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Rate constants for the reaction of NO and HO_2 with peroxy radicals formed from the reaction of OH, Cl or NO_3 with alkenes, dienes and α,β-unsaturated carbonyls

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Abstract

Rate constants for the gas-phase reaction of NO and HO_2 radicals with 33 peroxy radicals are presented. The peroxy radicals are derived from the addition of either OH, Cl, or NO_3 radicals, followed by addition of O_2, to a series of alkenes: tetrachloroethene, ethene, 1,2–dimethyl but–2–ene, butadiene, 2,3,4,5–tetramethyl hexa–1,3–diene, 1,1,2,3,4,4–hexachlorobutadiene but–1–ene–3–one (methyl vinyl ketone) and 2,3–dimethylpen–2–ene–4–one. The rate constants were predicted using a correlation between the singly occupied molecular orbital (SOMO) energy of the peroxy radical and the logarithm of the rate constant for reaction with NO or HO_2. A discussion of the accuracy of the method and the trends in the reactivity of the titled peroxy radicals is given. Peroxy radicals derived from halogenated alkenes have larger values of rate constants for reaction with NO relative to reaction with HO_2, indicating that they are more likely to react with NO, rather than HO_2, in the atmosphere. The reverse is true for peroxy radicals derived from alkylated alkenes.

Keywords

HOMO energy, SOMO energy, Halogenated alkenes, Alkylated alkenes, Troposphere oxidation, peroxy radical.

1.Introduction

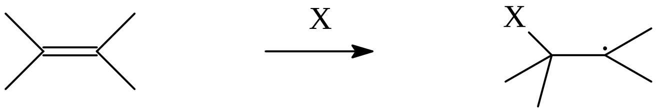
Organic peroxy radicals are formed in the atmosphere during the oxidation of organic species (Alfassi, 1997; Fowler *et al.*, 1997; Lightfoot *et al.*, 1992; Wayne, 2000). Alkenes are an important group of organic pollutants produced by biogenic and anthropogenic sources(Finlayson-Pitts and Pitts, 2000; Wayne, 2000). The addition of atmospheric oxidants, hydroxyl, nitrate or chlorine radicals, to the double bond of these species leads to an alkyl radical which, in the presence of oxygen, forms an organic peroxy radical, RO_2 (Alfassi, 1997; Lightfoot *et al.*, 1992; Wallington *et al.*, 1997). Under the correct conditions the peroxy radical forms part of a chain reaction leading to ozone formation (Fowler *et al.*, 1997). The reaction of NO with RO_2 (1) leads to NO_2 formation, thus the reaction of RO_2 with NO is a propagating reaction in the ozone formation cycle, whereas the reaction of RO_2 with HO_2 (2) is a terminating reaction.(Alfassi, 1997; Fowler *et al.*, 1997; Lightfoot *et al.*, 1992)

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (1)$$

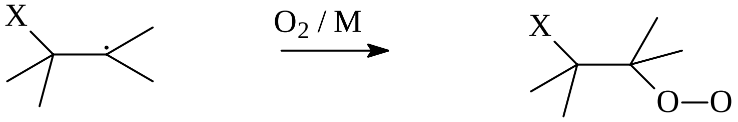
$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (2)$$

Hence, the concentrations of HO_2 and NO in the atmosphere and the reactivity of a peroxy radical towards NO or HO_2 are important in calculating the ozone forming potential of an organic compound as it is oxidised in the atmosphere (Derwent *et al.*, 1996; Derwent *et al.*, 1998). Rate constants for the reaction of NO and HO_2 with a number of organic peroxy radicals are known (Alfassi, 1997; Lightfoot *et al.*, 1992; Wallington *et al.*, 1997). However peroxy radicals are difficult to synthesise, especially multifunction peroxy radicals resulting from the reaction of nitrate, hydroxyl or chlorine with an alkene, hence a method of estimating these rate constants would be extremely useful.

In this work, estimated values for the rate constants for the reaction of NO and HO_2 with 33 organic peroxy radicals are reported. The peroxy radicals studied are those that would result from the addition of OH, Cl or NO_3 to a double bond of an alkene followed by the subsequent addition of O_2. The alkenes chosen are tetrachloroethene, ethene, 1,2-dimethyl but-2-ene, butadiene, 2,3,4,5-tetramethyl hexa-1,3-diene, 1,1,2,3,4,4–hexachlorobutadiene, but-1-ene-3-one (methyl vinyl ketone) and 1,1,2-trimethyl but-1-ene-3-one. The alkenes were chosen to represent a wide range of compounds and produce peroxy radicals likely to have very different reactivity towards the radicals NO and HO_2. Tetrachloroethene, ethene and 1,2-dimethyl but-2-ene, are alkenes which contain only one double bond. The addition of NO_3, Cl or OH followed by the addition of O_2 to these alkenes produces only one peroxy radical isomer. In the case of the addition of X (X = NO_3, Cl or OH) to 1,2-dimethyl but-2-ene:

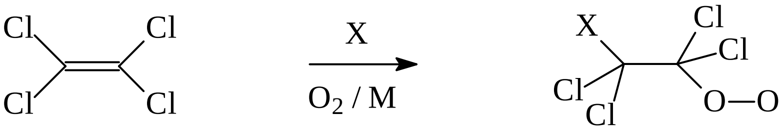


(3)



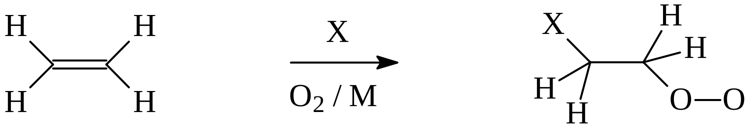
(4)

and in the case of the attack of X with tetrachloroethene:



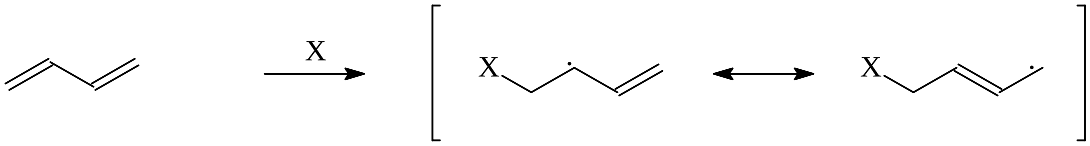
, (5)

and ethene:



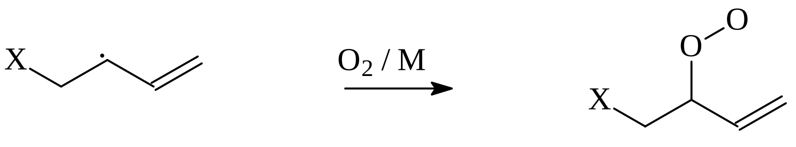
(6)

However, the reaction of NO_3, Cl or OH with a conjugated diene, followed by addition of O_2, can lead to different peroxy radical isomers. The reaction of X with butadiene results in the resonance stabilised radical shown below:

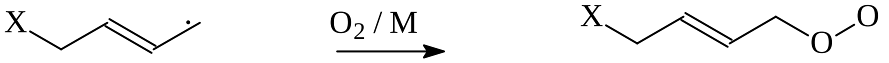


(7)

The radical can add oxygen in one of two positions leading to two isomeric peroxy radicals:

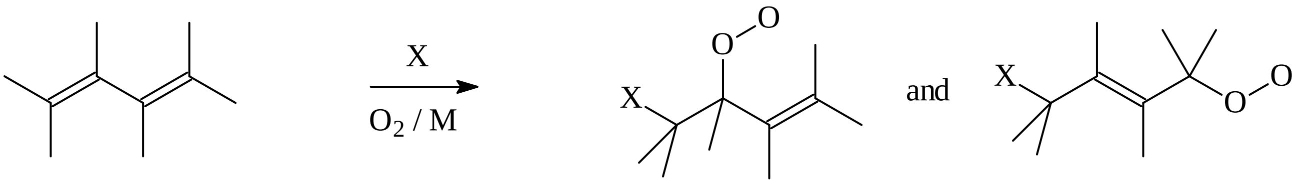


(8a)



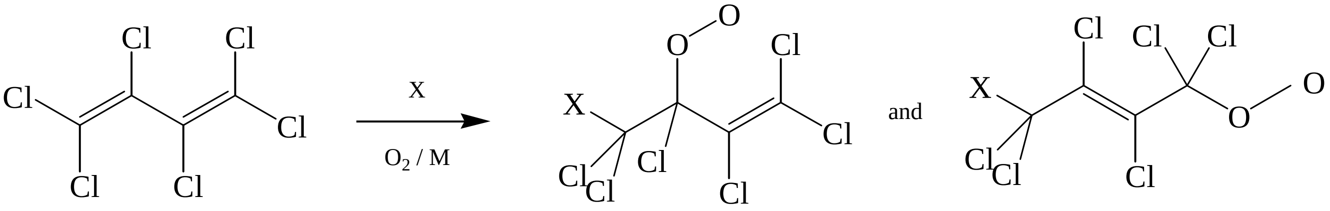
(8b)

Applying a similar mechanism to 2,3,4,5-tetramethyl hexa-1,3-diene results in the following two possible peroxy radical isomers.



(9)

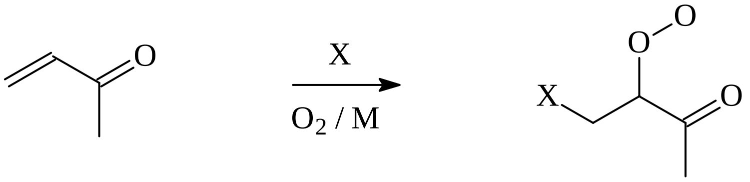
and similarly for 1,1,2,3,4,4-hexachlorobutadiene,



(10)

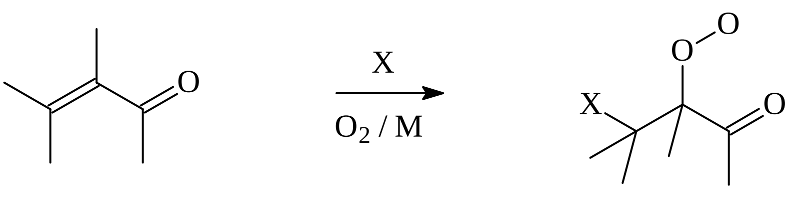
Both of the peroxy radical isomers that can result from the addition of NO_3, Cl or OH to a conjugated diene are considered in this paper to see if either isomer is more reactive with NO or HO_2. It is not the aim of this paper to predict the relative ratios of the peroxy radicals formed in reactions 7–10.

The reaction of α,β-unsaturated carbonyl compounds with NO_3, Cl and OH is similar to that of monoalkenes except that there is a strong tendency for the radical to add to the β-carbon. Thus, for methyl vinyl ketone the following peroxy radical is formed:



(11)

and for 2,3-dimethyl pen-2-ene-4-one,



(12)

The aim of this work is to determine the reaction rate constants for the reaction of the peroxy radicals formed in reactions 4–6 and 8–12 with NO and HO_2. The method used to determine the value of the rate constants will now be explained.

A correlation exists between the singly occupied molecular orbital (SOMO) energy, E_{SOMO}, of an organic peroxy radical and the logarithm of the rate constants for the reaction between NO or HO_2 and the organic peroxy radical. The correlation takes the mathematical form:

$$-\ln (k / \mathrm{cm}^3 \text{ molecule}^{-1} \mathrm{s}^{-1}) = -\mathrm{m}\, E_{\mathrm{SOMO}} + \mathrm{c} \qquad \text{(I)}$$

where the values of *m* and *c* are determined based on experimentally measured values for the rate constants, *k*, and values of E_{SOMO} that have been calculated using quantum mechanical methods. The estimation technique is based on our previous work (King *et al.*, 2001), reported in this journal. The reactions between organic peroxy radicals and NO or HO_2 have been shown to be controlled by the frontier molecular orbitals, *i.e.* the important orbital interactions during the reaction are between the singly occupied molecular orbital (SOMO) of the organic peroxy radical and the SOMO of

NO or HO_2(King *et al.*, 2001). Our previous work,(King *et al.*, 2001), in which values of *m* and *c* for equation (I) were determined, was exploratory. The calculations used to determine values of E_{SOMO} were undertaken at a very modest level of theory (ROB3LYP/6-31G*//AM1) and the database of experimental rate constants for the reaction of organic peroxy radicals with NO and HO_2 used was not complete. We have therefore chosen to re-determine the coefficients *m* and *c* for equation (I) using a more robust level of theory to calculate E_{SOMO} and we have attempted to use all known experimental determinations of the value of rate constants of the reactions of NO or HO_2 with organic peroxy radicals. Information on frontier molecular orbital theory can be found in (Albright *et al.*, 1985; Dewar and Dougherty, 1975; Fleming, 1996) and information on the correlation of frontier orbital energies with the logarithm of rate constants can be found in (King *et al.*, 1999a; King *et al.*, 1999b; King *et al.*, 2001; Klopman, 1968; Marston *et al.*, 1999; Salem, 1968a; Salem, 1968b).

2. Method.

The NIST reaction data base (NIST standard reference data 17 version 7.0, web version public release 1.1)(NIST, 2000) was used to provide values of rate constants for the reactions of HO_2 and NO with organic peroxy radicals with which to determine the values of *m* and *c*. If more than one determination of a rate constant existed the IUPAC recommendation (2001 web version December 2001) based on evaluations (Atkinson *et al.*, 1997a; Atkinson *et al.*, 1997b; Atkinson *et al.*, 1999; Atkinson *et al.*, 2000; Atkinson *et al.*, 1997c) was used, otherwise the values were simply averaged. The database presented here is considerably larger than the previous work. The values of E_{SOMO} were calculated using the Gaussian 98 computer program (Frisch *et al.*, 1995)at the ROB3LYP/6-311+G(2d,p)//ROB3LYP/6-31+G(d,p) level of theory. Conformers of the peroxy radicals were investigated at the ROB3LYP/6-31G*//AM1 level of theory and the conformer with the lowest Self Consistent Field energy was used for the calculation of E_{SOMO} at the higher level of theory. Table 1 details the values of E_{SOMO} and *k* used to determine *m* and *c* by fitting to a re-arranged equation (I)

$$k = e^{c} \times e^{-mE_{\mathrm{SOMO}}} \qquad \text{(II)}$$

with each data point receiving equal weighting. In our previous work (King *et al.*, 2001) equation (I) was used to calculate *m* and *c*.

3. Results

Table 1 contains the calculated SOMO energies of the peroxy radicals under study. Table 2 contains the predicted rate constants for the reaction of the peroxy radicals formed in reactions 4–6 and 8–12 with NO and HO_2. Figure 1 demonstrates the linear correlation (equation (I)) between the logarithm of rate constant and the E_{SOMO} for reactions of NO and HO_2 with organic peroxy radicals from table 1. Equation (II) is fitted to the data in figure 1 and the values of *m* and *c* displayed in table 3.

4. Discussion

The discussion presented here will focus on two aspects of the work. The first aspect will be the reliability of the correlation using equation (I) and the second will be the consideration of the reactivity of the peroxy radicals in table 2 towards NO and HO_2. The ability of the correlation to predict accurate rate constants can be estimated by comparing the rate constant predicted, $k_{\mathrm{predicted}}$, with the experimentally measured rate constant, k_{measured}. Histograms of $\ln\left(\frac{k_{\mathrm{predicted}}}{k_{\mathrm{measured}}}\right)$ values were compiled for the reactions of the organic peroxy radicals shown table 1 with NO and HO_2 and are plotted in figures 3 and 4. A normal function was fitted to the distributions in figure 2. The mean of the normal function is a measure of over- or under-prediction of a rate constant (relative to a measured rate constant). For reactions of peroxy radicals with NO and HO_2 the mean values of $\frac{k_{\mathrm{predicted}}}{k_{\mathrm{measured}}}$ are 1.01 and 0.931 respectively, (i.e. over predicts on average by ~1% and under predicts by ~7% for NO and HO_2 respectively). The probabilities of predicting a rate constant within a factor of 2 of a measured rate constants using the data from table 1, are 92% and 86% for reaction with NO and HO_2 respectively. Although it should be acknowledged that the span of rate constants is quite small.

For the reaction of the peroxy radicals included in table 2 with NO and HO_2, only four experimentally determined rate constants are reported in the literature (the values, and references, are included in table 1). The agreement between the values of the rate constants predicted in this work and the measured rate constants is excellent:

$$CH_2(OH)CH_2O_2 + NO \longrightarrow \text{products} \qquad (13)$$

$$k_{\mathrm{measured}} = 9 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},\ k_{\mathrm{predicted}} = 10.1 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$CH_2(OH)CH_2O_2 + HO_2 \longrightarrow \text{products} \qquad (14)$$

$$k_{\mathrm{measured}} = 1.0 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},\ k_{\mathrm{predicted}} = 0.916 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$C(CH_3)_2(OH)C(CH_3)_2O_2 + HO_2 \longrightarrow \text{products} \qquad (15)$$
$$k_{\text{measured}} = 2.01 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\ k_{\text{predicted}} = 1.50 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$CCl_3CCl_2(O_2) + NO \longrightarrow \text{products} \qquad (16)$$
$$k_{\text{measured}} = 6.19 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\ k_{\text{predicted}} = 7.46 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The peroxy radicals in table 2 range from fully chlorinated to fully methylated species and thus have associated values of E_{SOMO} that covers the full range of values expected for RO_2 radicals formed following the attack of OH, NO_3 and Cl radicals with alkenes commonly encountered in the atmosphere. Inspection of table 3 allows some interesting comments to be made about the reactivity of different types of peroxy radicals towards NO and HO_2.
First, a peroxy radical formed following the attack of a double bond by NO_3 has a larger value of rate constant for reaction with NO, and smaller value of rate constant for reaction with HO_2, than has the peroxy radical formed if Cl or OH had added to the double bond, and in turn peroxy radicals formed following Cl addition tend to be more reactive towards NO and less reactive towards HO_2 than if OH had added to the double bond. Hence the reaction between NO_3 and an alkene (in the presence of oxygen) leads to a peroxy radical that is more likely to propagate atmospheric oxidation (reaction (1)) and form ozone than the attack of the alkene by Cl or OH radicals. This last statement assumes the only loss of these peroxy radicals is by reactions with HO_2 or NO.

Secondly, the isomeric peroxy radicals formed from the addition of X/O_2 to a conjugated diene (reactions 7 and 8), are quite different in their reactivity towards HO_2 and NO.

Thirdly, relative to the peroxy radicals formed from the addition of X/O_2 to butadiene and 2,3,4,5–tetramethyl hexa–1,3–diene, the peroxy radicals formed from the addition of X/O_2 to methyl vinyl ketone and 2,3–dimethyl pen–2–ene–4–one react more slowly with HO_2 and faster with NO. Thus, the peroxy radicals resulting from the addition of X/O_2 to a conjugated diene are more likely to cause chain termination than the peroxy radicals formed resulting from the addition of X/O_2 to a structurally similar α,β–unsaturated carbonyl.

Finally it should be noted that as the value of E_{SOMO} becomes more negative, the ratio $\frac{k(NO)}{k(HO_2)}$ becomes larger and chain propagation (reaction (1)) becomes more important relative to chain termination (reaction (2)). Peroxy radicals substituted with electron donating chlorine groups have more negative E_{SOMO} values than those with electron donating methyl substituents. Thus, values of $\frac{k(NO)}{k(HO_2)}$ for chlorinated peroxy radicals are larger than form methylated peroxy radicals, suggesting that heavily chlorinated peroxy radicals will favour reaction with NO rather than HO_2 in the atmosphere and hence the peroxy radicals will participate in chain propagating reactions, leading to increased ozone formation. Similarly, peroxy radicals substituted with electron donating groups will favour reaction with HO_2 radicals and hence will tend to participate in chain terminating reactions. The preceding two sentences should be read with caution, however, because whether a peroxy radical reacts NO or HO_2 in the atmosphere depends on both the ratio $\frac{k(NO)}{k(HO_2)}$ and on the ratio $\frac{[\text{NO}]}{[\text{HO}_2]}$. As shown in table 2, the largest value of $\frac{k(NO)}{k(HO_2)}$, 3.29, was for the peroxy radical resulting from addition of NO_3/O_2 to $Cl_2C{=}CCl_2$ and the smallest value, 0.4, was for the peroxy radical resulting from the addition of OH/O_2 to 2,3,4,5–tetramethyl hexa–1,3–diene.

As can be seen from Figure 1, the rate of reaction of NO with an RO_2 radical increases with increasing SOMO energy of the RO_2 radical, whilst for the reaction of HO_2 with RO_2, the converse is true, the rate of reaction decreases with increasing SOMO energy of RO_2. Frontier molecular orbital theory explains this behavior in terms of the relative energies of the SOMO of the attacking species, either NO or HO_2, and the SOMO energy of the RO_2 radicals. As shown by Fleming (1996) frontier molecular orbital theory predicts,

$$\ln\left(k / cm^3 molecule^{-1} s^{-1}\right) \propto \frac{1}{E_{SOMO}(HO_2 or NO) - E_{SOMO}(RO_2)} \qquad \text{(III)}$$

which over a small range of values of E_{SOMO}, may be approximated to equation (I). The SOMO energy of NO is higher than the SOMO energies of all the RO_2 radicals considered in this work, and the SOMO energy of the HO_2 radical is lower than all the SOMO energies of the RO_2 radicals considered. Thus, if the difference between the SOMO energies of NO and a particular RO_2 radical is small then the difference in the SOMO energies of HO_2 and the same RO_2 radical will inevitably be large. Consequently the reaction between NO and the RO_2 radical would have a larger rate constant than that for the reaction between HO_2 and the RO_2 radical. A fuller description of this explanation for the trends in reactivity of the organic peroxy radicals to NO and HO_2 has been explained by us previously, (King et al., 2001).

5. Acknowledgements

MDK wishes to thank department of chemistry, Kings College London for supporting part of this work.

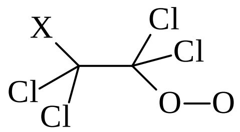
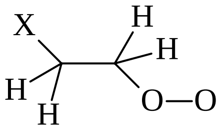
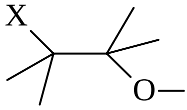
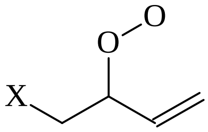
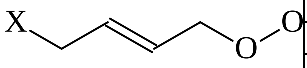
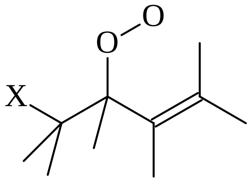
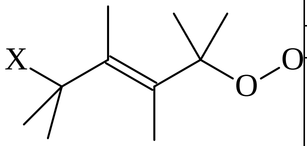
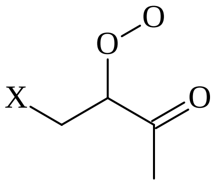
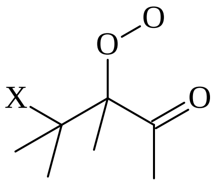
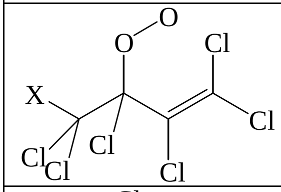
Table 1 Calculated SOMO energies and experimentally determined rate constants for reaction of organic peroxy radicals RO_2 with NO and HO_2.

Peroxy Radical RO_2	$-E$(SOMO) / eV	k(NO) / 10^{-12} cm^3 molecule^{-1} s^{-1}	Reference	k(HO_2) / 10^{-12} cm^3 molecule^{-1} s^{-1}	Reference
$C(CH_3)_3O_2$	3.6025	5.4	(Eberhard and Howard, 1997; Langer *et al.*, 1995a; Peeters *et al.*, 1992)		
Cyclo-$C_6H_{11}O_2$	3.6077	6.71	(Platz *et al.*, 1999a)	16.7	(Rowley *et al.*, 1992b)
$C(CH_3)_2(OH)C(CH_3)_2O_2$	3.6205			20.1	(Jenkin and Hayman, 1995)
$C(CH_3)_3C(CH_3)_2CH_2O_2$	3.6289	1.79	(Sehested *et al.*, 1993)		
$CH(CH_3)(CH_2CH_2CH_3)O_2$	3.6360	8	(Eberhard and Howard, 1997)		
$CH_3CH_2CH(CH_3)O_2$	3.6474				
Cyclo-$C_5H_9O_2$	3.6513	11	(Eberhard and Howard, 1997)	16	(Crawford *et al.*, 1997; Rowley *et al.*, 1992b)
$CH(CH_3)_2O_2$	3.6586	9	IUPAC		
$C(CH_3)_3CH_2O_2$	3.6733	4.7	(Sehested *et al.*, 1993)	14.7	(Rowley *et al.*, 1992a)
$C_6H_5CH_2O_2$	3.7136	2.49	(Kenley and Hendry, 1982)	10.1	(Noziere *et al.*, 1994)
$CH_3CH_2CH_2O_2$	3.7182	9.4	IUPAC		
$CH_3CH_2O_2$	3.7340	9	IUPAC	7.7	IUPAC
$CH_2{=}CHCH_2O_2$	3.7800	10.5	(Veyret *et al.*, 1982)	5.6	(Boyd *et al.*, 1996b)
$C(OH)(CH_3)_2CH_2O_2$	3.8047	4.9	(Langer *et al.*, 1994)	14.2	(Boyd *et al.*, 1996a)
$CH_3SCH_2O_2$	3.8382	12	IUPAC		
CH_3O_2	3.8406	7.5	IUPAC	5.2	IUPAC
$CH_3OCH_2O_2$	3.9073	9.1	(Langer *et al.*, 1995b)		
$CH(CH_3O)_2OCH_2O_2$	3.9378	9	(Platz *et al.*, 1999b)		
$CH_3CF_2CH_2O_2$	3.9498	8.5	(Mogelberg *et al.*, 1995b)		
1,4-dioxan-2-yldioxy	3.9603	12	(Platz *et al.*, 1997)		
$CH_3CH(OH)CH(CH_3)O_2$	3.9615			15	(Jenkin and Hayman, 1995)
$CH_2{=}C(CH_3)CH(CH_2OH)O_2$	3.9650	9	(Stevens *et al.*, 1999)		
$CH_2(OH)O_2$	4.0442	5.6	(Veyret *et al.*, 1982)	12	IUPAC
$CH_2(OH)CH_2O2$	4.0483	9	IUPAC	10	IUPAC
1,3,5-trioxan-2-yldioxy	4.0834	5.8	(Platz *et al.*, 1998)		
$CH_3OC(O)OCH_2O_2$	4.1021	12	(Bilde *et al.*, 1997)		
$CH_3C(O)CH_2O_2$	4.1111	8	(Sehested *et al.*, 1998)	9	IUPAC
$CFCl_2CH_2O_2$	4.2222	13	IUPAC	9.22	(Hayman and Battinleclerc, 1995)
$CF_2ClCH_2O_2$	4.2570	12	IUPAC	6.79	(Hayman and Battinleclerc, 1995)
CH_2BrO_2	4.2758	11	IUPAC	6.71	(Villenave and Lesclaux, 1995)
$CF_3CH_2O_2$	4.2891	12	(Nielsen *et al.*, 1994)		
CH_2ClO_2	4.2934	19	IUPAC	5	IUPAC
$CH_3CH_2C(O)O_2$	4.3421	28	IUPAC		
CH_2FO_2	4.3454	13	IUPAC		
$CH_3C(O)O_2$	4.3982	20	IUPAC	11	IUPAC
$CHCl_2O_2$	4.5106			5.87	(Catoire *et al.*, 1996)

$CF_3CH_2OCH(CF_3)O_2$	4.552	14.5	(Wallington *et al.*, 1998)		
CHF_2O_2	4.5979	13	IUPAC		
$CCl3CCl_2O_2$	4.6012	6.19	(Mogelberg *et al.*, 1995d)		
CCl_3O_2	4.6216	18	IUPAC	5.13	(Catoire *et al.*, 1996)
$CH(CF_3)_2O_2$	4.6233	11	(Mogelberg *et al.*, 1995c)		
$CFCl_2O_2$	4.6913	15	IUPAC		
CF_3CHFO_2	4.7231	13	IUPAC	3.8	IUPAC
$CF_3CCl_2O_2$	4.7465	18	IUPAC	1.9	IUPAC
CF_3CClHO_2	4.7664	10	(Mogelberg *et al.*, 1995a)		
$CF_3C(O)OCH(CF_3)O_2$	4.7710	15	(Stein *et al.*, 1999)		
CF_2ClO_2	4.7767	15	IUPAC	3.4	(Hayman and Battinleclerc, 1995)
$CF(CF_3)_2O_2$	4.8273	20.9	(Mogelberg *et al.*, 1996)		
CF_3CFClO_2	4.8350	16.8	(Bhatnagar and Carr, 1995)		
CF_3O_2	4.8714	16	IUPAC	2.9	(Hayman *et al.*, 1994)
$CF_3CF_2O_2$	4.9253			1.2	(Hayman and Battinleclerc, 1995)
$C_6H_5C(O)O_2$	5.0102	16	(Caralp *et al.*, 1999)		
$CF_3C(O)O_2$	5.0943	26	(Maricq *et al.*, 1996)		
$CF(O)O_2$	5.1082	25.1	(Wallington *et al.*, 1994)		

Note where the reference is given as IUPAC it refers to the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry Dec 2001, which is based on the original references (Atkinson *et al.*, 1997a; Atkinson *et al.*, 1997b; Atkinson *et al.*, 1999; Atkinson *et al.*, 2000; Atkinson *et al.*, 1997c).

Table 2 Calculated SOMO energies and rate constants for reaction with NO or HO_2 for the peroxy radicals formed by reactions 4–6 and 8–12. Values for rate constants calculated using equation (I) and values of *m* and *c* in table 3.

Peroxy radical	X=	$-E_{SOMO}$ / eV	k / 10^{-12} cm^3 $molecule^{-1}$ s^{-1}		$\frac{k_{NO}}{k_{HO2}}$
			NO	HO_2	
	OH	4.5441	14.2	5.15	2.76
	Cl	4.6015	14.8	4.82	3.07
	ONO_2	4.6379	15.2	4.62	3.29
	OH	4.0483	10.1	9.16	1.10
	Cl	4.0624	10.2	9.01	1.13
	ONO_2	4.1547	10.8	8.10	1.33
	OH	3.6205	7.46	15.0	0.50
	Cl	3.7778	8.33	12.5	0.67
	ONO_2	3.9095	9.13	10.8	0.85
	OH	3.9552	9.42	10.2	0.92
	Cl	3.9685	9.51	10.0	0.95
	ONO_2	4.0423	10.0	9.22	1.08
	OH	3.7508	8.17	12.9	0.63
	Cl	3.8880	8.99	11.0	0.82
	ONO_2	3.9990	9.72	9.70	1.00
	OH	3.6559	7.65	14.4	0.53
	Cl	3.7225	8.01	13.4	0.60
	ONO_2	3.8591	8.81	11.4	0.77
	OH	3.5010	6.86	17.3	0.40
	Cl	3.6175	7.44	15.1	0.49
	ONO_2	3.6951	7.86	13.8	0.57
	OH	4.1563	10.8	8.08	1.34
	Cl	4.1547	10.8	8.10	1.33
	ONO_2	4.3680	12.6	6.32	1.99
	OH	3.8316	8.64	11.8	0.73
	Cl	3.9938	9.68	9.76	0.99
	ONO_2	4.1008	10.4	8.62	1.21
	OH	4.2695	11.7	7.09	1.65
	Cl	4.3313	12.3	6.60	1.86
	ONO_2	4.5396	14.1	5.24	2.69
	OH	4.4447	13.3	5.78	2.30

	Cl	4.5016	13.8	5.41	2.55
	ONO_2	4.5291	14.1	5.24	2.69

Table 3 Values for *m* and *c* for the equation $-\ln (k / \text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) = -m\,E_{\text{SOMO}} + c$, for reactions of organic peroxy radicals with NO and HO_2. Uncertainties are one standard deviation.

Reaction of RO_2 with	*m* / eV	c
NO	0.698 ± 0.105	–28.150 ± 0.481
HO_2	–1.160 ± 0.228	–20.727 ± 0.884

Figure 1 Plot of $-\ln(k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ versus E_{SOMO} for reactions of organic peroxy radicals in table 1 with NO (a) and HO_2 (b).

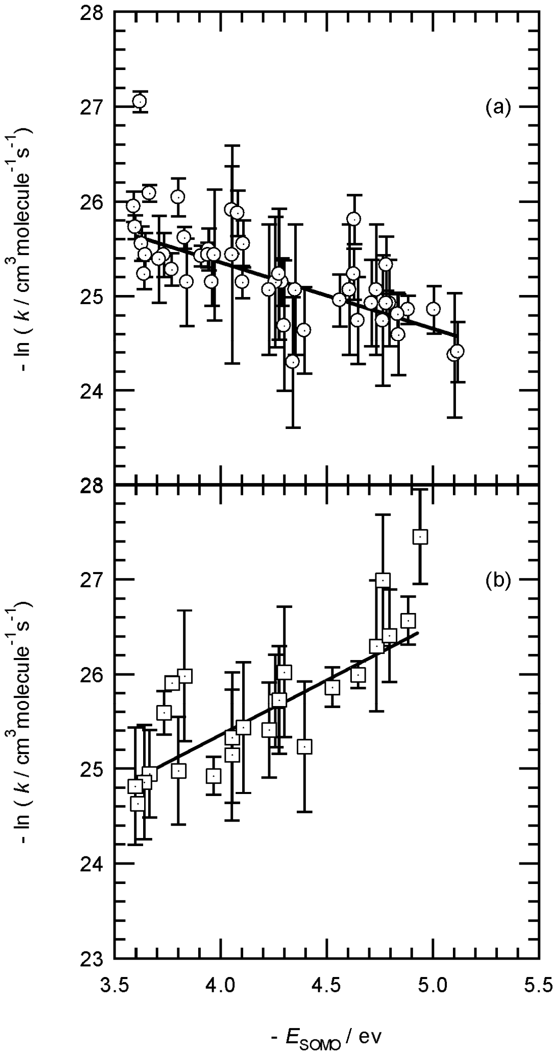
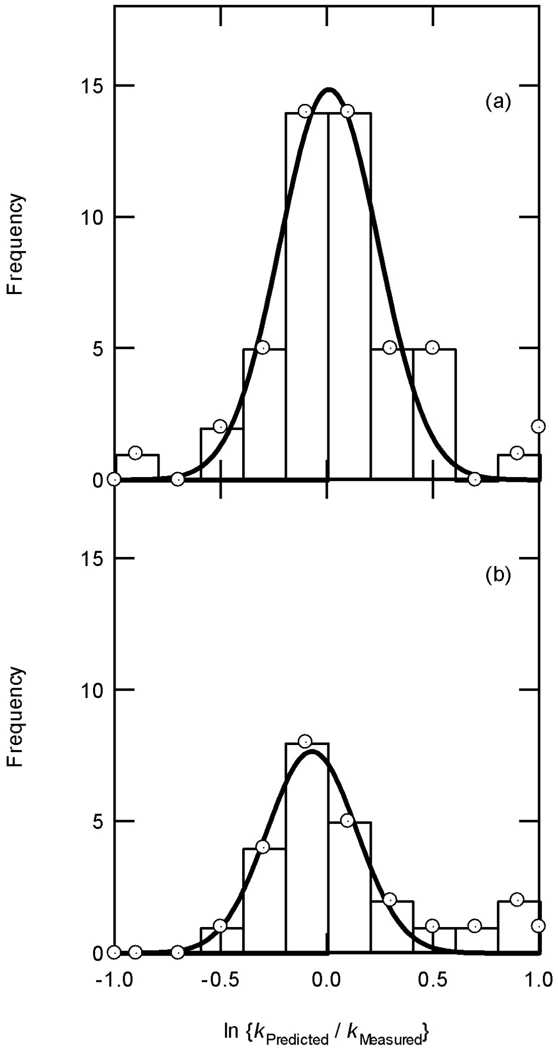


Figure 2 Histogram of the $\ln\left(\frac{k_{\text{predicted}}}{k_{\text{measured}}}\right)$ values for reactions of NO (a) and HO_2 (b) with organic peroxy radicals from table 1.



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