 <sup>-14</sup>	l
Containing allyl and $\beta$ -hydroxy	1.7 × 10 <sup>-14</sup>	1.6 × 10 <sup>-13</sup>	m
<i>Acyl peroxy radicals</i>			
	1.7 × 10 <sup>-11</sup>	5.0 × 10 <sup>-12</sup>	d

<sup>a</sup> *k*<sub>17</sub> for alkyl peroxy radicals also applied to some other cases (see text); <sup>b</sup> self-reaction rate coefficients at 298 K, except for CH<sub>3</sub>O<sub>2</sub>; <sup>c</sup> *k*<sub>17</sub> = 2/*k*<sub>15</sub> × *k*<sub>CH<sub>3</sub>O<sub>2</sub> + CH<sub>3</sub>O<sub>2</sub></sub>; <sup>d</sup> based on values of *k*<sub>15</sub> recommended by Lightfoot *et al.* (1992); <sup>e</sup> based on *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>; <sup>f</sup> based on *neo*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>; <sup>g</sup> based on CH<sub>2</sub>ClO<sub>2</sub>, CCl<sub>2</sub>O<sub>2</sub>, ClCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> and HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> (Lightfoot *et al.*, 1992; Catoire *et al.*, 1994; Jenkin and Hayman, 1995); <sup>h</sup> based on *c*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> and *c*-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>; <sup>i</sup> based on CH<sub>3</sub>CH(OH)CH(O<sub>2</sub>)CH<sub>3</sub> (Jenkin and Hayman, 1995); <sup>j</sup> based on the *k*<sub>15</sub> estimate for CH<sub>3</sub>=CH(CH<sub>3</sub>)CH(O<sub>2</sub>)CH<sub>2</sub>OH (Jenkin and Hayman, 1995); <sup>k</sup> based on *t*-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>; <sup>l</sup> based on (CH<sub>3</sub>)<sub>2</sub>C(OH)C(O<sub>2</sub>)(CH<sub>3</sub>)<sub>2</sub> (Jenkin and Hayman, 1995); <sup>m</sup> based on the *k*<sub>15</sub> estimate for HOCH<sub>2</sub>CH(CH<sub>3</sub>)(O<sub>2</sub>)CH=CH<sub>2</sub> (Jenkin and Hayman, 1995).

Table 9. Probabilities assigned to reactions of excited Criegee biradicals formed from a range of alkenes (see Section 3.7.1)

Parent alkene	Stabilisation (reaction (18))	OH formation <sup>a</sup> (reactions (19) or (20))	Other <sup>b</sup> (reactions (21) or (22))
CH <sub>2</sub> =CH <sub>2</sub>	0.37 <sup>c</sup>	0.12	0.51
CH <sub>2</sub> =CHR	0.24 <sup>d</sup>	0.36	0.40
CHR=CHR <sup>1</sup>	0.18 <sup>e</sup>	0.57	0.25
CH <sub>2</sub> =CRR <sup>1</sup>	0.18 <sup>f</sup>	0.82	0.00
CHR=CR <sup>1</sup> R <sup>2</sup>	0.11 <sup>g</sup>	0.89	0.00
CRR <sup>1</sup> =CR <sup>2</sup> R <sup>3</sup>	0.00 <sup>h</sup>	1.00	0.00
1,3-Butadiene	0.24 <sup>a</sup>	0.08	0.68
Isoprene	0.22 <sup>b</sup>	0.27	0.51

<sup>a</sup> Based on the estimation method of Atkinson and Aschmann (1993); <sup>b</sup> see section 3.7.1; <sup>c</sup> recommended by Atkinson (1994); <sup>d</sup> based on the data of Hatakeyama *et al.* (1984) for propene and Paulson and Seinfeld (1992) for 1-octene; <sup>e</sup> based on data for *cis*- and *trans*-2-butene (Niki *et al.*, 1977; Hatakeyama *et al.*, 1984); <sup>f</sup> based on data for methyl propene (Hatakeyama, 1984); <sup>g</sup> assumed to be 1-(OH yield); <sup>h</sup> assumed equivalent to CH<sub>2</sub>=CHR; <sup>i</sup> weighted mean of 0.6 and 0.4 of the values for CH<sub>2</sub>=CHR and CH<sub>2</sub>=CRR<sup>1</sup>, respectively.

(iii) Decomposition not generating OH radicals:

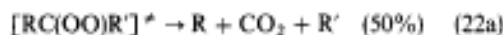
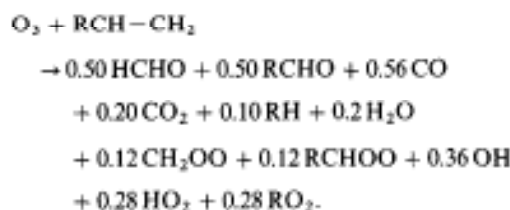
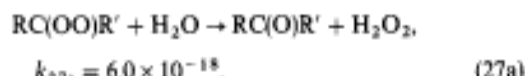
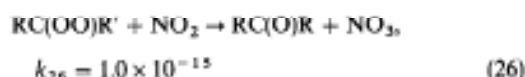
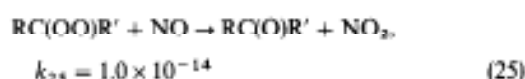


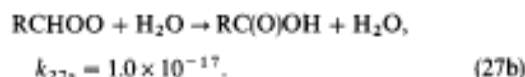
Table 9 shows the relative importance assigned to reactions in categories (i)–(iii) for excited biradicals formed from a range of alkene structures. For unsymmetric alkenes, these probabilities are assigned equivalently to both the excited Criegee biradicals generated. The probability of stabilised biradical formation via reaction (18) is based mainly on the data summarised by Atkinson (1994). The relative importance of OH formation where experimental data are unavailable follows the estimation method outlined by Atkinson and Aschmann (1993), with a minor adjustment to preclude yields greater than unity. Where the biradical contains an  $\alpha$ -H atom, OH formation is assumed to occur by reaction (19). In other cases, the “hydroperoxide” mechanism (reaction (20)), first postulated by Niki *et al.* (1987), is adopted. Any removal not explained by the stabilisation and OH formation routes is assumed to proceed by reaction (22) for all biradicals with the exception of  $[\text{CH}_2\text{OO}]^*$ , for which reaction (21) is the assumed fate. These assumptions are broadly based on the suggested major reaction routes for  $[\text{CH}_2\text{OO}]^*$  and  $[\text{CH}_3\text{CHOO}]^*$  as summarised by Atkinson (1994). Thus, for the reaction of ozone with  $\text{RCH}=\text{CH}_2$ , the above rules lead to the following product distribution:



3.7.2. *The reactions of the stabilised Criegee biradicals.* The stabilised Criegee biradicals, formed from the reactions of O<sub>3</sub> with alkenes, are assumed to react with SO<sub>2</sub>, CO, NO, NO<sub>2</sub> and H<sub>2</sub>O as shown below. Rate coefficients were assigned to these reactions on the basis of reported rate coefficients and relative rate coefficients for the reactions involving CH<sub>2</sub>OO, as summarised by Atkinson (1994) and Atkinson and Lloyd (1984) (units of rate coefficients, cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):



For biradicals containing H atoms  $\alpha$  to the radical centre, an additional channel for the reaction with H<sub>2</sub>O is included, leading to the formation of carboxylic acids:

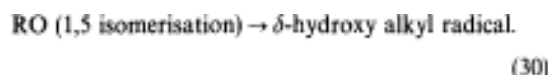


The values of these rate coefficients are extremely uncertain (Atkinson, 1994). However, the dominant fate of the stabilised biradicals under tropospheric conditions is believed to be the reaction with water vapour, which is consistent with the rate coefficients assigned above.

If not already considered, the degradation of the product carboxylic acids and carbonyl compounds formed from these reactions is treated, as described below in Sections 3.10.1 and 3.10.6.

### 3.8. Reactions of oxy radical intermediates

The behaviour of the oxy radicals, RO, under conditions relevant to the present work, is dominated by three modes of reaction, namely reaction with O<sub>2</sub>, thermal decomposition and isomerisation by a 1,5 H atom shift:



Available experimental information has been reviewed extensively by Atkinson and co-workers (Atkinson, 1994; Atkinson and Carter, 1991), although new data are constantly emerging. Where the behaviour of a given RO radical has been defined by experiment, the results are applied accordingly. In the absence of such data, the fates of the oxy radicals are defined by the criteria listed below. Where more than one reaction is possible, those calculated to account for <10% of the removal of a given RO radical are disregarded.

Carter and Atkinson (1985) defined a series of rules which provide an excellent basis for defining the behaviour of alkoxy radicals derived from alkanes in general, which have since been updated by Atkinson (1990, 1994). These rules are applied in the present work to unsubstituted and remotely substituted alkoxy radicals, and oxy radicals containing unsaturated carbon-carbon bonds.

For oxy radicals containing certain functional groups, the following rules are adopted on the basis of reported studies. CH<sub>3</sub>C(O)O has been shown to decompose rapidly and exclusively (Kenley and T aylor, 1975; Weaver *et al.*, 1975), and analogous routes are assumed for other acyl oxy radicals, yielding CO<sub>2</sub> and an organic radical:



Radicals containing an  $\alpha$ -carbonyl group are assumed to decompose exclusively to yield an acyl radical and a carbonyl compound, on the basis of the data of Jenkin *et al.* (1993c) and Bridier *et al.* (1993) for CH<sub>3</sub>C(O)CH<sub>2</sub>O, and the data of Cox *et al.* (1981) for CH<sub>3</sub>C(O)CH(O)CH<sub>3</sub>, e.g.



With the exception of HOCH<sub>2</sub>CH<sub>2</sub>O,  $\beta$ -hydroxy alkoxy radicals are assumed to decompose exclusively to yield a carbonyl compound and an  $\alpha$ -hydroxy alkyl radical, as discussed by Atkinson (1990), e.g.



For HOCH<sub>2</sub>CH<sub>2</sub>O, reaction with O<sub>2</sub> and thermal decomposition have been shown to be in competition at room temperature (Niki *et al.*, 1981):

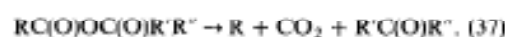


The rate of reaction (35) is assumed to be equivalent to that for the reaction of C<sub>2</sub>H<sub>5</sub>O with O<sub>2</sub> (Atkinson, 1994). The room temperature rate of reaction (34) is determined from the relative rate of reactions (34) and (35) (Niki *et al.*, 1981), with the temperature dependence defined assuming that the pre-exponential factor is equivalent to that for C<sub>2</sub>H<sub>5</sub>O decomposition (Batt, 1987).

Secondary and tertiary  $\alpha$ -alkoxy alkoxy radicals formed from ether oxidation are assumed to decompose exclusively by elimination of an alkyl radical to yield an ester, on the basis of the data of Wallington and Japar (1991), e.g.



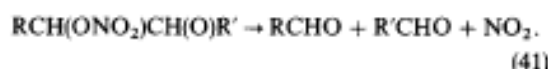
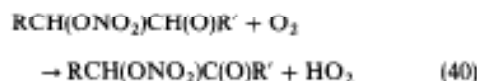
In the tertiary radicals, where there is a choice of organic radical that can be eliminated, the ejection of a tertiary radical is favoured over secondary over primary, and within these categories, larger over smaller. The corresponding H atom ejection from alkoxy methoxy radicals may be important (Jenkin *et al.*, 1993b), but these radicals are assumed to react with O<sub>2</sub> to yield HO<sub>2</sub> and a formate ester, as the ultimate products of these processes are indistinguishable. The similar oxy radicals formed from ester oxidation are assumed to decompose by C-O bond breaking, with subsequent decomposition of the acyl oxy radical (reaction (31)), as this leads to the formation of carbon dioxide:



On the basis of the results of Catoire *et al.* (1994), mono  $\alpha$ -chloro oxy radicals which contain  $\alpha$ -hydrogen atoms are assumed to react with O<sub>2</sub>, and di  $\alpha$ -chloro oxy radicals and those not possessing  $\alpha$ -hydrogen atoms are assumed to form a carbonyl compound by ejection of a Cl atom:



For primary and secondary  $\beta$ -nitro-oxy alkoxy radicals, formed from the NO<sub>3</sub>-initiated degradation of alkenes and dienes, both the reaction with O<sub>2</sub> and thermal decomposition are believed to occur (Barnes *et al.*, 1990; Hjorth *et al.*, 1990; Wayne *et al.*, 1991), e.g.

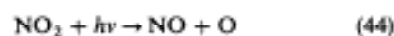
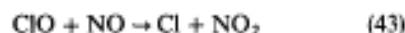


For primary and secondary radicals, the rate of reaction (40) is assumed to be equivalent to those for simple alkoxy radicals as discussed above. For oxy radicals formed from terminal alkenes (both primary and secondary), the decomposition reaction (41) is assumed to be a minor channel, accounting for only ca. 15% of the overall fate. It is therefore assigned a corresponding value of  $k_{41} = 7.0 \times 10^3 \text{ s}^{-1}$ . This is based on the observed low yields of HCHO in such systems (Barnes *et al.*, 1990; Hjorth *et al.*, 1990). For secondary oxy radicals formed from internal alkenes, reactions (40) and (41) are believed to be of similar importance, and the assigned decomposition rate is correspondingly higher,  $k_{41} = 4.0 \times 10^4 \text{ s}^{-1}$ . If the radical is tertiary, then exclusive thermal decomposition by a channel analogous to reaction (41) is assumed. The  $\beta,\gamma$  unsaturated  $\delta$ -nitro-oxy alkoxy radicals formed from the addition of  $\text{NO}_3$  to conjugated dienes (in the present work, isoprene and 1,3-butadiene) are assumed to react exclusively with  $\text{O}_2$ , forming  $\alpha,\beta$  unsaturated  $\gamma$ -nitro-oxy aldehydes and  $\text{HO}_2$ .

If not already considered, the degradation of the carbonyl compounds formed from these reactions is treated, as described below in Section 3.10.1.

### 3.9. Removal of chlorine atoms

The degradation of chlorinated organics leads ultimately to the release of Cl atoms (e.g. reaction (37)), which will be present in very low abundance. Cl may react with ozone, but also reacts very rapidly with most organic compounds. On the basis of available rate data (Atkinson and Aschmann, 1985; Wallington *et al.*, 1988; Atkinson *et al.*, 1992; Aschmann and Atkinson, 1995; Hooshiyar and Niki, 1995) and measured concentrations of ozone and organic compounds over rural England (PORG, 1993), it is apparent that removal by reactions with organic species is by far the dominant fate for Cl atoms, being at least an order of magnitude more rapid than the reaction with ozone. Furthermore, the predominant chemistry following the reaction with ozone regenerates Cl as part of the well-known "null cycle" (e.g. see Wayne *et al.*, 1995):



In the present work, therefore, Cl is assumed to be removed by reactions with all the alkanes in the chemical scheme, since these tend to be less reactive towards OH and are therefore generally present at higher concentrations than many other organics:



Rate coefficients have been measured for up to  $\text{C}_{10}$  alkanes (Atkinson and Aschmann, 1985; Wallington *et al.*, 1988; Atkinson and Aschmann, 1995;

Hooshiyar and Niki, 1995). The available data are in very good agreement, with values of  $k_{46}$  available for most of the alkanes considered in the present work. Atkinson and Aschmann (1995) and Hooshiyar and Niki (1995) have also developed structure-activity relationships allowing the estimation of rate coefficients in the absence of experimental data, and the calculation of product radical distributions from the reactions of Cl atoms with alkanes in general. The derived group rate coefficients and neighbouring group parameters from the two studies are almost identical. In the present study, the parameters recommended by Atkinson and Aschmann (1995) are used, on the basis that they were derived from the analysis of a larger number of alkanes.

### 3.10. Reactions of degradation products

The degradation of VOCs by the reactions summarised in the preceding subsections leads to a wide range of "first generation" oxygenated products of varying complexity, which are themselves further degraded. These products are a variety of carbonyl compounds, organic nitrates ( $\text{RONO}_2$ ), peroxy nitrates ( $\text{ROONO}_2$ ), hydroperoxides ( $\text{ROOH}$ ), percarboxylic acids ( $\text{RC(O)OOH}$ ), carboxylic acids ( $\text{RC(O)OH}$ ), alcohols ( $\text{ROH}$ ), and, in some cases, 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 VOCs by the procedures outlined in Sections 3.1–3.9. The rigorous treatment of the other products would also require these procedures to be applied. However, as indicated in Section 2, this would lead to chemical schemes of unrealistic complexity, since the degradation of minor products is often far more complex than the degradation of the parent VOC.

In order to limit the complexity of the degradation schemes constructed by the present protocol, the further degradation of first and subsequent generation products is simplified in comparison with the parent VOCs. The carbonyl compounds formed from the  $\text{NO}_x$  catalysed chemistry (i.e. resulting from the reactions of  $\text{RO}_2$  with  $\text{NO}$ ) are the major products under most conditions and are thus degraded following the above procedure, but with some degree of simplification as described below. The organic nitrates, 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 is designed to give the correct lifetimes of the products, to maintain the carbon and nitrogen balance and to represent radical propagation and termination processes adequately. It should be noted, however, that some of the reactions are unbalanced in terms of hydrogen and oxygen, usually because the production of  $\text{O}_2$  or  $\text{H}_2\text{O}$  has not been included in the representation of the simplified or composite reaction. Some further simplification in the treatment of peroxy

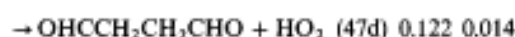


radicals formed from minor degradation products is also applied, as described in Section 3.10.10.

**3.10.1. Carbonyl compounds.** The degradation of these compounds follows the general rules outlined in Sections 3.1–3.9. Some simplification is achieved, however, by limiting the number of product channels which result from the attack of OH. The possible reaction channels and their relative importance are first defined, usually by SAR methods (Atkinson, 1987) as indicated in Section 3.1. For minor carbonyl compounds formed solely from the reactions of  $\text{RO}_2$  with  $\text{HO}_2$  or from the peroxy radical permutation reactions, only the major reaction channel is considered, with its rate scaled to account for total reaction rate assigned to the overall reaction. For the usually more significant carbonyl products formed from the  $\text{NO}_x$  catalysed chemistry, the overall importance of each channel, in terms of the degradation of the parent compound, is estimated as follows. The fractional conversion ( $\Psi$ ) of the parent compound into the carbonyl product under  $\text{NO}_x$ -rich conditions is calculated (disregarding nitrate formation). Any channel for which  $\Psi_{\text{SAR}} < 0.05$  (where  $f_{\text{SAR}}$  is the fractional contribution of a given OH + carbonyl reaction channel calculated using the SAR method) is disregarded, and the remaining channel(s) are scaled proportionately to account for the total reaction rate assigned to that overall reaction. If  $\Psi$  for a given carbonyl product is less than 0.05, only the major degradation route is included, once again scaled to account for the total reaction rate.

This procedure may be illustrated with the example of butane, the degradation scheme for which is shown schematically in Fig. 1. The minor degradation channel (which accounts for 14.7% of the reaction) leads to the production of two carbonyl products,  $n\text{-C}_3\text{H}_7\text{CHO}$  (24%) and  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO}$  (76%).  $n\text{-C}_3\text{H}_7\text{CHO}$  is a primary emitted compound (see the Appendix) and therefore treated independently.  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO}$  is not an emitted compound, and has to be degraded in the butane scheme. The value of  $\Psi$  for this compound is 0.112 ( $= 0.147 \times 0.76$ ). It has five possible OH-initiated degradation channels of calculated fractional contribution  $f_{\text{SAR}}$ :

$$f_{\text{SAR}} \quad \Psi_{\text{SAR}}$$



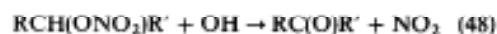
Since the product  $\Psi_{\text{SAR}}$  is only greater than 0.05 for channel (47a), the further degradation of this product is assumed to proceed by this channel alone, with its

rate scaled to account for the overall rate calculated by the SAR method.

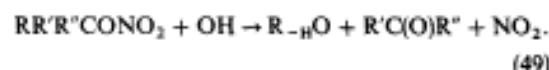
The SAR method of Atkinson (1987) is applicable to the majority of carbonyl products formed from the degradation of the species given in the Appendix, the major exceptions being the unsaturated carbonyls formed from isoprene and 1,3-butadiene. These are acrolein, methacrolein, methyl vinyl ketone and several  $\alpha,\beta$  unsaturated  $\gamma$  hydroxy aldehydes and ketones. Experimental data and recommended rate coefficients are available for the reactions of OH with acrolein, methacrolein, methyl vinyl ketone and the related compound, crotonaldehyde (Atkinson, 1989), and these data are used to infer rate coefficients and radical product distributions for all the related compounds. On the basis of these data, it is clear that the carbonyl group reduces the reactivity of the adjacent double bond towards OH. In the case of acrolein, the reaction is assumed to occur entirely by abstraction of the aldehydic H atom, and the associated rate coefficient ( $2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; Atkinson, 1989) is also assigned to aldehydic H abstraction in methacrolein, crotonaldehyde and the  $\alpha,\beta$  unsaturated  $\gamma$  hydroxy aldehydes. The recommended rate coefficients for methacrolein and crotonaldehyde then imply an OH addition rate coefficient to the double bond which is ca. 25% of those recommended by Atkinson (1994) for the corresponding alkenes, 2-methyl propene and 2-butene (*cis*- and *trans*-), respectively. Similarly, the recommended rate coefficient for methyl vinyl ketone at 298 K (Atkinson, 1989), compared with that for 1-butene (Atkinson, 1994), suggests that the OH addition rate to  $\alpha,\beta$  unsaturated ketones is ca. 60% of that of the corresponding alkene. Consequently, these factors and rate coefficients for the corresponding alkene (calculated using the method of Peeters *et al.*, 1994) are used to determine the OH addition rates to  $\alpha,\beta$  unsaturated  $\gamma$  hydroxy aldehydes and ketones. On the basis of data for allyl alcohol and propene (Atkinson, 1989, 1994), a hydroxy group is assumed to have no influence on the OH addition rate to an adjacent double bond.

**3.10.2. Organic nitrates ( $\text{RONO}_2$ ).** The degradation of organic nitrates may be initiated by reaction with OH, or photolysis. There is a significant body of kinetic data available for reactions of OH with alkyl nitrates (Atkinson, 1989, 1994). Where data are not available, the SAR method is applied to determine the overall rate coefficient (Section 3.1), but in the absence of product studies and as a scheme simplification measure, the chemistry is represented in each case by a single, generic product channel which regenerates  $\text{NO}_x$ , but removes  $\text{HO}_x$ :

primary and secondary nitrates:



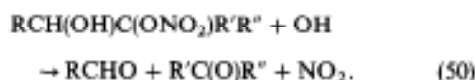
tertiary nitrates:





In the case of tertiary nitrates,  $R_{-H}O$  is a carbonyl product, which is assumed to be derived from the largest organic group containing an  $\alpha$ -hydrogen atom.

Organic nitrates possessing  $\beta$ -hydroxy groups may be generated from the reactions of  $\beta$ -hydroxy peroxy radicals with  $NO$ , or as alcohols ( $ROH$ ) from the  $NO_3$ -initiated oxidation of alkenes. Tertiary nitrates generated by the former are treated analogously to the following example:



The photolysis of all organic nitrates, other than those possessing  $\beta$ -hydroxy functionalities, is assumed to proceed by the reactions given in Table 4, with the appropriate photolysis parameter as shown.  $\beta$ -Hydroxy nitrates (or  $\beta$ -nitro-oxy alcohols) are assumed to be stable with respect to photolysis, on the basis of the significantly blue-shifted UV absorption spectrum reported for  $\beta$ -nitro-oxy ethanol (Roberts and Fajer, 1989).

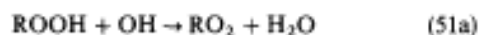
Where an organic nitrate also contains a remote carbonyl functionality, the inclusion of an additional photolysis pathway is also considered (see Section 3.10.9).

**3.10.3. Peroxy nitrates ( $ROONO_2$ ).** The major removal process for these species at low altitudes is thermal decomposition (Section 3.3.2). For the larger acyl peroxy nitrates in particular, however, removal by reaction with  $OH$  may make a minor contribution, and is also included. In the complete absence of mechanistic information, this is (notionally) assumed to enhance the thermal decomposition rate, i.e.



This reaction is strictly incorrect, since the release of  $NO_2$  (an odd electron species) should not be accompanied by the formation of an organic radical. However, the reaction is believed to be broadly acceptable from the point of view of boundary layer tropospheric chemistry, since it is only a minor fate for the peroxy nitrates. Literature rate coefficients are only available for the reactions of  $OH$  with  $CH_3C(O)OONO_2$  (Atkinson *et al.*, 1992) and  $CH_2=C(CH_3)C(O)OONO_2$  (Grosjean *et al.*, 1993b), and are consistent with reaction at the organic groups. In the case of  $CH_3C(O)OONO_2$ , the rate coefficient is in good agreement with the rate coefficient calculated using the SAR method, and the total reaction rate for other acyl peroxy nitrates is therefore also calculated using the SAR method.

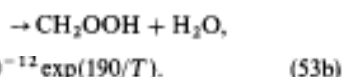
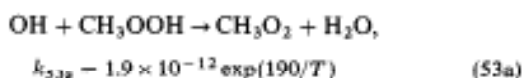
**3.10.4. Hydroperoxides ( $ROOH$ ).** The degradation of hydroperoxides may be initiated by reaction with  $OH$ , or photolysis. The reactions with  $OH$  are assumed to proceed by two channels, representing attack at the peroxide and organic groups, respectively:



For simplicity, the attack on the organic group is assumed to be exclusively adjacent to the  $-OOH$  group, with the species  $R_{-H}OOH$  decomposing rapidly to form a carbonyl compound,  $R_{-H}O$ , and  $OH$ , as is the case for  $CH_2OOH$ :



The rate of reaction (51a) is assumed to be the same as that for the analogous channel of the reaction of  $OH$  with  $CH_3OOH$  (Atkinson *et al.*, 1992):



The rate of reaction (53b) at 298 K,  $1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , indicates a significant activating influence of the  $-OOH$  group on the reactivity of the  $CH_3-$  group, which is consistent with a neighbouring group activation of  $\sim 13$ . This factor was therefore used to calculate the overall rate of reaction (51b) for hydroperoxides in general, using the SAR method. For tertiary hydroperoxides, reaction (51b) cannot be represented as described above owing to the absence of hydrogen atoms  $\alpha$  to the  $-OOH$  group. In these cases, therefore, the calculated overall rate of reaction by both channels is represented by channel (51a) alone.

The photolysis of all hydroperoxides is assumed to proceed as shown in Table 4, with the photolysis parameter equivalent to that for  $CH_3OOH$ . Where an organic hydroperoxide also contains a carbonyl functionality, the inclusion of an additional photolysis pathway is considered (see Section 3.10.9). Similarly to the  $\beta$ -nitro-oxy alcohols discussed in Section 3.10.2, the  $\beta$ -nitro-oxy hydroperoxides, formed from  $NO_3$ -initiated schemes, are assumed to have no "nitrate" photolysis channel.

**3.10.5. Percarboxylic acids ( $RC(O)OOH$ ).** Formed from the reactions of acyl peroxy radicals with  $HO_2$ , percarboxylic acids are assumed to be degraded in a similar way to the simple hydroperoxides, by the following reactions:



The overall rate of reaction of  $OH$  with  $RC(O)OOH$  at 298 K is determined by the SAR method, with the abstraction of the peroxide H assumed to occur at the same rate as reaction (53a). The total rate coefficient is assigned to reaction (54).

The photolysis of all percarboxylic acids is assumed to proceed by reaction (55) (see also Table 4), with the photolysis parameter equivalent to that for  $CH_3OOH$ . Where a percarboxylic acid also contains an additional carbonyl functionality, the inclusion of an additional photolysis pathway is considered (see Section 3.10.9).

3.10.6. *Carboxylic acids* (RC(O)OH). Simple carboxylic acids are degraded by reaction with OH radicals only. The total rate coefficient (measured or calculated) for the reaction with OH is assigned to the following single product channel:

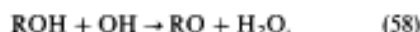


Although photolysis is unimportant for the simple acids, the inclusion of a photolysis pathway is considered for carboxylic acids containing an additional carbonyl functionality (see Section 3.4).

3.10.7. *Alcohols* (ROH). Simple alcohols are degraded by reaction with OH radicals only. The total rate coefficient (measured or calculated) for the reaction with OH is assigned to a single product channel, as follows. For primary and secondary alcohols:



For tertiary alcohols:



Where an alcohol also contains a remote carbonyl functionality, the inclusion of a photolysis pathway is also considered (see Section 3.4).

3.10.8. *The reactions of O<sub>3</sub> and NO<sub>3</sub> with unsaturated degradation products.* Many of the degradation products of dienes (in the present work, 1,3-butadiene and isoprene) contain an unsaturated linkage and therefore potentially react with O<sub>3</sub> and NO<sub>3</sub>. These reactions are considered only for the major carbonyl degradation products, which in the present work are acrolein, methacrolein, methyl vinyl ketone and some  $\alpha,\beta$  unsaturated aldehydes and ketones.

Rate coefficients for the reactions of O<sub>3</sub> with acrolein, methacrolein and methyl vinyl ketone have been recommended by Atkinson (1994), and those for the  $\alpha,\beta$  unsaturated aldehydes are taken as 6% of the values for the alkene of the same degree of substitution, as given in Table 1. This is based on a comparison between the recommended values for the reactions involving acrolein and methacrolein, and those for the corresponding alkenes, propene and 2-methyl propene. The available rate coefficients for methyl vinyl ketone and 3-pentene-2-one (Greene and Atkinson, 1994) are ca. 50 and 20%, respectively, of the corresponding rate coefficients for 1-butene and 2-butene (*cis*- and *trans*-) (Atkinson, 1994), suggesting that an adjacent ketone group does not reduce the reactivity of a double bond to O<sub>3</sub> to the same extent as an adjacent aldehyde group. Thus, the rate coefficients for  $\alpha,\beta$  unsaturated ketones are assumed to be 35% of the values for the corresponding alkene (Table 1). The degradation mechanism follows the rules described in Sections 3.2 and 3.7.

The rate coefficients for the reactions of NO<sub>3</sub> with acrolein and the related compound, crotonaldehyde, have been measured (Atkinson, 1991). By comparison with the reaction of NO<sub>3</sub> with acetaldehyde, the data are consistent with exclusive aldehydic H atom ab-

straction in acrolein, and predominant aldehydic H atom abstraction in crotonaldehyde. The measured rate coefficient for acrolein is used in the present work, and those for methacrolein and the  $\alpha,\beta$  unsaturated aldehydes are taken to be equivalent to that for the reaction involving acetaldehyde (Section 3.3.1), with the reaction assumed to proceed entirely by abstraction of the aldehydic H atom. Since these data imply a significant deactivating influence of an adjacent carbonyl group on the rate of reaction of NO<sub>3</sub> at a double bond, the rate coefficients for the reactions of methyl vinyl ketone and other  $\alpha,\beta$  unsaturated ketones with NO<sub>3</sub> are assumed to be at least five orders of magnitude lower than the rate coefficient for their reactions with OH, and the reactions are therefore excluded on the basis of the relation given in Section 3.3.

3.10.9. *The photolysis of multifunctional compounds.* Some degradation products contain more than one functionality for which photolysis may occur, and therefore possible competing photolysis reactions. In order to decide which photolysis routes should be represented for a multifunctional compound, the various photolysis routes are first assigned and their rates estimated (for a solar zenith angle of 65°) on the basis of the reactions and parameters given in Tables 3 and 4. The compound is assumed to be photolysed by the major photolysis route, and any other routes for which the estimated rate is  $\geq 20\%$  of the major route. Thus, for a compound containing a primary aldehyde group ( $J_1 = 6.57 \times 10^{-6} \text{ s}^{-1}$ ) and a ketone group ( $J_2 = 1.02 \times 10^{-6} \text{ s}^{-1}$ ), only the aldehyde photolysis pathway is assumed to occur. A primary nitrate ( $J_3 = 4.39 \times 10^{-7} \text{ s}^{-1}$ ) which also contains a remote ketone group, however, is assumed to photolyse by both the associated pathways, as given in Table 4.

3.10.10. *Reactions of peroxy radicals formed from minor products.* Peroxy radicals (RO<sub>2</sub>) formed solely from the degradation of certain minor products, which are themselves only formed from reactions of RO<sub>2</sub> with HO<sub>2</sub> or peroxy radical permutation reactions, are assumed to undergo a simplified series of reactions. These are similar to those outlined in Section 3.6 in that the considered reaction partners are NO, NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub> and other peroxy radicals, but the number of product channels is reduced, and the reaction products are removed by simplified reactions.

The reactions with NO are assumed not to produce organic nitrates, irrespective of the size or nature of the organic group. The reactions with HO<sub>2</sub> (reaction (14)) and the permutation reactions (reaction (17)) are assumed to proceed exclusively via the major channels (14a) and (17a), respectively. The reactions of OH with the product hydroperoxides and percarboxylic acids are assumed to regenerate the peroxy radicals exclusively by reactions (51a) and (54), with the total rate coefficient calculated as described above in Sections 3.10.4 and 3.10.5.

## 4. DISCUSSION

The rules presented above are designed as guidelines for the generation of detailed chemical degradation schemes which give a comprehensive description of the chemistry of VOCs under tropospheric conditions. The resultant schemes incorporate differences in reactivity and a series of possible initiation reactions for the VOCs and oxidised organic products, in addition to taking account of the influence of structural differences on the rates and products of the reactions of the reactive radical intermediates with a range of key species. Consequently, schemes generated using this protocol are believed to be particularly appropriate for comparative assessments of the formation of oxidants (e.g. ozone) from the degradation of organic compounds.

These schemes aim to reflect recent advances in the availability of kinetic and mechanistic data relevant to the tropospheric degradation of VOCs. However, it is recognised that there are still uncertainties in some aspects of VOC degradation, particularly concerning radical and  $\text{NO}_x$  sinks, which can influence predictions of ozone formation. Future work will therefore concentrate on the validation of chemical mechanisms constructed using this protocol: this will be achieved both by comparison of product simulations with environmental chamber data, and by incorporation of the chemical mechanisms into suitable tropospheric models (e.g. as described by Derwent *et al.*, 1996), allowing comparison of model predictions with atmospheric observational data.

Although the rules presented above lead to the generation of detailed degradation schemes, they

Table 10. Mechanism describing the OH-initiated oxidation of isoprene to first generation products at 298 K<sup>a</sup>

Reaction	Rate coefficient $\times$ branching ratio <sup>b</sup> ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
<i>Initiation</i>	
$\text{OH} + \text{isoprene} (+ \text{O}_2) \rightarrow \text{R1O}_2$	$1.01 \times 10^{-10} \cdot 0.164$
$\text{OH} + \text{isoprene} (+ \text{O}_2) \rightarrow \text{R2O}_2$	$1.01 \times 10^{-10} \cdot 0.491$
$\text{OH} + \text{isoprene} (+ \text{O}_2) \rightarrow \text{R5O}_2$	$1.01 \times 10^{-10} \cdot 0.086$
$\text{OH} + \text{isoprene} (+ \text{O}_2) \rightarrow \text{R6O}_2$	$1.01 \times 10^{-10} \cdot 0.259$
<i>Peroxy radical permutation reactions</i>	
$\text{R1O}_2 \rightarrow \text{R1O}$	$1.30 \times 10^{-12} \cdot 0.60 \cdot \text{RO2}$
$\rightarrow \text{R15OH}$	$1.30 \times 10^{-12} \cdot 0.20 \cdot \text{RO2}$
$\rightarrow \text{C51}$	$1.30 \times 10^{-12} \cdot 0.20 \cdot \text{RO2}$
$\text{R2O}_2 \rightarrow \text{R2O}$	$1.60 \times 10^{-12} \cdot 0.70 \cdot \text{RO2}$
$\rightarrow \text{R23OH}$	$1.60 \times 10^{-12} \cdot 0.30 \cdot \text{RO2}$
$\text{R5O}_2 \rightarrow \text{R5O}$	$1.30 \times 10^{-12} \cdot 0.60 \cdot \text{RO2}$
$\rightarrow \text{R15OH}$	$1.30 \times 10^{-12} \cdot 0.20 \cdot \text{RO2}$
$\rightarrow \text{C55}$	$1.30 \times 10^{-12} \cdot 0.20 \cdot \text{RO2}$
$\text{R6O}_2 \rightarrow \text{R6O}$	$1.40 \times 10^{-12} \cdot 0.60 \cdot \text{RO2}$
$\rightarrow \text{R46OH}$	$1.40 \times 10^{-12} \cdot 0.20 \cdot \text{RO2}$
$\rightarrow \text{C56}$	$1.40 \times 10^{-12} \cdot 0.20 \cdot \text{RO2}$
<i>Peroxy radical reactions with HO<sub>2</sub></i>	
$\text{R1O}_2 + \text{HO}_2 \rightarrow \text{R1OOH} + \text{O}_2$	$1.63 \times 10^{-11}$
$\text{R2O}_2 + \text{HO}_2 \rightarrow \text{R2OOH} + \text{O}_2$	$1.63 \times 10^{-11}$
$\text{R5O}_2 + \text{HO}_2 \rightarrow \text{R5OOH} + \text{O}_2$	$1.63 \times 10^{-11}$
$\text{R6O}_2 + \text{HO}_2 \rightarrow \text{R6OOH} + \text{O}_2$	$1.63 \times 10^{-11}$
$(\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2)$	$2.84 \times 10^{-12}$
<i>Peroxy radical reactions with NO</i>	
$\text{R1O}_2 + \text{NO} \rightarrow \text{R1O} + \text{NO}_2$	$3.80 \times 10^{-12} \cdot 0.90$
$\rightarrow \text{R1ONO}_2$	$3.80 \times 10^{-12} \cdot 0.10$
$\text{R2O}_2 + \text{NO} \rightarrow \text{R2O} + \text{NO}_2$	$3.80 \times 10^{-12} \cdot 0.90$
$\rightarrow \text{R2ONO}_2$	$3.80 \times 10^{-12} \cdot 0.10$
$\text{R5O}_2 + \text{NO} \rightarrow \text{R5O} + \text{NO}_2$	$3.80 \times 10^{-12} \cdot 0.90$
$\rightarrow \text{R5ONO}_2$	$3.80 \times 10^{-12} \cdot 0.10$
$\text{R6O}_2 + \text{NO} \rightarrow \text{R6O} + \text{NO}_2$	$3.80 \times 10^{-12} \cdot 0.90$
$\rightarrow \text{R6ONO}_2$	$3.80 \times 10^{-12} \cdot 0.10$
$(\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2)$	$8.30 \times 10^{-13}$
<i>Oxy radical reactions (assumed instantaneous)</i>	
$\text{R1O} (\text{isom.}/\text{O}_2) \rightarrow \text{C55} + \text{HO}_2$	
$\text{R2O} (\text{decomp.}/\text{O}_2) \rightarrow \text{MVK} + \text{HCHO} + \text{HO}_2$	
$\text{R5O} (\text{isom.}/\text{O}_2) \rightarrow \text{C51} + \text{HO}_2$	
$\text{R6O} (\text{decomp.}/\text{O}_2) \rightarrow \text{MACR} + \text{HCHO} + \text{HO}_2$	

<sup>a</sup> Species nomenclature after Jenkin and Hayman (1995). Key to species identity given in Fig. 4.

<sup>b</sup>  $T = 298 \text{ K}$ ;  $P = 1 \text{ atm}$ .

incorporate a degree of strategic simplification designed to limit the total number of reactions in a given scheme. As outlined in Section 2, this is partially achieved by disregarding minor channels resulting from the attack of OH on some VOCs, and also by parameterising the "permutation reactions" of the peroxy radical intermediates. As an illustration, the mechanism describing the OH-initiated degradation of isoprene to first generation products, written using the present protocol (shown in Table 10), has been used to calculate the yields of the products, both in the presence of high  $\text{NO}_x$  concentrations

and in the absence of  $\text{NO}_x$ , for comparison with product yields obtained in laboratory studies (Gu *et al.*, 1985; Atkinson *et al.*, 1989; Tuazon and Atkinson, 1990; Becker *et al.*, 1994). The experimental results, and the results of the calculations, are summarised in Table 11. Also presented are the yields calculated recently by Jenkin and Hayman (1995), using a detailed chemical mechanism containing 40 reactions with 83 product channels, which was shown to give a reasonable description of the observed product yields both in the presence and absence of  $\text{NO}_x$ .

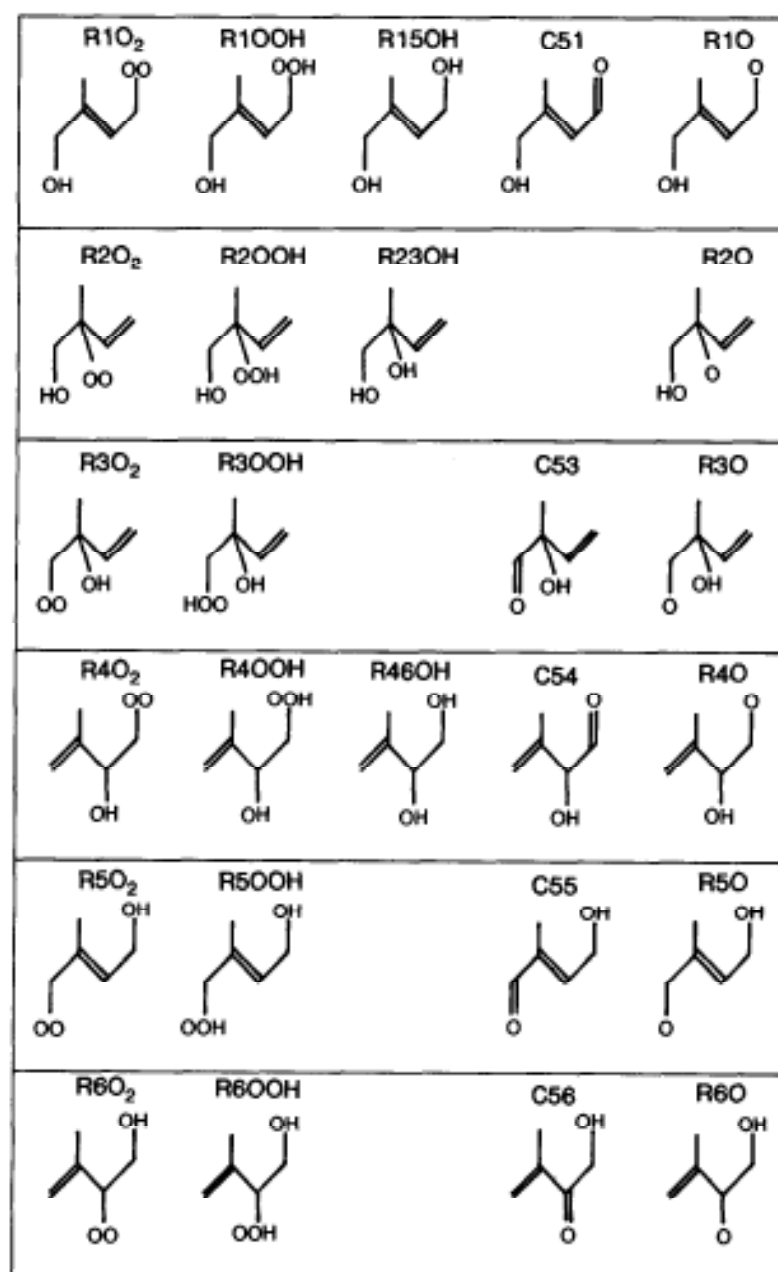


Fig. 4. Identification chart for the species in the chemical mechanism in Table 10.

Table 11. Reported and calculated molar product yields from the OH-initiated oxidation of isoprene

Product <sup>a</sup>	NO <sub>x</sub> present			NO <sub>x</sub> absent			
	% b	% c	% d	% e	% f	% c	% d
HCHO	67 ± 7	(65.4)	(67.5)	32 ± 3	~ 34	(29.1)	(27.4)
MVK	36 ± 3	(42.2)	(44.2)	15 ± 2	~ 17	(13.7)	(13.7)
MACR	25 ± 3	(23.2)	(23.3)	17 ± 3	~ 22	(15.4)	(13.7)
3-Methyl furan	4 ± 2	( 4.2)	—	1.5 ± 0.3		( 2.3)	—
Organic nitrates	14 ± 5	(10.0)	(10.0)			( 0.0)	(0.0)
Hydroperoxides		( 0.0)	(0.0)	~ 48		(42.4)	(40.2)
Alcohols		( 0.0)	(0.0)			( 7.6)	(10.4)
Carbonyls	21 ± 5	(20.4)	(22.5)	18 ± 7		(18.6)	(22.0)
<i>Hydroperoxides<sup>a</sup></i>							
R1OOH		( 0.0)	(0.0)			( 3.8)	(2.8)
R2OOH		( 0.0)	(0.0)			(30.4)	(31.6)
R3OOH		( 0.0)	—			( 0.9)	—
R4OOH		( 0.0)	—			( 0.9)	—
R5OOH		( 0.0)	(0.0)			( 2.1)	(1.5)
R6OOH		( 0.0)	(0.0)			( 4.3)	(4.5)
<i>Alcohols<sup>a</sup></i>							
R15OH		( 0.0)	(0.0)			( 2.5)	(4.3)
R23OH		( 0.0)	(0.0)	~ 5		( 2.2)	(5.9)
R46OH		( 0.0)	(0.0)	~ 2		( 2.9)	(4.5)
<i>Carbonyls<sup>a</sup></i>							
C51 <sup>b</sup>		( 7.0)	(7.7)			( 5.9)	(7.3)
C53		( 0.0)	—			( 0.8)	—
C54		( 0.0)	—			( 0.8)	—
C55 <sup>a</sup>		(13.4)	(14.8)			( 8.4)	(10.1)
C56		( 0.0)	(0.0)			( 2.7)	(4.6)

<sup>a</sup> MVK = methyl vinyl ketone, MACR = methacrolein, carbonyls = carbonyl species other than MVK, MACR and HCHO. <sup>b</sup> Yields quoted by Paulson *et al.* (1992) on the basis of their results, and those of Gu *et al.* (1985), Atkinson *et al.* (1989) and Tuazon and Atkinson (1990). <sup>c</sup> Yields calculated using the detailed mechanism of Jenkin and Hayman (1995) (see text). <sup>d</sup> Yields calculated using the mechanism based on current protocol (see Table 10). <sup>e</sup> Data of Becker *et al.* (1993, 1994). <sup>f</sup> Data of Miyoshi *et al.* (1994). <sup>g</sup> Species nomenclature after Jenkin and Hayman (1995). See Fig. 4 for species identity. <sup>h</sup> These species have been detected, but not quantified (Kwok *et al.*, 1995).

The mechanism of Jenkin and Hayman (1995) described the formation of six peroxy radicals from the addition of OH to isoprene, and treated the permutation reactions of the peroxy radicals explicitly, with rate coefficients based on trends of reactivity of less complex peroxy radicals possessing similar structural features. The assignment of structure-dependent rate coefficients to these reactions was found to be crucial in explaining the relative yields of the products in the absence of NO<sub>x</sub>, in particular the difference in the relative yield of methyl vinyl ketone (MVK) and methacrolein (MACR) compared with that observed (and calculated) in the presence of NO<sub>x</sub>. However, this chemistry made a large contribution to the size of the mechanism, requiring 21 reactions with 51 product channels. In comparison, the present mechanism is considerably reduced in size, possessing only 17 reactions with 31 product channels in total. The reduction is achieved by neglecting two of the six peroxy radicals, which together only represent about 9.5% of the initial radical yield (Section 3.1), and as a result of the parameterised representation of the permutation re-

actions (Section 3.6.5), which only requires four reactions with 11 product channels. As shown in Table 11, the yields of the products calculated using the present scheme compare well with those calculated with the more complex scheme of Jenkin and Hayman (1995), and are also in reasonable agreement with the results of laboratory studies. The only notable difference in the yields calculated using the two mechanisms is the absence of the experimentally observed minor product, 3-methyl furan, which is produced in the mechanism of Jenkin and Hayman (1995) from the chemistry of the two minor peroxy radicals eliminated from the present mechanism.

It should also be noted that the effect of the parameterisation of the peroxy radical permutation reactions is a strong function of the number of peroxy radicals in the scheme (see also Madronich and Calvert, 1990). In a scheme involving  $n$  peroxy radicals, the explicit representation requires  $\frac{1}{2}n(n+1)$  reactions, whereas the parameterised representation is only  $n$  reactions. Thus, in the scheme describing the degradation of the VOCs given in the Appendix,

which involves approximately 500 peroxy radicals, the parameterised representation of about 500 reactions is clearly a colossal (and essential) reduction on the approximately 12,500 reactions necessary for an explicit representation.

It is clear that, even with the simplification measures described above, the degradation schemes generated using the protocol are very complex. Consequently, a full mechanism treating a large number of VOCs (e.g. as shown in the Appendix) may only generally be used in chemical box models, or in models with a comparatively economical representation of meteorology and transport. Since the mechanisms are designed to be applicable to a wide range of ambient conditions, however, there is considerable scope for mechanism reduction for models of specific tropospheric environments requiring a more sophisticated representation of transport processes. Thus, the detailed mechanisms generated by the protocol described above provide a suitable starting point for the generation of reduced chemical mechanisms, where the reductions are achieved by a rigorous procedure using objective methods, rather than by making significant *a priori* assumptions.

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APPENDIX: VOLATILE ORGANIC COMPOUNDS FOR WHICH DEGRADATION SCHEMES HAVE BEEN WRITTEN USING THE PRESENT PROTOCOL (see Section 1)

Alkanes

Methane

Ethane

Propane

Butane (*n*-butane)

2-Methyl propane (*i*-butane)

Pentane (*n*-pentane)

2-Methyl butane (*i*-pentane)

2,2-Dimethyl butane

2,3-Dimethyl butane

Cyclohexane

Heptane (*n*-heptane)

2-Methyl hexane

3-Methyl hexane

Octane (*n*-octane)

2,2-Dimethyl propane ( <i>neo</i> -pentane)	Nonane ( <i>n</i> -nonane)
Hexane ( <i>n</i> -hexane)	Decane ( <i>n</i> -decane)
2-Methyl pentane	Undecane ( <i>n</i> -undecane)
3-Methyl pentane	Dodecane( <i>n</i> -dodecane)
<i>Alkenes</i>	
Ethene (ethylene)	<i>trans</i> -2-Pentene
Propene (propylene)	2-Methyl 1-butene
Methyl propene (butylene)	3-Methyl 1-butene
1-Butene	2-Methyl 2-butene
<i>cis</i> -2-Butene	1-Hexene
<i>trans</i> -2-Butene	<i>cis</i> -2-Hexene
1-Pentene	<i>trans</i> -2-Hexene
<i>cis</i> -2-Pentene	
<i>Dialkenes</i>	
1,3-Butadiene	2-Methyl 1,3-butadiene (isoprene)
<i>Alkynes</i>	
Ethyne (acetylene)	
<i>Aldehydes</i>	
Methanal (formaldehyde)	Butanal (butyraldehyde)
Ethanal (acetaldehyde)	Methyl propanal ( <i>i</i> -butyraldehyde)
Propanal (propionaldehyde)	Pentanal (valeraldehyde)
<i>Ketones</i>	
2-Propanone (acetone)	2-Hexanone
2-Butanone (methyl ethyl ketone)	3-Hexanone
2-Pentanone	2-Methyl 4-pentanone (methyl <i>i</i> -butyl ketone)
3-Pentanone	3,3-Dimethyl 2-butanone (methyl <i>t</i> -butyl ketone)
3-Methyl 2-butanone (methyl <i>t</i> -propyl ketone)	Cyclohexanone
<i>Alcohols and glycols</i>	
Methanol	2-Methyl 1-butanol
Ethanol	2-Methyl 2-butanol ( <i>t</i> -amyl alcohol)
1-Propanol ( <i>n</i> -propanol)	3-Methyl 1-butanol ( <i>i</i> -amyl alcohol)
2-Propanol ( <i>i</i> -propanol)	3-Methyl 2-butanol
1-Butanol ( <i>n</i> -butanol)	Cyclohexanol
2-Butanol ( <i>sec</i> -butanol)	4-Hydroxy 4-methyl 2-pentanone (diacetone alcohol)
2-Methyl 1-propanol ( <i>i</i> -butanol)	Ethane 1,2-diol (ethylene glycol)
2-Methyl 2-propanol ( <i>t</i> -butanol)	Propane 1,2-diol (propylene glycol)
3-Pentanol	
<i>Ethers and glycol ethers</i>	
Dimethyl ether	2-Methoxy ethanol
Diethyl ether	1-Methoxy 2-propanol (methoxypropanol)
Di- <i>i</i> -propyl ether	2-Ethoxy ethanol
Methyl <i>t</i> -butyl ether	2-Butoxy ethanol (butyl glycol)
Ethyl <i>t</i> -butyl ether	1-Butoxy 2-propanol
<i>Esters</i>	
Methyl methanoate (methyl formate)	<i>i</i> -Propyl ethanoate ( <i>n</i> -propyl acetate)
Methyl ethanoate (methyl acetate)	<i>n</i> -Butyl ethanoate ( <i>n</i> -butyl acetate)
Ethyl ethanoate (ethyl acetate)	<i>sec</i> -Butyl ethanoate ( <i>sec</i> -butyl acetate)
<i>n</i> -Propyl ethanoate ( <i>n</i> -propyl acetate)	<i>t</i> -Butyl ethanoate ( <i>t</i> -butyl acetate)
<i>Organic acids</i>	
Methanoic acid (formic acid)	Propanoic acid (propionic acid)
Ethanoic acid (acetic acid)	
<i>Chloro- and hydrochlorocarbons</i>	
Chloromethane (methyl chloride)	Trichloroethene
Dichloromethane (methylene chloride)	Tetrachloroethene (perchloroethene)
Trichloromethane (chloroform)	<i>cis</i> -1,2-Dichloroethene
1,1,1-Trichloroethane (methyl chloroform)	<i>trans</i> -1,2-Dichloroethene