

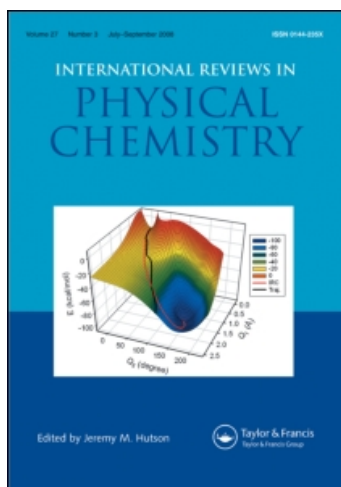
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Reactions of alkoxy and alkyl peroxy radicals

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Unimolecular and bimolecular reactions of alkoxy and alkyl peroxy radicals have evoked considerable interest because of their relevance to both atmospheric chemistry and combustion. In addition to the reactions of these radicals, their electronic spectra and thermochemistry are also considered. In particular group additivity values are tabulated so that the latter values may be calculated.

1. Introduction

Although in principle the reactions of all oxy-radicals RO_x should be considered, this review is confined mainly to the reactions of RO and RO_2 because other polyoxy radicals are unstable. Thus Nangia and Benson (1980 b) have shown that the formation of RO_3 from RO and O_2 (1) is endothermic by 60 kJ mol^{-1} . No review on these



reactions would be complete without the inclusion of both the thermochemistry and the spectra of these radicals. Either absorption or emission spectra provide a direct measure of the concentration of a particular species during reaction.

Benson (1976) has emphasized the importance of a thermochemical kinetic approach. This means that heats of formation and entropies together with heat capacities are considered because of their essential thermodynamic relationship. It is also valuable to be able to calculate these thermodynamic quantities via group additivity rules although one has to realize the limitations of such calculations. These calculations are not limited to the radicals alone since the same rules may be applied to transition states of particular reactions. This review also presents an opportunity to tabulate these quantities in SI units for the first time.

2. Thermochemistry

Several methods are available for the determination of the heats of formation of alkoxy radicals. Four involve thermochemical kinetic studies of the compounds ROX where $X = OR, NO, NO_2$ or Me . Here classical kinetic studies were made of the rate of breaking of the $RO-X$ bond:



By making the usual assumption that the reverse step has zero activation energy, the heat of formation of various alkoxy radicals may be determined from the relationship:

$$E_2 + RT = \Delta H_2^\ominus = D(RO-X) = \Delta H_f^\ominus(RO) + \Delta H_f^\ominus(X) - \Delta H_f^\ominus(ROX) \quad (A)$$

In the special case where $X = RO$ we have:

$$\Delta H_f^\ominus(RO) = \frac{1}{2}[D(RO-X) + \Delta H_f^\ominus(RO-OR)] \quad (B)$$

Using equation (B), the errors involved in the determination of $D(RO-OR)$ and $\Delta H_f^\ominus(RO-OR)$ are halved. It turns out that the bond dissociation energies $D(RO-X)$

Table 1. Bond dissociation energies for RO-X.

Compound	$D(\text{RO-X}) \text{ kJ mol}^{-1}$	Reference
ROOR	159.0 ± 4.2	Benson and Shaw (1970)
ROOR	158.2 ± 0.8	Batt and McCulloch (1976 b)
RONO	173.6 ± 2.1	Batt and Robinson (1982 a)
RONO ₂	173.0 ± 0.4	Longoria (1983)
MeO-Me	343.1 ± 1.3	Batt <i>et al.</i> (1982)
ROH	436.2 ± 1.3	Batt and McCulloch (1976 b)

are independent of the nature of R (table 1). Using expressions (A) and (B) to determine heats of formation of the alkoxy radicals, Batt and McCulloch (1976 b) found that $D(\text{RO-H})$ was also independent of the nature of R (table 1), confirming the earlier predictions of Benson and Shaw (1968, 1970). This value may be used to determine the heats of formation of other alkoxy radicals (Benson and Choo 1981) unless a radical stabilization energy is involved. Heats of formation may also be determined from appearance potentials but these are subject to larger errors (Reed and Brauman 1975, Holmes and Lossing 1984). Table 2 lists experimentally determined heats of formation for C₁-C₅ whereas table 3 gives mean and/or recommended values for all C₁-C₄ and one C₅ alkyl groups. Of these n-Bu and i-Bu were not available experimentally and so were determined by assuming $D(\text{RO-H}) = 436.2 \text{ kJ mol}^{-1}$ (Batt 1979, Benson and Choo 1981). The vinoxy radical is not considered here because it is a carbon-centred rather than an oxygen-centred radical. Benson and O'Neal (1969) have pointed out that the value of entropies and heat capacities for free radicals cannot be measured

Table 2. Heats of formation of alkoxy radicals.

R	$\Delta H_f^\ominus (\text{kJ mol}^{-1})$	Determination method	References
CF ₃	-655.6 ± 6.3	$\Delta(\text{CF}_3\text{O})_2$	Batt and Walsh (1982, 1983)
	17.6 ± 4.6	ΔMeONO	Batt <i>et al.</i> (1977)
	15.9 ± 0.8	$\Delta(\text{MeO})_2$	Batt and McCulloch (1976 b)
Me	15.1 ± 3.8	ΔMeONO_2	Longoria (1983)
	23.4 ± 8.4	Appearance potential	Holmes and Lossing (1985)
Et	16.3 ± 1.3	$\Delta\text{Me}_2\text{O}$	Batt <i>et al.</i> (1982)
	-17.2 ± 3.4	$\Delta(\text{C}_2\text{H}_5\text{O})_2$	Leggett and Thynne (1967)
	-13.8 ± 5.9	$\Delta\text{C}_2\text{H}_5\text{ONO}$	Batt and Milne (1977 b)
HC≡CO	-15.9 ± 2.5	$\Delta\text{C}_2\text{H}_5\text{ONO}_2$	Longoria (1983)
	120.5 ± 8.4	Appearance potential	Holmes and Lossing (1985)
n-Pr	-37.2 ± 4.6	$\Delta\text{n-PrONO}_2$	Benson <i>et al.</i> (1975)
i-Pr	-49.8 ± 5.4	$\Delta\text{i-PrONO}$	Batt and Milne (1977)
	-54.0 ± 2.1	$\Delta\text{i-PrONO}_2$	Longoria (1983)
HC≡CCH ₂ O	241.4 ± 8.4	Appearance potential	Holmes and Lossing (1985)
s-Bu	-69.5 ± 5.4	$\Delta\text{s-BuONO}$	Batt and McCulloch (1976 a)
t-Bu	-91.2 ± 3.4	$\Delta(\text{t-BuO})_2$	Islam (1977)
			Batt and Benson (1962)
t-Am	-89.5 ± 4.1	$\Delta\text{t-BuONO}$	Batt and Milne (1976)
	-110.9 ± 3.4	$\Delta\text{t-AmONO}$	Batt <i>et al.</i> (1978 a)

Table 3. Thermodynamic quantities for alkoxy radicals (RÖ).

R	ΔH_{F300}^\ominus (kJ mol ⁻¹)	S_{300}^\ominus (J mol ⁻¹ K ⁻¹)	C_p^\ominus (J mol ⁻¹ K ⁻¹)						
			300	400	500	600	800	1000	1500
Me	16.2	227.2	34.7	43.9	51.5	57.8	69.0	77.0	90.4
Et	-16.6	269.9	59.4	73.6	87.0	98.3	116.3	129.3	146.1
n-Pr	-37.2	313.0	82.4	101.7	120.5	136.4	161.9	180.8	205.7
i-Pr	-51.9	297.5	82.8	103.8	123.9	139.8	164.4	182.8	—
n-Pr	-56.5†	351.5	104.2	129.3	150.6	174.5	207.1	231.4	264.3
i-Bu	-64.9†	337.2	104.1	130.3	154.8	176.2	209.0	232.8	266.4
s-Bu	-69.5	347.3	107.5	133.1	157.8	177.8	209.6	232.6	268.1
t-Bu	-90.4	314.6	107.5	135.1	160.3	180.8	212.1	235.1	270.8
t-Am	-110.9	351.0	125.9	159.4	191.2	218.0	257.7	286.2	330.4

† Derived from group additivity values in table 4.

experimentally. Benson and O'Neal (1969) started with known values of an analogous reference compound and corrected for any small differences which might be anticipated between the reference molecule and the radical of interest, as used previously (Trotman-Dickenson 1953, Purnell and Quinn 1964, Benson 1960). These differences are the following:

- (i) Mass (M): both translation and external rotation partition functions depend on M . Thus mass corrections, by proper choice of reference compound (A), may be made very small and are given by:

$$\Delta S^\ominus = \frac{3}{2}R \ln(M_R/M_A) \quad \text{and} \quad \Delta C_p^\ominus = 0$$

- (ii) Vibrational frequencies.
 (iii) Moments of inertia for internal rotations.
 (iv) Electronic degeneracy. For a radical with one unpaired electron,

$$g_e = 2S + 1 = 2 \quad \Delta S_e^\ominus = R \ln 2.$$

- (v) Symmetry (σ).
 (vi) Rotational barriers.

Corrections (i) and (iii) are usually very small and can be ignored. It is assumed that rotational barriers are the same as in the parent compounds, except where noted below.

For the alkoxy radicals, two suitable reference compounds are the corresponding alkyl fluorides (RF) and alcohols (ROH).

- (a) RF

$$S^\ominus(\text{RO}) \simeq S^\ominus(\text{RF}) + R \ln 2 \quad (C_p^\ominus(\text{RO}) \simeq C_p^\ominus(\text{RF})).$$

- (b) ROH

$$S^\ominus(\text{RO}) \simeq S^\ominus(\text{ROH}) - S^\ominus(\text{R-OH})_{4,0} - S^\ominus(\text{C} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \text{H}) \\ - S^\ominus(\text{O-H}) + R \ln 2$$

where $S^\ominus(\text{R-OH})_{4,0}$ represents the entropy due to restricted rotation about the R-O bond with a barrier of 4 kJ mol^{-1} .

$$C_p^\ominus(\text{RO}) \approx C_p^\ominus(\text{ROH}) - C_p^\ominus(\text{R-OH})_{4,0} - C_p^\ominus(\text{C} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{H} \end{array})$$

In the cases where data were available for both fluoride and alcohol, mean values were taken, but in some cases data were available for only the alcohol. Smoothing of the data for C_p^\ominus resulted in some corrections. This data was used to obtain group values (table 4) which were usually identical with those derived earlier by Benson (1976). Group values for alkyl groups are also included (Benson 1976). These group values may be used to obtain data for other alkoxy radicals. In table 3, the data were determined in this way for the radical *i*-BuO.

In contrast to alkoxy radicals, very little experimental data is available for alkyl peroxy radicals so that one has to rely heavily on the use of group additivity rules. Almost all of the information is due to Benson and co-workers (Benson and Shaw 1968, 1970, Benson 1976, Benson and Shum 1983). $\Delta H_f^\ominus(\text{RO})$ stems from essentially three sources. The first depends upon the heat of formation of the hydroperoxy radical, for which a timely review was made by Benson and Shum (1983). They recommend a value of $14.6 \pm 4.0 \text{ kJ mol}^{-1}$. By making use of the values $\Delta H_f^\ominus(\text{H}_2\text{O}_2) = -136.1 \text{ kJ mol}^{-1}$ and $\Delta H_f^\ominus(\text{H}) = 217.6 \text{ kJ mol}^{-1}$ (Stull *et al.* 1970), and $D(\text{HO}_2-\text{H}) = 368.2 \text{ kJ mol}^{-1}$, Benson and Shaw (1968) assumed that $D(\text{HO}_2-\text{H}) = D(\text{RO}_2-\text{H})$. Benson and Shaw (1968) also made use of the principle of group additivity to determine $\Delta H_f^\ominus(\text{RO}_2\text{H})$ since there are no experimental values available. Thus $\Delta H_a^\ominus = 0$ for example:



Table 4. Group thermodynamic quantities.

Group	$\Delta H_f^\ominus_{300}$ (kJ mol^{-1})	S^\ominus_{300} ($\text{J mol}^{-1} \text{K}^{-1}$)	$C_p^\ominus(\text{J mol}^{-1} \text{K}^{-1})$						
			300	400	500	600	800	1000	1500
$\text{C(H)}_3(\text{C})$ and $\text{C(H)}_3(\text{O})^\dagger$	-42.2	127.2	25.9	32.8	39.3	45.2	4.5	61.8	71.0
$\text{C(H)}_2(\text{C})_2$	-20.6	39.4	23.0	29.1	34.5	39.1	46.3	51.5	59.6
$\text{C(H)}(\text{C})_3$	-8.0	-50.5	19.0	25.1	30.0	33.7	39.0	42.1	46.7
$\text{C(H)}_2(\text{C})(\text{O})$	+25.6	153.3	33.3	39.6	46.2	52.1	61.0	67.1	72.5
$\text{C}(\text{C})_2(\text{H})(\text{O})$	+34.0	62.0	31.8	38.3	44.3	48.9	54.8	58.3	61.3
$\text{C}(\text{C})_3(\text{O})$	+36.3	-35.0	27.5	34.3	40.6	44.3	48.3	49.5	50.0
$\text{C}(\text{C})(\text{H})_2(\text{O})$	-33.9	41.0	20.9	28.7	34.7	39.5	46.5	51.6	58.0
$\text{C}(\text{C})_2(\text{O})(\text{H})$	-30.1	-46.0	20.1	27.8	33.9	37.5	41.1	43.5	45.5
$\text{C}(\text{C})_3(\text{O})$	-27.6	-140.4	18.1	25.9	30.3	32.2	34.3	34.5	35.0
$\text{O}(\text{C})(\text{O})$	67.4	154.9	34.2	54.0	59.6	62.3	73.4	81.7	98.0

\dagger $\text{C(H)}_3(\text{C})$ and $\text{C(H)}_3(\text{O})$ are assigned identical values.

Example of the use of Table 4

$$\begin{aligned} \Delta H_f^\ominus(\text{t-BuO})_{300} &= 3\Delta H_f^\ominus[\text{C(H)}_3(\text{C})] + \Delta H_f^\ominus[\text{C}(\text{C})_3(\text{O})] \\ &= -90.3 \text{ kJ mol}^{-1} \quad (-90.4)^\ddagger \\ S^\ominus(\text{t-BuO})_{300} &= 3S^\ominus[\text{C(H)}_3(\text{C})] + S^\ominus[\text{C}(\text{C})_3(\text{O})] - R \ln 81\ddagger \\ &= 310.1 \text{ J mol}^{-1} \text{K}^{-1} \quad (314.6)^\ddagger \\ C_p^\ominus(\text{t-BuO}) &= 3C_p^\ominus[\text{C(H)}_3(\text{C})] + C_p^\ominus[\text{C}(\text{C})_3(\text{O})] \\ &= 105.2 \text{ J mol}^{-1} \text{K}^{-1} \quad (107.5)^\ddagger \end{aligned}$$

\ddagger Experimental values listed in parenthesis.

\S Symmetry contribution.

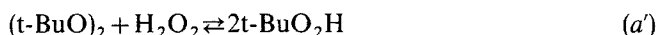
Hence with $\Delta H_f^\ominus(\text{MeO})_2 = -125.5 \text{ kJ mol}^{-1}$, $\Delta H_f^\ominus(\text{MeO}_2\text{H}) = -130.8 \pm 5 \text{ kJ mol}^{-1}$ and $\Delta H_f^\ominus(\text{MeO}_2) = 19.9 \pm 5 \text{ kJ mol}^{-1}$. Heneghan and Benson (1983), studied the equilibrium:



They found that $\Delta H_b^\ominus = 12.1 \pm 6.7 \text{ kJ mol}^{-1}$. From the result:



they also find $D(\text{t-BuO}_2\text{-H}) = 378.2 \pm 6.7 \text{ kJ mol}^{-1}$. By again invoking the principle of group additivity, $\Delta H_f^\ominus(\text{t-BuO}_2\text{H})$ may be determined:



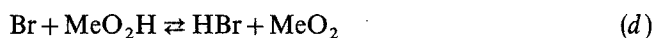
Using $\Delta H_f^\ominus(\text{t-BuO})_2 = -349.0 \pm 8 \text{ kJ mol}^{-1}$ (Batt and Islam 1977, unpublished), we find $\Delta H_f^\ominus(\text{t-BuO}_2\text{H}) = -242.6 \pm 4 \text{ kJ mol}^{-1}$ and hence

$$\Delta H_f^\ominus(\text{t-BuO}_2) = -82.0 \pm 7.8 \text{ kJ mol}^{-1}.$$

A third approach is to take a mean of $D(\text{HO}_2\text{-H})$ and $D(\text{t-BuO}_2\text{-H}) = 373.6 \pm 4 \text{ kJ mol}^{-1}$ close to the theoretical value of Benson and Heneghan (1983) whence

$$\Delta H_f^\ominus(\text{MeO}_2) = 25.2 \text{ kJ mol}^{-1}.$$

A similar study by Kondo and Benson (1984) using the equilibrium (d) is in essential agreement with this result.



This may be compared with the thermochemical estimate of Nangia and Benson (1979) of 25.9 kJ mol^{-1} . In this way, $\Delta H_f^\ominus(\text{t-BuO}_2)$ is $-86.6 \text{ kJ mol}^{-1}$. Using the mean value for $D(\text{RO}_2\text{-H})$ and the group additivity value for $\Delta H_f^\ominus(\text{RO}_2\text{H})$, group values have been derived for $[\text{O}(\text{C})\text{O}]$ incorporating the entropy and heat capacity values of Benson and Shaw (1968, 1970) (table 4). Thus, thermodynamic quantities can be derived for a series of alkyl peroxy radicals. An example of their use is given by the work of Khachatryan *et al.* (1982). They studied the equilibrium:



in the oxidation of methane over the temperature range 706–786 K. They obtained the result, $\Delta H_e^\ominus = -119.2 \pm 10.2 \text{ kJ mol}^{-1}$. Using the group additivity data for the methyl peroxy radical, Benson and O'Neal's data for the methyl radical, and Benson's data for oxygen ($\Delta C_p^\ominus = -14.7 \text{ J mol}^{-1} \text{ deg}^{-1}$), $\Delta H_e^\ominus(300) = -125.5 \pm 10.2 \text{ kJ mol}^{-1}$. Thus with $\Delta H_f^\ominus(\text{Me}) = 146.9 \text{ kJ mol}^{-1}$ (Benson *et al.* 1981), $\Delta H_f^\ominus(\text{CH}_3\text{O}_2)$ is $21.4 \pm 10 \text{ kJ mol}^{-1}$ in very good agreement with the above conclusions and the group value. Very recently, Gutman *et al.* (1985) have measured K_e and K_f directly over the temperature range 694–811 K and find $\Delta H_e^\ominus = -135.6 \pm 2.9 \text{ kJ mol}^{-1}$ and $\Delta H_f^\ominus = -157.7 \pm 7.5 \text{ kJ mol}^{-1}$. These values certainly upset the values predicted



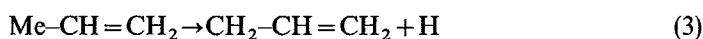
from group additivity rules. Earlier it was mentioned that one had to be aware of the limitations of group additivity rules (GAR). To date, these only exist in multi-substituted systems such as CF_3CH_3 , $\text{NO}_2\text{CH}_2\text{NO}_2$ etc. and highly strained systems. The data agree to $\pm 4 \text{ kJ mol}^{-1}$ for all mono and di-substituted halides, alcohols, ethers, esters, acids, nitrites, nitrates, cyanides and dialkyl peroxides. Gutman's data

would imply alkyl hydroperoxides would not fit. Much work, including my own, has shown that $D(\text{RO-X})$ where $\text{X}=\text{H}$, Alkyl, NO , NO_2 and OR , is independent of the nature of X . It does seem unlikely that this would not follow for $\text{X}=\text{OH}$. It is clear that a study of $D(\text{R-O}_2)$ has to be pursued further.

A value for the heat of formation and entropy of the allyl peroxy radical can be derived from the data of Pilling *et al.* (1981, 1982). They found that $\Delta S_g^\ominus = -(122 \pm 5) \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_g^\ominus = -(76.2 \pm 2.1) \text{ kJ mol}^{-1}$



Compared to ΔH_c^\ominus , this means that the resonance stabilization energy of the allyl radical is $43 \pm 10 \text{ kJ mol}^{-1}$. This is in agreement with the result $\Delta H_3^\ominus = 367 \text{ kJ mol}^{-1}$ derived using the data of Benson (1976) compared to a



primary C-H bond strength of 410 kJ mol^{-1} . Using $\Delta H_f^\ominus(\text{C}_3\text{H}_5) = 170 \text{ kJ mol}^{-1}$ (Benson 1976), $\Delta H_f^\ominus(\text{C}_3\text{H}_5\text{O}_2) = 93.8 \pm 4.5 \text{ kJ mol}^{-1}$. Similarly from the entropies of the allyl radical and oxygen (Benson 1976) we find

$$S^\ominus(\text{C}_3\text{H}_5\text{O}_2) = 342.8 \pm 8.7 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Entropies and heat capacities (C_p^\ominus) may also be estimated by analogy with model compounds $-\text{RCH}=\text{CH}_2$, RCHO (Benson 1965) and the suitably modified alkoxy methyl radical ROCH_2 . For the entropy $R \ln 2$ at least needs to be added to the listed entropies for the radical species. Data for table 5 were calculated in this way. Group values are also derived thereby.

Finally via a re-examination of the data for the pyrolysis of bis(trifluoromethyl) peroxide Batt and Walsh (1982, 1983) led to values of

$$\Delta H_f^\ominus(\text{CF}_3\text{O}_2) = -674.9 \text{ kJ mol}^{-1}$$

and

$$D(\text{CF}_3\text{-O}_2) = 204.2 \text{ kJ mol}^{-1}.$$

Table 5. Thermodynamic quantities for alkyl peroxy radicals (RO_2).

R	$\Delta H_f^\ominus(300)$ (kJ mol^{-1})	$S^\ominus(300)$ ($\text{J mol}^{-1} \text{ K}^{-1}$)	$C_p^\ominus(\text{J mol}^{-1} \text{ K}^{-1})$						
			300	400	500	600	800	1000	1500
CF_3	-619.7	320.5	92.4	95.4	105.4	114.5	127.7	134.8	—
Me	25.2	273.0	65.1	79.9	94.4	107.5	127.9	143.5	169.0
Et	-8.7	314.0	86.0	115.5	133.6	147.0	174.4	195.1	227.0
n-Pr	-29.3	353.4	109.0	144.6	172.1	196.1	220.7	246.7	286.6
i-Pr	-47.1	354.1	111.1	147.4	172.1	190.2	223.5	248.8	285.5
Allyl	93.8	342.8	105.4	131.0	152.7	170.7	199.2	220.5	—
n-Bu	-49.9	392.8	132.0	173.7	212.6	235.2	267.0	298.3	346.2
i-Bu	-58.9	381.5	130.9	173.4	202.9	225.9	267.9	299.0	344.7
s-Bu	-67.7	390.2	134.1	176.5	206.6	229.3	269.8	300.4	345.1
t-Bu	-86.8	359.6	135.0	178.3	207.8	230.1	271.2	301.6	346.0

This bond strength is some 85 kJ mol^{-1} stronger than the corresponding $D(\text{CH}_3\text{-O}_2)$. However, recent studies (Batt and Stewart 1985, unpublished) suggest that $D(\text{CF}_3\text{-O}_2) = 149 \text{ kJ mol}^{-1}$. More data are required for the important class of compounds CX_3O_2 where X is halogen.

3. Electronic spectra

Despite extensive searches (for example McGrath and McGarvey 1964, Callear and Wood 1971) very little information is available on the electronic absorption spectra of alkoxy radicals. However Wendt and Hunziker (1979) were able to obtain an absorption spectrum for the methoxy radical via the $\text{Hg}({}^3\text{P}_0)$ photosensitized decomposition of both methyl formate and acetate. It consisted of a long, single progression of bands starting at 317 nm and continuing to shorter wavelengths. The absorption corresponded to the $\bar{A}^2\text{A}_1\text{-}\bar{X}^2\Sigma$ electronic transition which is analogous to the $\bar{A}^2\Sigma^+\text{-}\bar{X}^2\Pi_i$ transition of the hydroxyl radical. Yarkony *et al.* (1974) have calculated the electronic structure of these two states and predicted a transition energy close to that of the hydroxyl radical with the $\text{CH}_3\text{-O}$ bond length increasing from 1.44 Å in the ground state of 1.65 Å in the excited state. A similar, but unsuccessful study was carried out on the ethoxy radical (Wendt and Hunziker 1979). The absorption spectrum is also available for the vinoxy radical (Hunziker *et al.* 1981) but *ab initio* calculations (Dupuis *et al.* 1982) indicate that this radical is essentially a carbon-centred radical, viz $\cdot\text{CH}_2\text{-CH=O}$.

By contrast, as a result of mainly Japanese work, there is considerably more information on the emission spectra of alkoxy radicals. Emission spectra were first observed by Style and Ward (1953) who photolysed a number of methoxy and ethoxy precursors, including methyl and ethyl nitrites, using a hydrogen continuum lamp. The species giving the emission bands in the near ultraviolet to visible region were proposed to be the methoxy and ethoxy radicals respectively. Ohbayashi *et al.* (1977) repeated this work with methyl, ethyl, isopropyl and t-butyl nitrites using iodine (206, 187 nm), mercury (185 nm), xenon (147, 130 nm), krypton (124, 117 nm) and a deuterium continuum lamp. With the xenon and krypton lamps and the four nitrites, β and γ bands of nitric oxide were observed. With the iodine and mercury lamps and t-butyl nitrite no NO emission was observed but there were emission spectra between 290 and 450, 330 and 500, and 360 and 520 nm for methyl, ethyl and isopropyl nitrites respectively. The ratios of quenching to fluorescence were determined for 13 added gases and from the self-quenching rates the fluorescence lifetimes were estimated as MeO ($\sim 3 \mu\text{s}$), EtO ($\sim 1 \mu\text{s}$) and i-PrO ($\sim 0.3 \mu\text{s}$). Confirmatory work was provided by studying the reaction of metastable argon and krypton with methanol (Sutoh *et al.* 1980). From the point of view of kinetic studies, a major step forward was made by studying the laser-induced fluorescence (LIF) of methoxy (Inoue *et al.* 1979, 1980) ethoxy (Inoue *et al.* 1981) and vinoxy (Inoue and Akimoto 1981) radicals. (The latter is of less interest for the reasons stated). For the other radicals, formation was achieved in a fast flow system via reaction of fluorine atoms with the corresponding alcohol. Mention must also be made of the laser magnetic resonance rotational spectrum of the methoxy radical obtained by Radford and Russell (1977). Once again the radical was obtained via the reaction of fluorine atoms with methanol. Their high resolution study made in the far infrared region has now been extended to the microwave by Endo *et al.* (1982).

Unlike the alkoxy radicals, no vibrational structure is shown in the U.V.-absorption spectra of alkyl peroxy radicals (Parkes *et al.* 1973). Similar to the hydrogen

peroxy radical, which has a maximum at 210 nm and extends to 280 nm (Troe 1969, Kijewski and Troe 1972), the spectra of peroxy radicals consist of a broad band from 200–280 nm, with maxima at 240 nm with molar absorption coefficients between 1000 and $1500 \text{ M}^{-1} \text{ cm}^{-1}$ i.e. some 200 times stronger than the methoxy radical. Spectra have been determined via the flash photolysis of the appropriate azo compound in the presence of oxygen for MeO_2 (Adachi *et al.* 1980), EtO_2 (Parkes *et al.* 1973, Adachi *et al.* 1979), and $n\text{-PrO}_2$ and $i\text{-PrO}_2$ (Adachi and Basco 1982 a). Similar results were obtained for the acetylperoxy radical (Addison *et al.* 1980) formed from the modulated photolysis of chlorine in the presence of acetaldehyde and oxygen. However, the continued rise in the absorption spectrum at wavelengths $< 210 \text{ nm}$ may indicate interference from another species but could be accounted for by the CO chromophore. In addition, the I.R.-absorption spectrum of the *t*-butyl peroxy radical has been observed (Parkes and Donovan 1975).

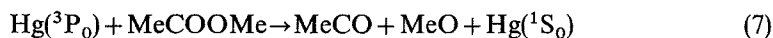
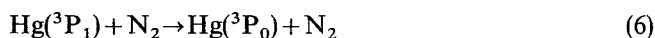
4. Reactions of alkoxy radicals

4.1. Introduction

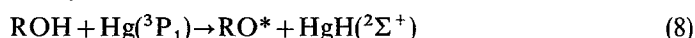
The reactions of alkoxy radicals were last reviewed in 1967 (Gray *et al.*) and thus provide a starting point here. One should first consider sources of radicals. Two recent reviews have considered alkyl nitrites and alkyl nitrates (Batt 1982) and dialkyl peroxides (Batt and Liu 1984) as thermal sources. Alkyl nitrites are also clean photochemical sources such that thermally equilibrated radicals are formed at total pressures $> 100 \text{ Torr}$ (Batt and Rattray 1979, Batt, Hisham and McKay 1984, unpublished). Mention must also be made of two other photochemical sources of alkoxy radicals. The first of these is organic esters such as methyl acetate:



The photochemistry of these processes has been comprehensively reviewed by Calvert and Pitts (1966). It appears that although other primary processes occur, reaction (4) is the major path. Absorption takes place in the far U.V. region with a maximum at 215 nm. Since the MeCO-OMe bond strength is 404 kJ mol^{-1} , one or both fragments will carry excess vibrational energy. It appears that most of this excess energy resides in the MeCO fragment. Excess energy is less of a problem when using mercury Hg^3P_1 (Kearle and Lossing 1959, Pottie and Lossing 1961) or Hg^3P_0 (Wendt and Hunziker 1979) sensitization:



The electronic excitation of $\text{Hg}(^3\text{P}_0)$ corresponds to 452 kJ mol^{-1} thus leaving some 48 kJ mol^{-1} of excess energy, well below the threshold for the decomposition of the methoxy radical. Secondly, Knight and Gunning (1961 a, b, 1962, 1963) have shown that the major process in the $\text{Hg}(^3\text{P}_1)$ sensitized decomposition of alcohols (ROH) is the production of alkoxy radicals where $\text{R} = \text{Me, Et, } i\text{-Pr and } t\text{-Bu}$. In the last two cases, vibrationally excited species are formed which indicates that the processes are:



such that $\Delta H_8^\ominus = -70 \text{ kJ mol}^{-1}$, numerically equal to the activation energy for the decomposition of the *t*-butoxy radical (Batt and Robinson 1982 b). Addition of carbon

tetrafluoride > 300 Torr is sufficient to equilibrate these radicals thermally. A similar abstraction process involving the alcohols using fluorine atoms in a fast flow system can be used:



Here thermally equilibrated radicals are produced but hydroxymethyl radicals are the major product:



There are two methods available for the study of alkoxy radicals. The first is a direct method which involves laser-induced fluorescence (LIF) which monitors the decay of the alkoxy radical. This should be complemented by product analysis. The method is limited by diffusion losses at very low pressures, < 5 Torr, and by quenching of fluorescence at high pressures, > 100 Torr. The second method involves the measurement of relative rates and involves the combination of the alkoxy radical either with nitric oxide or nitrogen dioxide



Because both processes take place at almost every collision, very low pressures are accessible and allow the effect of inert gas to be explored. This method is limited by the precision of the rate constants, k_{11} and k_{12} .

4.2. The reaction of alkoxy radicals with nitric oxide and nitrogen dioxide

McDonald *et al.* (1980) have measured the rate of the reaction of methoxy radicals with nitric oxide using the LIF technique. The radicals were produced by the U.V. laser photolysis (266 nm) of methyl nitrite. This wavelength corresponds to $449.5 \text{ kJ mol}^{-1}$ and since $D(\text{MeO}-\text{NO})$ is $171.5 \text{ kJ mol}^{-1}$, the excess energy of 278 kJ mol^{-1} may be enough to cause some decomposition or isomerization (Batt *et al.* 1981) of the methoxy radical especially at short delays. There are two possible channels for the reaction, corresponding to either combination or disproportionation

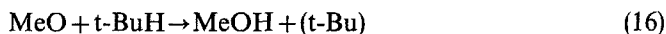


Reaction (13) would be expected to be pressure dependent and both McDonald *et al.* (1980) and Zellner *et al.* (1984) using the same technique found experimental evidence for pressure dependence. Serious discrepancies appear in the literature for the ratio k_{14}/k_{13} which vary from zero to 0.5. Failure to account for either the pressure dependence of reaction (13) or re-dissociation of methyl nitrite may resolve many of the discrepancies. Of the most recent studies $k_{14}/k_{13} < 0.1$ as $M \rightarrow \infty$ (McDonald *et al.* 1980), 0.17 (Zellner *et al.* 1984) and 0.05 (Batt *et al.* 1978 b), the first and last value for k_{14}/k_{13} are preferred, i.e. 0.05, because this was determined under limiting pressure conditions. Further work is clearly desirable. In respect of the rate constant k_1 , McDonald *et al.* (1980) find a value of $10^{10.0 \pm 0.1} \text{ M}^{-1} \text{ s}^{-1}$ which slowly decreases over the temperature range 295–608 K. They attribute this fall to the temperature dependence of k_{13} , i.e. reaction (13) has a small positive activation energy, $6 \pm 2 \text{ kJ mol}^{-1}$. Zellner *et al.* (1984) find a value of $10^{10.2 \pm 0.1} \text{ M}^{-1} \text{ s}^{-1}$ at room temperature in good agreement.

Batt *et al.* (1977) determined the rate constant for the reverse of reaction (13):



This was carried out by decomposing methyl nitrite (1 Torr) in a bath of isobutane, *t*-BuH (1 atm) such that all the methoxy radicals produced in reaction (15) were converted to methanol:



Thus the rate constant for reaction (15) was found to be

$$k_{15} = 10^{15.9 \pm 0.4} \exp(-20800 \pm 400/T) \text{ s}^{-1}.$$

The thermochemistry for reaction (15) shows that $E_{13} = 0$. Hence the pre-exponential factor $A_{13} = k_{13}$. This is in good agreement with the two previous results. However, this result is obtained at higher pressures under pressure-independent conditions whereas k_{13} still shows some pressure dependence at the pressures studied for the direct determination of k_{13} . On the basis that $k_{14}/k_{13} = 0.05$, $k_{14} = 10^{8.9} \text{ M}^{-1} \text{ s}^{-1}$.

McDonald *et al.* (1981) also measured the rate of reaction of ethoxy radicals with nitric oxide. Pressure dependence was less marked. It should be emphasized that this study measures only the rate of disappearance of ethoxy radicals and does not differentiate between combination and disproportion



They find that the rate constant is a factor of 2 higher than that for methoxy and nitric oxide, i.e. $k_{17} + k_{18} = 10^{10.3} \text{ M}^{-1} \text{ s}^{-1}$. Batt and Milne (1977 b) studied the decomposition of ethyl nitrite. By using small concentrations of nitrite and small extents of decomposition they were able to isolate reaction (19)



Since $R_{20} \gg R_{17}$ the rate of formation of formaldehyde was a direct measure of reaction (23). Its rate of reaction was given by $k_{19} = 10^{16.0 \pm 0.4} \exp(-21000 \pm 500/T) \text{ s}^{-1}$. Using the method for the study of the decomposition of methyl nitrite (Batt *et al.* 1975), k_{17} was found to be $10^{10.3 \pm 0.4} \text{ M}^{-1} \text{ s}^{-1}$ in good agreement with the direct study. Similar studies were carried out with other nitrites in order to determine the rate constants for the combination of other alkoxy radicals with nitric oxide. The values are given by $10^{10.3 \pm 0.2} \text{ M}^{-1} \text{ s}^{-1}$ (table 6).

Recent studies of the disproportionation:combination ratio for ethoxy, isopropoxy radicals and nitric oxide (Batt and Longoria 1983, unpublished) show that in each case the value is < 0.05 . Previous higher values are attributed to heterogeneous effects (Batt *et al.* 1975).

No direct studies have been made of the reaction of alkoxy radicals with nitrogen dioxide. Batt and Alvarado (1979, unpublished) determined the rate constant for reaction (21):



Table 6. Rate constants for the combination process $\text{RO} + \text{NO} \rightarrow \text{RONO}$ (11).

R	$k/\text{M}^{-1} \text{s}^{-1}$	Reference
Me	$10^{10.2 \pm 0.4}$	McDonald <i>et al.</i> (1981)
Me	$10^{10.0 \pm 0.1}$	Zellner <i>et al.</i> (1984)
Me	$10^{10.2 \pm 0.1}$	Batt <i>et al.</i> (1977)
Et	$10^{10.3 \pm 0.4}$	McDonald <i>et al.</i> (1981)
Et	$10^{10.3 \pm 0.1}$	Batt and Milne (1977 a)
i-Pr	$10^{10.5 \pm 0.4}$	Batt and Milne (1977 b)
i-Bu	$10^{10.4 \pm 0.4}$	Batt and McCulloch (1976 a)
t-Bu	$10^{10.4 \pm 0.4}$	Batt and Milne (1976)
t-Am	$10^{10.5 \pm 0.2}$	

by decomposing methyl nitrate in the presence of nitric oxide and inert gas, when the methoxy radicals formed either combined or disproportionated with nitric oxide. As discussed already, reaction (14) plays a very minor role except perhaps at the lower pressures of added inert gas. The rate of formation of methyl nitrite is clearly pressure dependent. This probably reflects the pressure dependence of reaction (21). At the highest pressures used (760 Torr) the reaction was studied over the temperature range 380–420 K. This gave the result $k_{21} = 10^{16.6 \pm 0.4} \exp(-20100 \pm 400/T) \text{ s}^{-1}$. Since E_{22} is zero, k_{22} may be calculated from ΔS_{19}^\ddagger , and turns out to be $10^{10.0 \pm 0.4} \text{ s}^{-1}$. This value may be compared



with two competitive studies. Arden *et al.* (1964) found that $k_{13}/k_{22} = 2$ whereas Batt and Rattray (1979) found that $k_{13}/k_{22} = 2.03 \pm 0.47$ (393–433 K) at 500 Torr (CF_4). This means that k_{22} is $10^{9.9 \pm 0.3} \text{ M}^{-1} \text{ s}^{-1}$ in good agreement with the above result. Similar studies were made on the decomposition of ethyl and isopropyl nitrate (Batt and Longoria 1983, unpublished). The rate constants for the combination of ethoxy and isopropoxy radicals with nitrogen dioxide are given in table 7.

The ratio of disproportionation to combination for the methoxy radical with nitrogen dioxide, k_{23}/k_{22} :



has recently been measured by decomposing methyl nitrite (1 Torr) in the presence of nitrogen dioxide (1 Torr) and inert gas (CF_4 , 760 Torr). The value was 0.04 ± 0.01 (443–474 K) independent of temperature (Batt and Longoria 1983, unpublished) (although there is some evidence that reaction (23) may have a small activation energy of 8–12 kJ mol⁻¹). This may be compared with an identical earlier result at 433 K (Baker and Shaw 1965) and means that $k_{23} = 10^{8.6 \pm 0.4} \text{ M}^{-1} \text{ s}^{-1}$. Barker *et al.* (1977) found a larger value for the ratio of k_{23}/k_{22} of 0.3 but this was probably a reflection of the pressure dependence of reaction (22). Similar studies for the ethoxy and isopropoxy radicals (Batt and Longoria 1983, unpublished) gave values for the ratio of disproportionation to combination of 0.1 ± 0.01 and 0.027 ± 0.006 independent of temperature. However, in each case evidence was produced for a slight temperature dependence for the ratios. The values for the rate constants are given in table 7.

Table 7. Rate constants for the combination and disproportionation of alkoxy radicals with nitrogen dioxide: $\text{RO} + \text{NO}_2 \rightarrow \text{RONO}_2$ (12), $\text{RO} + \text{NO}_2 \rightarrow \text{RO}_{-H} + \text{HNO}_2$ (24).

R	k_{24}/k_{12}	$\log k_{12}(\text{M}^{-1} \text{s}^{-1})$	$\log k_{24}(\text{M}^{-1} \text{s}^{-1})$
Me	0.04 ± 0.01	10.0 ± 0.4	8.6 ± 0.4
Et	0.1 ± 0.01	10.4 ± 0.4	9.4 ± 0.4
i-Pr	0.027 ± 0.006	10.4 ± 0.7	8.8 ± 0.7

See text for references.

4.3. Other radical reactions

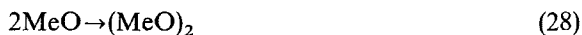
The first type of reaction of alkoxy radicals to be considered here is their mutual reaction of either combination or disproportionation:



No direct measurements have been made. Several studies have been made on the decomposition of dimethyl peroxide (for a review see Batt and Liu (1984)) in order to determine the rate constant k_{27} :



An analysis of the data of Batt and McCulloch (1976) leads to the result $k_{27} = 10^{15.3 \pm 0.4} \exp(-18500 \pm 400/T) \text{s}^{-1}$. By making use of Benson's Group Additivity Rules (1968), one may calculate ΔS_{27}^\ddagger to be $139.8 \pm 4 \text{J mol}^{-1} \text{K}^{-1}$. Hence $k_{28} = 10^{9.9 \pm 0.4} \text{M}^{-1} \text{s}^{-1}$. A similar calculation



for the results of the decomposition of bistrifluoromethyl peroxide (Batt and Walsh 1982, 1983) gives a value for k_{29} of $10^{10.3 \pm 0.2} \text{M}^{-1} \text{s}^{-1}$.



Since ΔS_{27}^\ddagger is a group value for all dialkyl peroxides, this value may be used to calculate rate constants for the combination of the corresponding alkoxy radicals. These values for k_{25} are given in table 8. It is important to notice that these values are quite different

Table 8. Rate constants for the combination of alkoxy radicals, $2\text{RO} \rightarrow (\text{RO})_2$ (25).

R	$\log k_{25}(\text{M}^{-1} \text{s}^{-1})$	Reference
Me	9.9 ± 0.4	Batt and McCulloch (1976 b)
CF_3	10.3 ± 0.2	Batt and Walsh (1982)
Et	10.7 ± 0.7	Batt and McCulloch (1976 b)
n-Pr	9.8 ± 0.4	—
i-Pr	10.0 ± 0.4	Batt and McCulloch (1976 b)
t-Bu	10.3 ± 0.2	Batt and McCulloch (1976 b)
t-Am	10.5	Perona and Golden (1978)

from those quoted by Gray *et al.* (1967). One other related combination process may be cited which concerns the trifluoromethoxy radical and a fluorine atom:



This may be determined as above (Batt and Walsh 1982) and turns out to be $10^{9.4} \text{M}^{-1} \text{s}^{-1}$. Batt *et al.* (1982) showed that dimethyl ether was a good high-temperature source of alkoxy radicals by pyrolysing the ether in a bath of methane.



Clearly the rate of process (31) is given by the rate of formation of ethane. It turned out that k_{31} is given by $k_{31} = 10^{16.3 \pm 0.3} \exp(-41000 \pm 150/T) \text{s}^{-1}$. Using a value for ΔS_{31}^\ddagger of $156.0 \text{J mol}^{-1} \text{K}^{-1}$ gives a value for k_{36} of $10^{9.8 \pm 0.4} \text{M}^{-1} \text{s}^{-1}$



We turn now to the disproportionation process (26) between alkoxy radicals. In the absence of direct measurement some uncertainty exists because the alcohol and aldehyde may well arise from other reactions. Most of this work has been covered by the review of Gray *et al.* (1967) but it is worth while to reconsider the disproportionation process:



Calvert and Dever (1962) studied the oxidation of methyl radicals in excess oxygen using a 40-m path I.R. system. Failure to observe the formation of any dimethyl peroxide led to the result $k_{37}/k_{28} > 60$, whereas Heicklen and Johnston (1962) found the ratio to be 9.3 ± 0.6 using mass spectrometric analysis. This illustrates the considerable uncertainty in the value for the rate constant for reaction (37). In terms of simple collision theory $(k_{28} + k_{37}) = 2.6 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$ which fits better with the lower of the two values. This would make $k_{37} = 10^{10.4 \pm 0.4} \text{M}^{-1} \text{s}^{-1}$. Wijnen (1958) found that the ratios $k_{38}/k_{39} = 1.4$ and $k_{40}/k_{41} = 1.8$, both independent of temperature from 303 to 363 K.



Although some isotope effect is to be expected, it is probably expedient at this time to take the mean of 1.6 ± 0.2 for the ratio. This means that the disproportionation of methyl and methoxy radicals has a rate constant of $10^{10.0 \pm 0.4} \text{M}^{-1} \text{s}^{-1}$.

4.4. Decomposition or isomerization processes

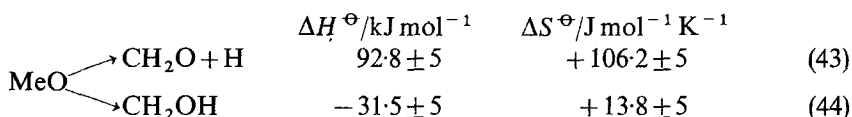
A comprehensive survey of the work on the gas-phase decomposition of alkoxy radicals by Gray *et al.* (1967) revealed serious



discrepancies which have been emphasized by Benson and O'Neal (1970) and Barker *et al.* (1977) who compared literature results with thermochemical kinetic estimates. The reasons for the discrepancies are well documented (Batt 1979) and therefore do not need to be dwelt on. One factor should be emphasized. As unimolecular processes are involved, their pressure dependence needs particular attention (Herchenson and Benson 1962). The extrapolation method used for the determination of $k_{4.1}(\infty)$ may affect the Arrhenius parameters that would be obtained from an Arrhenius plot. Michel and Rabinovitch (1959) drew attention to the errors involved in a Hinshelwood–Lindemann plot using the experimental rate constant (k_{obs}) as a function of pressure (p) and plotting $1/k_{\text{obs}}$ versus $1/p$. Large errors are to be expected from such a plot unless measurements are taken very close to the high-pressure limiting conditions. Michel and Rabinovitch (1959) recommended that a plot of $1/k_{\text{obs}}$ versus $p^{-0.5}$ be used for data that are not close to the high-pressure limit. The last two statements imply that the best plot would be $1/k_{\text{obs}}$ versus $p^{-\alpha}$ where $0 < \alpha < 1$ which was subsequently suggested by Oref and Rabinovitch (1968). Semi-logarithmic plots are also used, viz. $\log k_{\text{obs}}$ versus $p^{-0.5}$ or $p^{-\alpha}$. My own experience is that none of these methods is satisfactory. Our method has been to use the Oref–Rabinovitch approach as a starting point followed by a curve-fitting procedure in terms of the RRKM analysis program. Mathematically, this means that a polynomial expression should be used.

In theory it is possible for the alkoxy radicals to both decompose and isomerize, although in practice the latter process has not been given much attention. Isomerization processes may have some importance in both combustion processes and atmospheric chemistry. Some radicals may have more than one decomposition path although one path usually dominates.

There are two decomposition paths that should be considered for the methoxy radical: C–H bond breaking, and isomerization

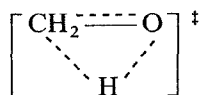


By using the thermodynamic values for the methoxy radical in table 3 and literature values for formaldehyde and the hydrogen atom (Benson 1976), $\Delta H_{4.3}^\ominus$ and $\Delta S_{4.3}^\ominus$ may be calculated. It is worth pointing out that although reaction (44) has been given less attention than reaction (43), it is an exothermic process unlike reaction (44).

Despite the importance of reaction (43) (Batt 1979, Schaefer *et al.* 1983) there is little information available. By means of an Evans–Polanyi plot, Batt (1979) estimated $E_{4.3}$ to be 115 kJ mol^{-1} whereas Gray *et al.* (1962) give a value of $125.5 \text{ kJ mol}^{-1}$. The more sophisticated Evans–Polanyi plot of Benson and Choo (1981) favours the higher value for $E_{4.3}$. Two recent theoretical studies recommend barriers of 144 kJ mol^{-1} (Schaefer *et al.* 1983) and 147 kJ mol^{-1} (Adams *et al.* 1982). Very little experimental information is available. Baldwin *et al.* (1970), in a study of the oxidation of acetaldehyde at 813 K, attributed formaldehyde formation to reaction of the methoxy radical either with

oxygen or decomposition (47). On this premise we found (Batt 1979) that $k_{43} = 10^{4.4} \text{ s}^{-1}$. It was concluded that process (43) was in the fall-off region under the conditions (160 Torr).

Despite the exothermicity of reaction (44), although noted (Gray *et al.* 1967) the process was not considered to be a competitive path with reaction (43). This is because of the thermodynamic restrictions in forming the 3-centred transition state.



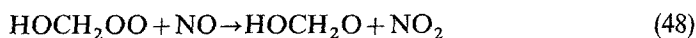
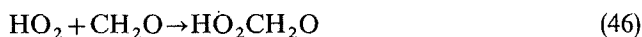
However, Schaefer (1979) considers that 1,2-hydrogen shifts may be important. Early evidence for such a process was provided by Takesaki and Takeuchi (1954). They studied the sensitized decomposition of methanol by dimethyl peroxide at 440 K and found it necessary to include the isomerization step in order to explain the observed kinetics. Twenty-five years later Wendt and Hunziger (1979) revived interest in the process. In experiments involving the reaction of fluorine atoms with methanol and the pyrolysis of dimethyl peroxide, Radford (1980) found evidence for the isomerization process. However, Christie and Pilipovich (1971) discarded this step because no ethylene glycol was formed. Batt *et al.* (1981) argued against this step at room temperature on thermochemical grounds, but concluded that isomerization may compete with the bond fission process at higher temperatures. This view is supported by the results of Dulcey and Hudgeons (1983) and Bogan (1983, personal communication). Theoretical studies by Adams *et al.* (1982) and Schaefer *et al.* (1983) led to values for E_{44} varying from 149 and $150.6 \text{ kJ mol}^{-1}$ respectively. It is clear that these two reactions merit further study.

Adams *et al.* (1982) also considered a third decomposition process,



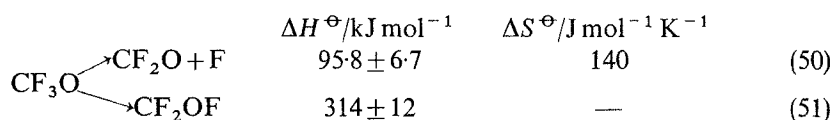
Preliminary results indicated that reaction (45) has a much larger energy barrier than either reactions (43) or (44).

Veyret *et al.* (1982) considered the formation and dissociation of the hydroxy-methoxy radical in the flash photooxidation of formaldehyde in the presence of nitric oxide



The simulated reaction gave agreement with the experimental results if a value of $k_{49} = 10^{14} \exp(-7100/T) \text{ s}^{-1}$ was used. However, if HOCH_2O is formed reaction with oxygen may be much faster than reaction (49) (Batt 1979).

It is interesting to compare the decomposition of the trifluoromethoxy radical with that of the methoxy radical. It turns out that ΔH_{50}^\ominus is almost identical with ΔH_{43}^\ominus .



However ΔH_{51}^\ominus is even more endothermic than reaction (50) and would therefore always be ruled out as a competitive path for the decomposition of the trifluoromethoxy radical.

In the decomposition of neat bis(trifluoromethyl) peroxide (Kennedy and Levy 1972, Descamps and Forst 1976, Batt and Walsh 1982), the rate-determining step is reaction (50). The mechanism is:



The rate of reaction is given by:

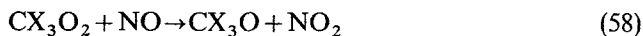
$$-d[(\text{CF}_3\text{O})_2]/dt = k_{50} \left(\frac{k_{52}}{k_{53}} \right)^{1/2} [(\text{CF}_3\text{O})_2]^{1/2}$$

Kennedy and Levy appreciated that the conditions for the above relationship were not fully met by their experimental conditions, but they were nevertheless able to interpolate a value for k_{50} . This was given by $k_{50} = 10^{14.5 \pm 0.2} \exp(-15600 \pm 300/T)$. Unlike Kennedy and Levy, Descamps and Forst (1976) found that the rate of reaction depended upon the concentration of added inert gases. However, Kennedy and Levy were working at much higher pressures. The pressure dependence is almost certainly due to reaction (50). An extrapolation is required (Descamps and Frost 1976) in order to obtain $k_{50}(\infty)$. This leads to the result $k_{50} = 10^{12.8 \pm 0.3} \exp(-13400/T) \text{ s}^{-1}$. One would expect the parameters to lie in between these two sets of reported results. The fall-off data of Descamps and Forst (1976) were matched almost precisely in a RRKM analysis using a weak collision exponential model with a step size of 200 cm^{-1} and Arrhenius parameters $\log(A_\infty/\text{s}^{-1}) = 13.47$ and $E_\infty = 118.9 \text{ kJ mol}^{-1}$ at 533 K (Batt, Reid and Stewart 1984, unpublished).

In connection with the photolysis of halogenomethanes (CX_3Cl),



a great deal of work has been carried out on the reactions of the halogen atoms generated in the photolytic act, but much less is known about the chemistry of the fragment CX_3 . A sequence of reactions such as the following seem likely (Batt and Walsh 1983).

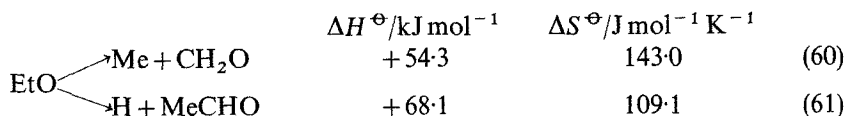


The question arises whether the radical CX_3O decomposes under stratospheric conditions



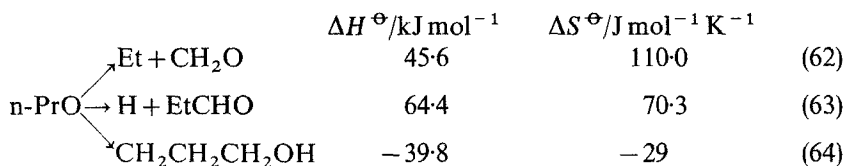
For $\text{CX}_3 = \text{CF}_3$, the process is clearly slow enough to be unimportant. For other radicals where $\text{CX}_3 = \text{CF}_2\text{Cl}$, CFCl_2 and CCl_3 , decomposition may be more facile.

There are two decomposition processes that need to be considered for the ethoxy radical. Process (60) is clearly favoured thermodynamically.



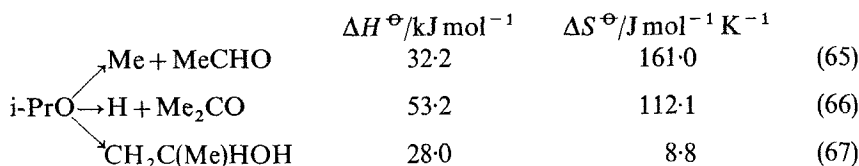
Wijnen (1960) found little evidence for the participation of reaction (61) whereas Leggett and Thynne (1967) found that the ratio $k_{60}/k_{61} > 10$, in keeping with the difference in the endothermicities. Leggett and Thynne found that k_{60} was independent of added carbon dioxide (up to 100 Torr). This is a most unexpected result especially when there is clear evidence for the pressure-dependent decomposition of the t-butoxy radical (see later). Conversely Batt and Milne (1977 b) found that there was a fall-off in the observed rate constant in the decomposition of ethyl nitrite at low pressures (~ 1 Torr) which may indicate the pressure dependence of reaction (60).

No experimental data is available for the decomposition of the n-propoxy radical but Golden *et al.* (1977) estimate that $k_{62} = 10^{13.8} \exp(-9800/T) \text{ s}^{-1}$



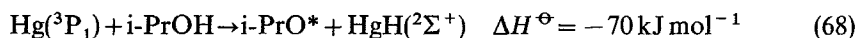
with a rate constant, taking into account fall-off, of $2.8 \times 10^{-1} \text{ s}^{-1}$ at 300 K and 1 atm (air). In terms of ΔH^\ominus_{63} , process (63) would not compete with reaction (62). Carter *et al.* (1976) estimate that $k_{64} \approx 2 \times 10^2$ at 300 K while Golden *et al.* (1977) estimate that $k_{64} = 10^{11.7} \exp(-6600/T) \text{ s}^{-1}$, i.e. $k_{64} = 1.5 \times 10^2 \text{ s}^{-1}$ in good agreement, making this the dominating unimolecular process!

There are three possible decomposition processes involving the isopropoxy radical of which the isomerization reaction (67) has not been considered before. Assuming a four-centre transition state



one may estimate that $A_{67} \approx 10^{13} \text{ s}^{-1}$ and $E_{67} \approx 138 \text{ kJ mol}^{-1}$ by the Benson (1976) method (see also Carter *et al.* (1976), Golden *et al.* (1977)). This value for k_{67} means that reaction (67) never competes with the two other decomposition processes of the isopropoxy radical. Thynne and Yee Quee (1968) found clear evidence that both reactions (65) and (66) take place. They studied the decomposition of the isopropoxy radical using diisopropyl peroxide as a thermal source over the temperature range

395–428 K. Under these conditions $k_{66}/k_{65} < 0.01$ such that $E_{66} \approx 84 \text{ kJ mol}^{-1}$. Both Phillips *et al.* (1966) and Thynne and Yee Quee (1968) were able to show that reaction (65) was a pressure-dependent process, but the conditions were such that neither set of workers was able to construct proper fall-off curves. Batt and Milne (1977) showed that k_{65} was reduced by some two powers of ten in 1 Torr of isopropyl nitrite compared to 0.9 atm of added isobutane. Longaria and Batt (1983) studied the decomposition of the isopropoxy radical using isopropyl nitrate as a thermal source. The fall-off curve obtained at 443 K is shown in figure 2. Knight and Gunning (1963) found that in the mercury-sensitized decomposition of isopropyl alcohol, vibrationally excited alkoxy radicals were produced. Batt and Milne (1976) concluded, on thermochemical grounds, that the radicals were produced from reaction (68):



There is one other system where the decomposition of the isopropoxy radical is important. An unexpected product in the pyrolysis of acetaldehyde is acetone (Laidler *et al.* 1964, 1967). A kinetic and thermodynamic analysis has shown that this acetone arises as a result of the displacement of a hydrogen atom by a methyl group involving the isopropoxy radical as an intermediate (Batt 1967, 1969).

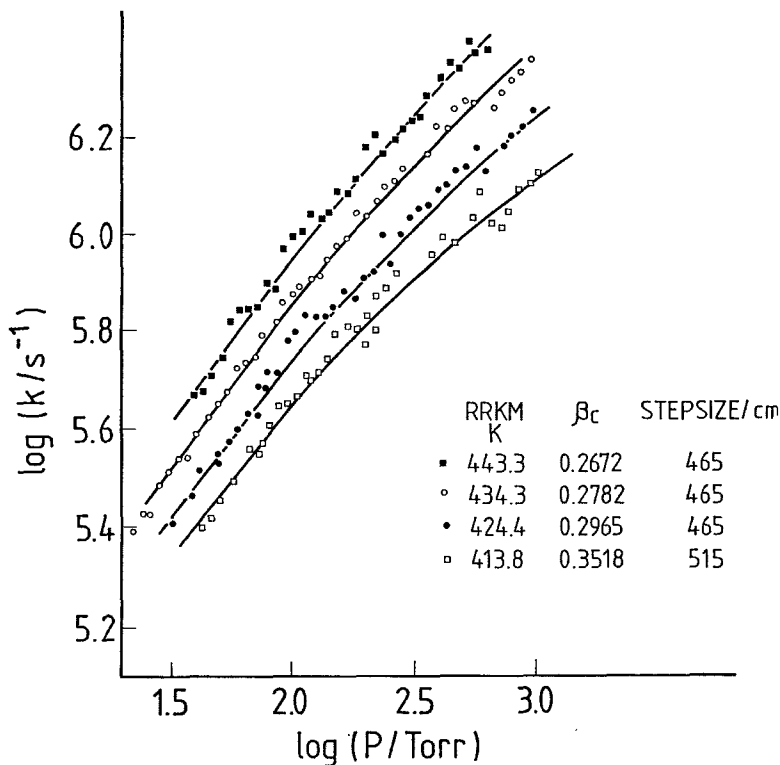
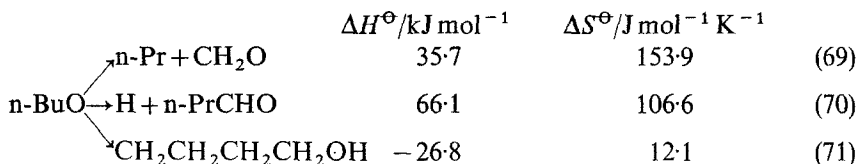
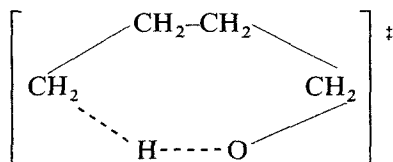


Figure 1. Falloff curve for decomposition of t-BuO with CF_4 .

No experimental information exists on the bond fission processes (69) and (70).

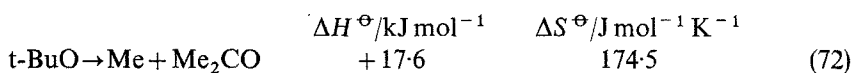


Baldwin and Golden (1978 b) estimate that $A_{69} = 10^{13.6} \text{ s}^{-1}$ and $E_{69} = 80 \text{ kJ mol}^{-1}$. The decomposition of n-butyl nitrate has been studied in the liquid phase at 493 K (Lur'e and Svetlov 1976). It was suggested that n-butanol, a major product, arose as a result of reaction (71) followed by hydrogen atom abstraction to form the alcohol. Baldwin and Golden (1978 b) pyrolysed n-butyl nitrite in the presence of deuterium iodide using a very low-pressure pyrolysis apparatus. The formation of C-D butanol indicated that the isomerization process (71) occurred. They estimate that $A_{71} = 10^{11.4} \text{ s}^{-1}$ and $E_{71} = 32.2 \text{ kJ mol}^{-1}$. The latter activation energy assumes little or no strain energy in forming the six-centre transition state

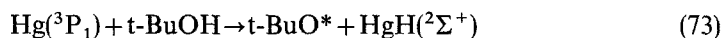


Assuming high-pressure limiting conditions, at 493 K, $k_{71}/k_{69} \approx 10^3$ so that isomerization is the dominating, if not only, process. Similar conclusions were reached by Carter *et al.* (1976).

The decomposition of the t-butoxy radical has been the most studied. It is the simplest system in that only one decomposition path is available and isomerization cannot easily occur. Also, no disproportionation process with another radical is possible.

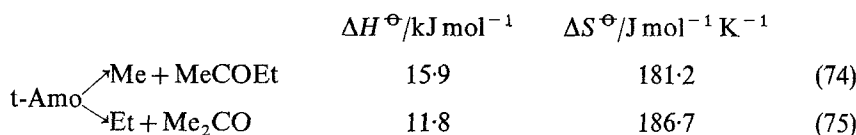


Knight and Gunning (1963) were able to show that vibrationally excited t-butoxy radicals were formed in the Hg(³P₁) sensitized decomposition of the t-butyl alcohol:



Vibrationally excited radicals are also formed in the U.V. (313, 256, 249 nm) photolysis of di-t-butyl peroxide (Dorer and Johnston 1971). Recent work by Batt and Robinson (1982) provided unequivocal evidence for the pressure dependence of reaction (72). Fall-off curves (Batt, Hisham, MacKay, Robinson and Stewart 1985, unpublished) are shown in figure 1. Best fits were obtained with $(k_{72}(\infty)/\text{s}^{-1}) = 10^{14.21} \exp(-7429/T)$.

There are two possible paths for the decomposition of the t-amloxy radical, of which reaction (75) is less endothermic and therefore should be more likely.



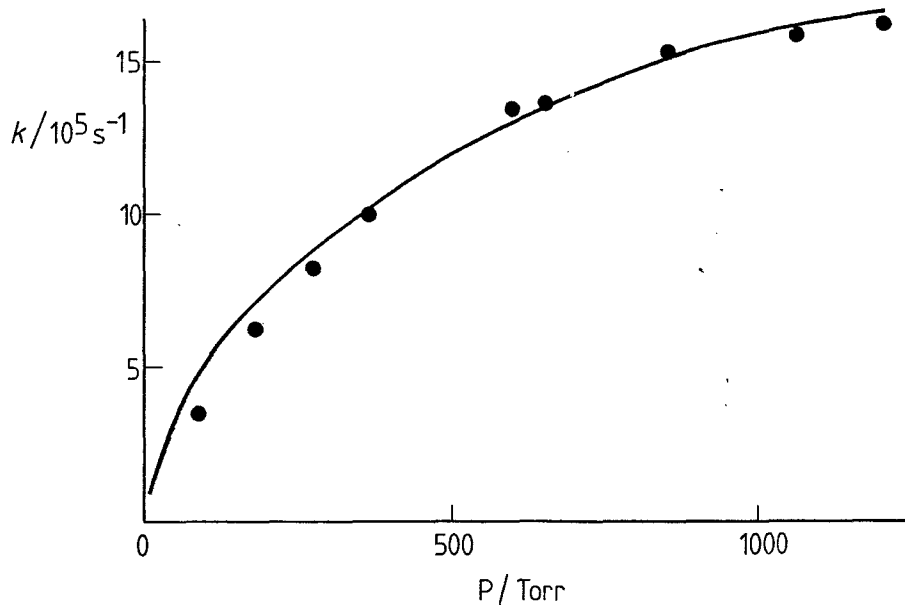


Figure 2. Falloff curve for decomposition of *i*-PrO (443K and CF₄).

Perona and Golden (1973) studied the decomposition of di-*t*-amyl peroxide using the VLPP technique over the temperature range 523–633 K. A specific search was made for the product methyl ethyl ketone but none was detected. Therefore reaction (75) appears to be the dominating path. This is in agreement with the results of Batt *et al.* (1978 a) although earlier results are conflicting. They found that the ratio $k_{75}/k_{74} = 80$ at 433 K. They studied reaction (75) via the pyrolysis of *t*-amyl nitrite in the presence of nitric oxide and found $k_{75} = 10^{14.7 \pm 0.2} \exp(-7200/T) \text{ s}^{-1}$. No pressure dependence of k_{75} was either expected or observed. In contrast to the experimental value for k_{75} , Choo and Benson (1981) estimate a value of $k_{75} = 13.6 \exp(-6900/T) \text{ s}^{-1}$.

Recommended Arrhenius parameters are given in table 9. These values differ in some respects from the estimated values of Choo and Benson (1981) in that the values cited in table 9 are based mainly on experimental results.

Table 9. Recommended Arrhenius parameters for the decomposition of alkoxy radicals.

Reaction	$\log(A/\text{s}^{-1})$	$E(\text{kJ mol}^{-1})$
MeO → CH ₂ O + H	13.4	115
EtO → CH ₂ O + Me	13.9	90
<i>i</i> -PrO → MeCHO + Me	14.6 ± 0.5	72.0 ± 4
<i>s</i> -BuO → MeCHO + Et	14.9 ± 0.5	64
<i>t</i> -BuO → Me ₂ CO + Me	14.0 ± 0.4	62.5 ± 0.6
<i>t</i> -AmO → Me ₂ CO + Et	14.7 ± 0.2	59.8 ± 4
CF ₃ O → CF ₂ O + F	13.5	104
HOCH ₂ OH → H + HCOOH	14	59†

† Lesclaux (1983).

4.5. Hydrogen atom abstraction reactions

There are two types of hydrogen atom abstraction reactions to consider: reaction with organic compounds (R'H) and reaction with oxygen.



Early work on reaction (76) has been considered by Gray *et al.* (1967). Most recent work has centred on t-butoxy radicals. Here the rate constant k_{76} has been determined relative to the decomposition of the t-butoxy radical by choosing the 'most reliable' value for k_{72}



Arrhenius parameters for reaction (76) are given in table 10. Choo *et al.* (1982) used the far U.V. (250–280 nm) photolysis of ditertiary butyl peroxide as a source of t-butoxy radicals. Under these conditions the radicals contain considerable excess energy and the rate constant used for reaction (72) would not adequately characterize their decomposition. Waddington *et al.* (1981) used ditertiary butyl peroxide as a thermal source of t-butoxy radicals. They studied reaction (76) using formaldehyde, acetaldehyde and acetone. Reaction of alkoxy radicals with formaldehyde in particular may have a significant role in the combustion of organic compounds which release methyl radicals. However, it should be pointed out that the *A* factors quoted appear to be too high by 1–2 orders of magnitude.

The second type of hydrogen atom abstraction mentioned has consequences for both atmospheric chemistry and combustion. In addition the reaction itself is used as a source of hydroperoxy radicals (Sahetchian *et al.* 1982).

Three relative studies and one direct study using laser-induced fluorescence have been made for R = Me. The results are given in table 11. The results quoted in (e) (Cox *et al.* 1980) for 300–423 K are in good agreement with the direct study (Gutman *et al.* 1982) in the range 300–473 K. One direct study and one relative study have been made for R = Et which are in reasonable agreement (table 11). However, the Arrhenius parameters quoted in the direct study (Gutman *et al.* 1982) are not in accord with the rate constants quoted at 296 and 353 K of 4.8×10^6 and $5.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Both Baldwin *et al.* (1977) and Gutman *et al.* (1982) have attempted to correlate the Arrhenius parameters with the nature of the alkyl group in the alkoxy radical.

5. Reactions of alkyl peroxy radicals

5.1. Introduction

An obvious source of alkyl peroxy radicals is via the addition of the appropriate alkyl or other radical to oxygen (Addison *et al.* 1980). The problem therefore reduces to sources of alkyl radicals. One other source is the alkyl hydroperoxide via hydrogen atom abstraction. Benson *et al.* (1983, 1984) found that using bromine atoms, hydrogen abstraction occurred exclusively from the O–H site:



Niki *et al.* (1983) generated methyl peroxy radicals using hydroxyl radicals:



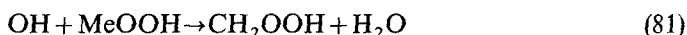
Table 10. The hydrogen abstraction reactions of alkoxy radicals with organic compounds.

Reaction	$T(K)$	$P(Torr)$	$\log A(M^{-1} s^{-1})$	$E(kJ mol^{-1})$	Reference
$\dot{C}CO \rightarrow t\text{-BuOH} + HCO$	399-434	20-200	9.9 ± 0.2	19.3 ± 2.3	Waddington <i>et al.</i> (1981)
$\dot{C}CHO \rightarrow t\text{-BuOH} + CH_2CHO$			(9.9)	25.9 ± 0.4	
$\dot{C}CHO \rightarrow t\text{-BuOH} + MeCO$			(9.9)	15.2 ± 0.8	
$\dot{C}_2CO \rightarrow t\text{-BuOH} + Me_2COCH_2$			10.1 ± 0.1	25.7 ± 1.3	
$D_3COCD_3 \rightarrow t\text{-BuOD}$					
$\dot{C}OCD_2$	316-338	10-200	10.2 ± 0.2	31.6 ± 3.0	Choo <i>et al.</i> (1982)
$\dot{C}iMe_3 \rightarrow \text{Products}$			8.5	15.5	
$\dot{C}Me_3 \rightarrow \text{Products}$			8.4	18	
$\dot{C}Me_3 \rightarrow \text{Products}$	392-429	50-660	8.6 ± 0.6	10.0 ± 4.6	Batt and Robinson (unpublished)

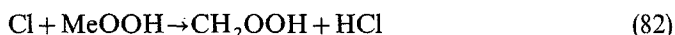
Table 11. Arrhenius parameters for the reaction of alkoxy radicals with oxygen.

R	$\log A(\text{M}^{-1} \text{s}^{-1})$	$E(\text{kJ mol}^{-1})$	Reference
Me	8.5 ± 1.5	17 ± 12	Barker <i>et al.</i> (1977)
Me	9.0 ± 0.6	20 ± 4.6	Batt and Robinson (1979)
Me	7.9 ± 0.4	11.2 ± 2.8	Cox <i>et al.</i> (1980)
Me	7.8	10.9	Gutman <i>et al.</i> (1982)
Et	7.6 ± 0.2	9.8 ± 1.0	Batt and Patrick (unpublished)
Et	7.6	5.4	Gutman <i>et al.</i> (1982)

However, C-H hydrogen atom abstraction also occurs to the extent that $k_{80}/k_{81} = 1.30 \pm 0.03$ at room temperature



In contrast, hydrogen atom abstraction using chlorine atoms results in almost exclusive attack at the C-H site



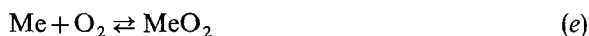
Although the addition of radicals to oxygen is inevitably involved in both sources of alkyl peroxy radicals and their dissociation, the kinetics of the addition processes, such as reaction (83), are only referred to briefly here.



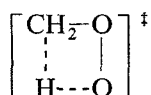
For methyl and halogen-substituted methyl radicals (for a review see Caralp and Lesclaux (1983)) the addition process is pressure dependent under the conditions studied. The fall-off is usually modelled using the semi-empirical method of Troe (1983). The possibility of a second bimolecular channel for the reaction of methyl radicals and oxygen (84) has been the subject of considerable controversy (Bayes 1983). Baldwin and Golden (1978 a) find no evidence for this process up to 1220 K.



Any reaction this way most likely involves a prior addition process probably dominated by the equilibrium (e) followed by an isomerization process which would have a four-centre transition state:

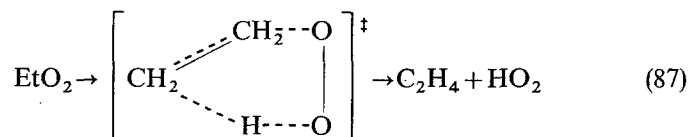


This process is endothermic only to the extent of 19 kJ mol^{-1} but the strain energy involved in forming the four-centre transition state may make $E_{85} > D(\text{Me}-\text{O}_2)$.

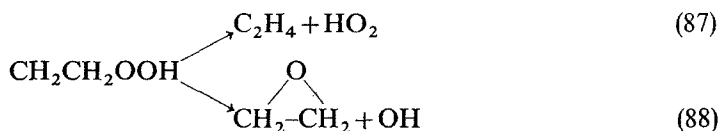


Therefore conditions may never exist for the isomerization process to compete with re-dissociation or other reactions of the methyl peroxy radical. However, once isomerization has occurred, the exothermic (114 kJ mol^{-1}) dissociation of the hydroperoxy radical occurs rapidly. This is supported by Niki's (1983) studies on the chlorine atom

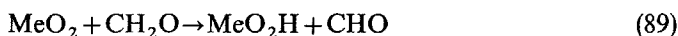
sensitized decomposition of methyl hydroperoxide. Isomerization of higher peroxy radicals is an important process in connection with combustion processes. Also, it now appears that the other bimolecular process involving alkyl radicals and oxygen (86) also involves the alkyl peroxy radical as an intermediate (Gutman 1986):



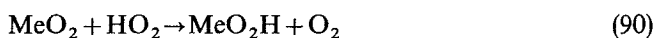
Here a five-centre transition state would be involved. If this were so, a major controversy would be raised since this implies that the major route for the decomposition of $\text{CH}_2\text{CH}_2\text{OOH}$ would be to ethylene and HO_2 , as indicated by reaction (87). In fact most other work favours epoxide formation with the production of OH .



External hydrogen abstraction reactions proceed very slowly because of the very weak $\text{RO}_2\text{-H}$ bond strength unless perhaps the process involves formaldehyde which also has a weak C-H bond strength



otherwise methyl hydroperoxide would be formed more rapidly via disproportionation with the hydroperoxy radical.



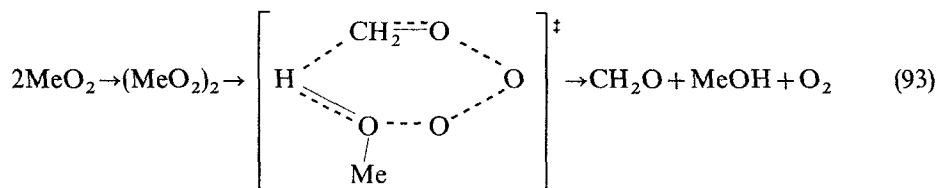
At high temperatures the equilibrium (e) would lie to the left-hand side (Benson 1965), so that the methyl peroxy radical would also disappear via reaction with a methyl radical, thereby producing two methoxy radicals.



Methoxy radicals may also be formed via the mutual destruction of two methyl peroxy radicals (92). An alternative process (97) is known as the Russell mechanism (1957).



Since this process involves a 1,5 hydrogen atom shift which may have a high activation energy,



Benson and Nangia (1980 b) argue that for alkyl peroxy radicals having α -hydrogen atoms, the same products may be accounted for via the production of a Criegee zwitterion (e.g. CH_2OO). No evidence has been found for the reaction of methyl peroxy radicals with sulphur dioxide (Sander and Watson 1981 a).

Although some of these reactions of alkyl peroxy radicals play a role in atmospheric chemistry, of more immediate relevance is their reaction with nitric oxide and nitrogen dioxide.

5.2. The reactions of alkyl peroxy radicals with nitric oxide and nitrogen dioxide

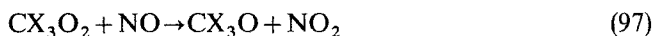
The obvious processes to consider are the addition processes with both nitrogen oxides



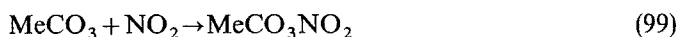
In fact for the methyl peroxy radical, interaction with nitric oxide is responsible for the latter's rapid conversion to nitrogen dioxide. Because of its importance in both the upper and lower atmosphere, reaction (96) has been studied in several laboratories (table 12).



The low value found by Adachi and Basco (1979 c) has been attributed to interference via the very rapid formation of methyl nitrite (Sander and Watson 1980). By analogy with reaction (96), Heicklen *et al.* (1979) propose that the halogenated methyl peroxy radicals CX_3 , where $\text{CX}_3 = \text{CCl}_3, \text{CCl}_2\text{F}$, react similarly



A similar reaction has been proposed for the acetylperoxy radical (Cox *et al.* 1976) such that the ratio $k_{98}/k_{99} = 1.7$ (1 atm).



Based upon a direct measurement of reaction (99) (Addison *et al.* 1980)—which is pressure dependent—at 715 Torr, makes $k_{98} = 4.8 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Adachi and Basco (1979 a) measured the reaction of ethyl peroxy radicals with NO



by kinetic spectroscopy giving a value for $k_{100} = (1.6 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ such that reaction (100) was the only fate. Plumb *et al.* (1982) found, in essential agreement, that >80% of the products were given by reaction (100). However, they found that $k_{100} = (5.4 \pm 1.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and suggest that the discrepancy is due to an interfering absorption of ethyl nitrite in Adachi and Basco's study. The latter study was carried out at 80 Torr (Ar) whereas Ryan and Plumb's study was at 5 Torr (He). At atmospheric pressure Atkinson *et al.* (1982) found reaction (100) accounted for >99% of the overall reaction.

Table 12. Rate constants for the reaction $\text{MeO}_2 + \text{NO} \rightarrow \text{MeO} + \text{NO}_2$ (96).

System†	P(Torr)	$\log A(\text{M}^{-1} \text{s}^{-1})$	$E(\text{J mol}^{-1})$	$k(10^9 \text{M}^{-1} \text{s}^{-1})$	Reference
FP-UV	75-100(Ar)			1.8 ± 0.1	Adachi and Basco (1979 c)
DF-MS	2-3(Ar)			4.8 ± 1.2	Plumb <i>et al.</i> (1979)
MMS	50(Ar + CH ₄)			3.9 ± 1.2	Sander and Watson (1980)
FP-UV	75-600(HC ₄)			4.3 ± 0.8	Cox and Tyndall (1979)
LFP-UV		9.6 ± 0.4	-715 ± 930 ‡	4.5 ± 1.0	Ravishankara <i>et al.</i> (1981)
FP-UV	70-600(CH ₄)	9.1 ± 0.3	-3160 ± 2080 §	4.6 ± 0.5	Simonaitis and Heicklen (1981)

† FP-UV, flash photolysis; ultraviolet absorption; DF-MS, discharge flow-mass spectrometry; MMS, molecular modulation spectroscopy; LFP-UV, laser flash photolysis-ultraviolet absorption.

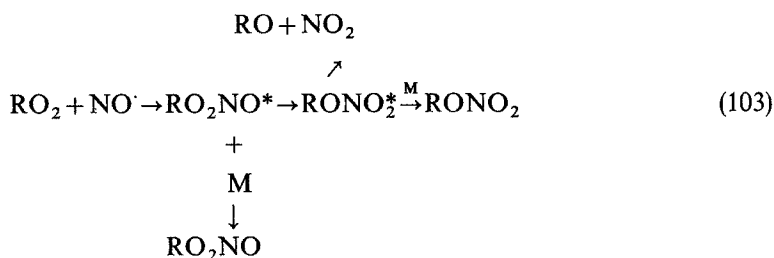
‡ 240-339 K.

§ 218-365 K.

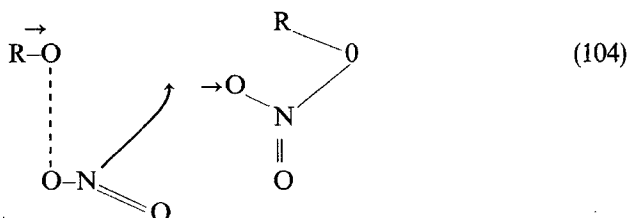
Conversely for C₃–C₈ alkyl peroxy radicals there was increasing evidence for the addition process (101) (Atkinson *et al.* 1982, 1983) although Adachi and Basco (1982 a) consider that all *i*-propyl peroxy radicals disappear via reaction (102).



The results are based upon direct alkyl nitrate formation which is significant in relation to both the chain length for the atmospheric oxidation of hydrocarbons and the regeneration of nitrogen dioxide. Atkinson *et al.* (1983) found that the processes are both temperature and pressure dependent. A rather complex mechanism was proposed. This involves the production of an alkyl peroxy nitrite which either



dissociates or is collisionally stabilized, or spontaneously isomerizes to form the alkyl nitrate. The latter has the choice of also forming an alkoxy radical + nitrogen dioxide, or being collisionally stabilized. No evidence was found for peroxy nitrite formation but this nitrite could also rapidly isomerize to the more stable alkyl nitrate. By analogy with the fact that $D(\text{RO}-\text{NO}) \simeq D(\text{RO}-\text{NO}_2)$ (Batt and Robinson 1982 a), Atkinson *et al.* (1983) assumed that $D(\text{ROO}-\text{NO}) \simeq D(\text{RO}_2-\text{NO}_2) = 85 \text{ kJ mol}^{-1}$. On this basis they concluded that the isomerization process from peroxy nitrite to nitrate had little or no activation energy. This would mean that as the RO–ONO bond starts to break the complex is very flexible. At O–O bond distances of $\sim 4 \text{ \AA}$ this can lead to a configuration such as:

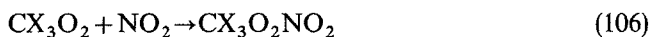


A slight rotation is sufficient to cause nitrate formation (Benson 1985, personal communication).

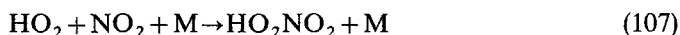
Niki *et al.* (1978) have shown by the use of FTIR spectroscopic studies that alkyl peroxy nitrates are formed via reaction (105)



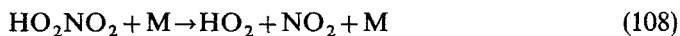
for $\text{R} = \text{C}_n\text{H}_{2n+1}$ where $n = 0-6$ and for $\text{CX}_3 = \text{CCl}_3, \text{CFCl}_2$ and CF_2Cl . Heicklen *et al.* (1979) have also shown that the ratio $k_{97}/k_{106} = 0.58 \pm 0.10$ for $\text{CX}_3 = \text{CCl}_2\text{F}$ and 0.68 for $\text{CX}_3 = \text{CCl}_3$ independent of temperature.



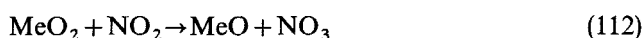
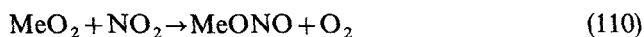
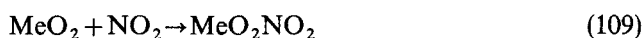
The combination of the hydroperoxy radical with nitrogen dioxide has recently been reviewed by Kaufman and Sherwell (1983) and so will not be considered further here.



It should be mentioned that HO_2NO_2 can be used as a source of HO_2 radicals



Although Niki *et al.* (1978) have shown that methyl peroxy nitrate is formed from methyl peroxy radicals and nitrogen dioxide, other products have also been proposed.



Heicklen *et al.* (1973) conclude that reactions (109) and (111) predominate with $k_{109}/k_{111} = 3.75$. Cox and Tyndall (1980) and Adachi and Basco (1980) measured the rate of disappearance of the methyl peroxy radical directly. They both consider reaction (109) as the dominant path. Little or no evidence was found for pressure dependence. Conversely both Sander and Watson (1980) and Ravishankara *et al.* (1981) found evidence for pressure dependence. This provides supporting evidence for reaction (109) and means that the contribution due to reaction (111) remains uncertain. Sander and Watson analysed their results in terms of the Troe method such that the broadening factor $F_c = 0.4 \pm 0.1$. The curve fitting procedure produced values for both k_0 and k_∞ . Ravishankara *et al.* (1980) also examined the temperature dependence of reaction (109). They followed the procedure adopted by Sander and Watson and expressed the temperature dependence of k_0 and k_∞ such that their data fitted Sander and Watson's at room temperature.

Addison *et al.* (1980) studied the addition of acetyl peroxy radicals to nitrogen dioxide via MMS following the disappearance of the peroxy radical via its U.V. absorption at 245–255 nm. Pressure dependence was observed (28–715 Torr O_2/N_2) for $k_{103} = (1.3\text{--}2.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Hendry and Kenley

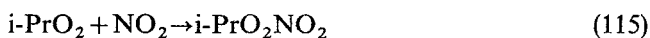


(1977) studied the decomposition of peroxy acetyl nitrate in excess nitric oxide over the temperature 298–303 K which gave $\log A_{114}/\text{s}^{-1} = 16.3 \pm 0.6$. They



estimated ΔS_{113}^\ddagger and found $k_{103} = 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Adachi and Basco (1979 a, 1982 a) studied the combination of ethyl peroxy and *i*-propyl peroxy radicals with nitrogen dioxide and found that both processes were pressure independent.



The values for k_{114} and k_{115} are given in table 13.

Table 13. Rate constants for the reaction $\text{RO}_2 + \text{NO}_2 \rightarrow \text{RO}_2\text{NO}_2$ (95).

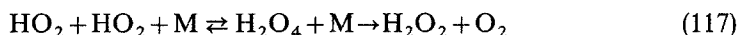
R	$k(10^9 \text{ M}^{-1} \text{ s}^{-1})$	Reference
MeCO	(1.3–2.8)	Addison <i>et al.</i> (1980)
	0.63	Hendry and Kenley (1977)
Et	0.75 ± 0.04	Adachi and Basco (1979 a)
i-Pr	3.4 ± 0.1	Adachi and Basco (1982 a)

5.3. Bimolecular reactions of alkyl peroxy radicals

Studies of the reaction between two hydroperoxy radicals indicate that the reaction has both pressure-independent and pressure-dependent mechanisms (Takacs and Howard 1984). One route involves a direct abstraction reaction



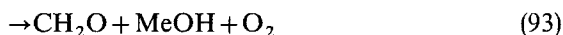
and the other a weakly bonded adduct complex leading to the same products



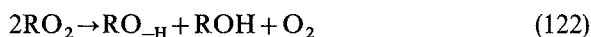
(Benson and Mozurkewich 1985). However, there is some evidence that hydrogen is also produced (Sahetchian *et al.* 1982).



A similar controversy also exists for the bimolecular reactions of alkyl peroxy radicals. Four paths have been suggested for the reactions of primary and secondary radicals of which Raley *et al.* (1951) proposed the first, Russell (1957) added the next two and Nangia and Benson (1980 b) the last.



Reaction (119) has been excluded on both thermochemical (Nangia and Benson 1980 b) and analytical grounds. Both Kan *et al.* (1979) and Niki *et al.* (1981), using FTIR spectroscopy, found little or no evidence for the formation of dimethyl peroxide at room temperature. The last two sets of workers also searched for the presence of the zwitterion CH_2O_2 . No evidence was found despite the sensitive tests used. The fate for the bimolecular reaction of alkyl peroxy radicals appear to be reactions (92) and (93), and these are given in table 14. The values are in very good agreement and give a mean value of $(2.5 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Values for other alkyl peroxy radicals are also given in tables 14 and 15. Ratios for the rate constants k_{121}/k_{122} are given in table 16.



These results reveal two puzzling features about the bimolecular reaction between alkyl peroxy radicals. The first is the fall in rate constant from primary \rightarrow secondary \rightarrow tertiary, which is accompanied by an increased activation energy (table 15). The second is the value for the ratio k_{121}/k_{122} and the viability of

Table 14. Rate constants for the bimolecular reaction of alkyl peroxy radicals (RO₂).

Method	R	$k(\text{M}^{-1}\text{s}^{-1})$	Reference
MMS	Me	2.8×10^8	Parkes <i>et al.</i> (1973)
FP-UV	Me	$(2.3 \pm 0.3) \times 10^8$	Hochanadel <i>et al.</i> (1977)
MMS	Me	$(2.7 \pm 0.6) \times 10^8$	Parkes (1977)
FP-UV	Me	$(2.2 \pm 0.2) \times 10^8$	Kan <i>et al.</i> (1979)
FP-UV	Me	$(2.5 \pm 0.3) \times 10^8$	Adachi <i>et al.</i> (1980)
FP-UV	Et	$(6.0 \pm 0.6) \times 10^7$	Adachi <i>et al.</i> (1979)
FP-UV	n-Pr	$2.0 \pm 0.2 \times 10^8$	Adachi and Basco (1982 a)
FP-UV	i-Pr	7.8×10^5	Adachi and Basco (1982 a)
P-UV	i-Pr	$8.1 \pm 0.5 \times 10^5$	Kirsch <i>et al.</i> (1978, 1979)

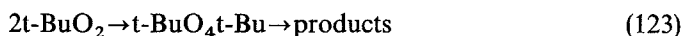
Table 15. Arrhenius parameters for the bimolecular reaction of alkyl peroxy radicals (RO₂).

R	$\log A(\text{M}^{-1}\text{s}^{-1})$	$E(\text{kJ mol}^{-1})$	Reference
t-Bu	9.3	37.0	Derived from Nangia and Benson (1980 a)
i-Pr	9.15 ± 0.03	18.65 ± 0.5	Cowley <i>et al.</i> (1982)
i-Pr	9.16 ± 0.3	18.7 ± 0.5	Kirsch <i>et al.</i> (1978)
Et	8.49 ± 0.02	4.2 ± 0.06	Anastasi <i>et al.</i> (1983)
Me	7.93 ± 0.06	$-(1.9 \pm 0.3)$	Sander and Watson (1981 b)

Table 16. Values for the ratio k_{121}/k_{122} .

R	k_{121}/k_{122}	T/K	Reference
Me	0.75 ± 0.1	298	Kan <i>et al.</i> (1979)
	0.54	298	Niki <i>et al.</i> (1981)
	0.53	298	Parkes (1977)
Et	1.75 ± 0.05	302	Anastasi <i>et al.</i> (1983)
	2.45 ± 0.15	373	
	1.3	298	Niki <i>et al.</i> (1981)
	1.0	298	Adachi <i>et al.</i> (1979)
i-Pr	1.39 ± 0.04	302	Kirsch <i>et al.</i> (1978, 1979)
	1.83 ± 0.04	333	Cowley <i>et al.</i> (1982)
	2.80 ± 0.08	373	Cowley <i>et al.</i> (1982)

reaction (122). There is at present no convincing explanation for either phenomena. Chemiluminescent phenomena are linked to these interactions (Emanuel *et al.* 1967). For t-butyl peroxy radicals, evidence has accumulated for tetroxide formation. Bogan *et al.* (1984) have observed $\text{O}_2(\text{b}^1\Sigma_g^+ \rightarrow \text{X}^3\Sigma_g^-)$ chemiluminescence from the interaction of isopropyl peroxy radicals. They attribute this chemiluminescence to reaction (122)



so that the observed activation energy could be associated with the dissociation of the tetroxide to products other than the two peroxy radicals. This would be concerned with the breaking of the O-O bond.



followed by dissociation of the highly unstable (Nangia and Benson 1980 a) t-BuO₃ within one vibration.



It is possibly here that electronically excited oxygen is formed. Unfortunately reaction (124) is endothermic by some 100 kJ mol⁻¹.

5.4. Unimolecular reactions of alkyl peroxy radicals

5.4.1. Dissociation

An obvious unimolecular reaction to consider for alkyl peroxy radicals is simple dissociation



There is at present no direct information on this process and evidence is really available only on the reverse process, which is not relevant to this review.



For R = Me, taking the high-pressure rate constant $k_{126} = 10^{9.0} \text{ M}^{-1} \text{ s}^{-1}$ (Callear and Van den Bergh 1971, Parkes 1977), one may calculate that

$$\Delta S_{127}^\circ = -121.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

and hence $A_{126} = 10^{13.5} \text{ s}^{-1}$. Using the thermochemical results discussed earlier gives $E_{127} = 117 \text{ kJ mol}^{-1}$. Further discussion is not justified.

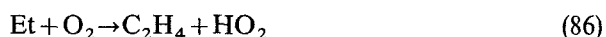
5.4.2. Isomerization

It has been generally accepted that a number of the primary products from the oxidation of hydrocarbons arise from the isomerization of the alkyl peroxy radical (128). Despite this there is no unequivocal data



for these processes mainly because the same products may arise from different sources both homogeneous and heterogeneous. The problem of the reaction of methyl radicals with oxygen to form formaldehyde and a hydroxy radical has already been referred to.

Baldwin *et al.* (1980, 1982) were able to set up a fairly clean system by adding small amounts of hydrocarbons to slowly reacting mixtures of hydrogen and oxygen in the presence of nitrogen (total pressure, 500 Torr). Thus ethyl radicals were generated from ethane



By assuming the equilibrium (h) and that the rate-determining step (129) was given by the yield of ethylene oxide (EO):

$$R_{\text{EO}} = K_{\text{h}} k_{129} [\text{Et}] [\text{O}_2]$$

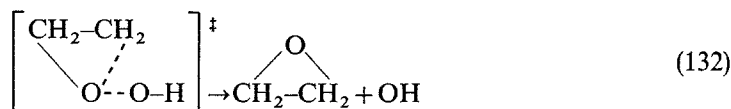
and the ratio $R_{\text{EO}}/R_{\text{C}_2\text{H}_4}$ by:

$$R_{\text{EO}}/R_{\text{C}_2\text{H}_4} = \frac{K_h}{k_{131}} k_{129}$$

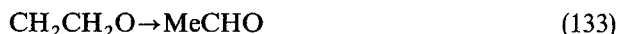
K_h could be calculated from the thermochemical data already cited. Further, from the trace amounts of butane formed and k_{132} , k_{131} , and hence k_{129} , could be determined.



Both systematic and random errors may arise from the assumptions made and the measurement of products—especially the yield of butane—respectively. Nevertheless this does provide a way of determining $k_{129} = 10^{13} \exp(-17380/T) \text{ s}^{-1}$ (Baldwin *et al.* 1980). The reactions involve a three-centre transition state involving the incipient



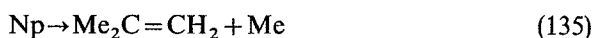
closing of a three-membered ring. At the temperature considered ($\sim 750 \text{ K}$) isomerization to acetaldehyde seems highly likely.



This introduces a further complication. The A factor is given by

$$A = ekT/h \exp(\Delta S^\ddagger/R) = 10^{13.6} \exp(\Delta S^\ddagger/R) \quad \text{at } 750 \text{ K}$$

Taking into account the entropy for loss in rotation of the methyl group and the reaction coordinate plus a symmetry factor $R \ln 3$, $A = 10^{13.0}$ in reasonable accord. Assuming a strain energy of 25 kJ mol^{-1} in the five-membered ring and an intrinsic activation energy for a primary hydrogen atom abstraction of 85 kJ mol^{-1} makes $E_{129} \approx 110 \text{ kJ mol}^{-1}$, somewhat lower than the quoted value. Baldwin *et al.* (1982) also considered the isomerization of the neopentyl peroxy radical using the same system. This time the reaction was studied relative to the decomposition of the neopentyl radical (Np)



This time R_{134}/R_{135} is given by

$$R_{134}/R_{135} = K_i k_{134}/k_{135}$$

K_i is estimated as before and k_{135} was estimated via thermochemical kinetic methods. This gave $k_{134} = 10^{12.8} \exp(-13700/T) \text{ s}^{-1}$. The A factor is in reasonable accord with an estimate as made previously. A similar five-centre transition state is involved so that one would expect the same activation energy as previously, i.e. 110 kJ mol^{-1} , in very good agreement. Baldwin *et al.* (1982) have estimated Arrhenius parameters for other isomerization processes and these are given in table 17. It is clear that an unequivocal method is required to determine data for these important reactions.

Table 17. Arrhenius parameters for the isomerization of alkyl peroxy radicals.†

Reaction	$\log A(\text{s}^{-1})$	$E(\text{kJ mol}^{-1})$
$\text{EtCH}(\text{OO})\text{Me} \rightarrow \text{EtCH}(\text{OOH})\text{CH}_2\text{EtO}_2 \rightarrow \text{C}_2\text{H}_4\text{OOH}$	13.3	145
$\text{Me}_3\text{CCH}_2\text{OO} \rightarrow \text{Me}_2\text{C}(\text{CH}_2\text{OOH})\text{CH}_2$	13.0	117
$\text{Me}_2\text{C}(\text{H})\text{CH}_2\text{OO} \rightarrow \text{MeC}(\text{H})(\text{CH}_2\text{OOH})\text{CH}_2$	12.8	117
$n\text{-BuOO} \rightarrow (\text{CH}_2)_4\text{OOH}$	11.5	98
$n\text{-Am}/\text{OO} \rightarrow (\text{CH}_2)_5\text{OOH}$	10.7	82
$\text{MeCH}(\text{OO})\text{Et} \rightarrow \text{MeCH}(\text{OOH})\text{CHMe}$	13.1	125
$\text{MeCH}(\text{OO})n\text{-Pr} \rightarrow \text{MeCH}(\text{OOH})\text{CHEt}$	13.1	125
$n\text{-BuOO} \rightarrow \text{MeCH}(\text{CH}_2)_2\text{OOH}$	12.3	100
$\text{MeCH}(\text{OO})n\text{-Pr} \rightarrow \text{MeCH}(\text{OOH})\text{CH}_2\text{CHMe}$	12.3	100
$n\text{-PrO}_2 \rightarrow \text{MeCH}(\text{CH}_2)_3\text{O}_2\text{H}$	11.5	80
$\text{MeCH}(\text{OO})\text{Et} \rightarrow \text{MeC}(\text{OOH})\text{Et}$	13.8	153
$\text{MeCHCH}_2\text{OO} \rightarrow \text{Me}_2\text{CCH}_2\text{OOH}$	12.9	110

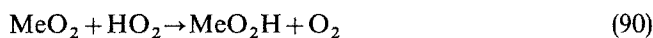
† From Baldwin *et al.* (1982).

5.4.3. Other alkyl peroxy radical reactions

There are no data on the hydrogen atom abstraction reactions by alkyl peroxy radicals from molecules, e.g.



This type of reaction is often cited as a source of methyl hydroperoxide in combustion studies. For RH formaldehyde, E_{93} has been estimated to be between 25 kJ mol^{-1} (Heicklen 1968, Griffiths and Skirrow 1968) and 50 kJ mol^{-1} (Baldwin *et al.* 1970). In this case the reaction is essentially thermoneutral. For primary C–H bonds, $E_{136} \approx 85 \text{ kJ mol}^{-1}$. The high values for E_{136} may mean that reaction (136) may never be a major source of methyl hydroperoxide. A more likely source is reaction with a hydroperoxy radical or other radicals which may donate a hydrogen atom to methyl peroxy.



Cox and Tyndall (1979, 1980) have studied this reaction using molecular modulation spectroscopy at three temperatures (table 18) and 1 atm N_2 . They find that the rate constant is given by $k_{90} = (4.6 \pm 7) \times 10^7 \exp(1296 \pm 364/T) \text{ M}^{-1} \text{ s}^{-1}$. At room temperature, k_{90} is about three times that of $2\text{HO}_2 \rightarrow \text{products}$ and about 10 times that of $2\text{MeO}_2 \rightarrow \text{products}$. Because the reaction has a negative temperature coefficient they suggest that the reaction may involve a complex mechanism similar to that of hydroperoxy radicals.

Table 18. Rate constants for $\text{MeO}_2 + \text{HO}_2 \rightarrow \text{MeO}_2\text{H} + \text{O}_2$ (90).†

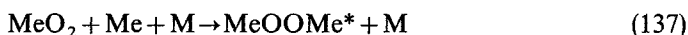
$T(\text{K})$	$k(10^9 \text{ M}^{-1} \text{ s}^{-1})$
274	5.1 ± 0.7
298	3.7 ± 0.6
338	2.1 ± 0.3

† Cox and Tyndall (1979, 1980).

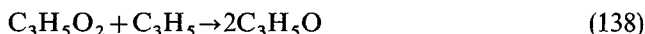
One other radical-radical reaction to be considered, which becomes more important as the temperature is raised, is that between alkylperoxy radicals and alkyl radicals



Although Adachi *et al.* (1980) suggest that the reaction may involve a peroxide intermediate the high exothermicity of the reaction may prevent thermal equilibration



Parkes (1977) finds that $k_{95} = (3.6 \pm 0.6) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ whereas Pilling (1984, personal communication) finds $(2.7 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. For the similar reaction involving the allyl radical, $k_{138} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.



In connection with atmospheric pollution, the methyl peroxy radical may also be responsible for the oxidation of sulphur dioxide. Both Kan *et al.* (1979)



and Sanhueza *et al.* (1979) found that sulphur dioxide was oxidized by methyl peroxy radicals much more rapidly than it was by hydroperoxy radicals. However, a later study by Sander and Watson (1981 b) over the temperature range 298–423 K found that the rate of reaction was immeasurably slow. An upper limit for k_{139} was determined to be $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

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References

- ADACHI, H., and BASCO, N., 1979 a, *Chem. Phys. Lett.*, **64**, 431.
 ADACHI, H., and BASCO, N., 1979 b, *Chem. Phys. Lett.*, **67**, 324.
 ADACHI, H., and BASCO, N., 1979 c, *Chem. Phys. Lett.*, **63**, 490.
 ADACHI, H., and BASCO, N., 1980, *Int. J. chem. Kinet.*, **12**, 1.
 ADACHI, H., and BASCO, N., 1982 a, *Int. J. chem. Kinet.*, **14**, 1125.
 ADACHI, H., and BASCO, N., 1982 b, *Int. J. chem. Kinet.*, **14**, 1243.
 ADACHI, H., BASCO, N., and JAMES, D. G. L., 1979, *Int. J. chem. Kinet.*, **11**, 1211.
 ADACHI, H., BASCO, N., and JAMES, D. G. L., 1980, *Int. J. chem. Kinet.*, **12**, 949.
 ADDISON, M. C., BURROWS, J. P., COX, R. A., and PATRICK, R., 1980, *Chem. Phys. Lett.*, **73**, 283.
 AL AKEEL, N. Y., SELBY, K., and WADDINGTON, D. J., 1981, *J. chem. Soc. Perkin II*, 1036.
 ANASTASI, C., WADDINGTON, D. J., and WOOLLEY, A., 1983, *J. chem. Soc. Faraday Trans. I*, **79**, 505.
 ARDEN, E. A., PHILLIPS, L., and SHAW, R., 1964, *J. chem. Soc.*, 5126.
 ATKINSON, R., ASCHMANN, S. A., CARTER, W. P. L., WINER, A. M., and PITTS, J. N. JR., 1982, *J. Am. chem. Soc.*, **86**, 4563.
 ATKINSON, R., CARTER, W. P. L., and WINER, A. M., 1983, *J. phys. Chem.*, **87**, 2012.
 BAKER, G., and SHAW, R., 1965, *J. chem. Soc.*, 6965.
 BALDWIN, A. C., BARKER, J. R., GOLDEN, D. M., and HENDRY, D. G., 1977, *J. phys. chem.*, **81**, 2483.
 BALDWIN, A. C., and GOLDEN, D. M., 1978 a, *Chem. Phys. Lett.*, **55**, 350.
 BALDWIN, A. C., and GOLDEN, D. M., 1978 b, *Chem. Phys. Lett.*, **60**, 108.
 BALDWIN, R. R., MATCHAM, M. J., and WALKER, R. W., 1970, *Combust. Flame*, **15**, 109.
 BALDWIN, R. R., PICKERING, I. A., and WALKER, R. W., 1980, *J. chem. Soc. Faraday Trans. I*, **76**, 2374.

- BALDWIN, R. R., HISHAM, M. W. M., and WALKER, R. W., 1982, *J. chem. Soc. Faraday Trans. I*, **78**, 1615.
- BARKER, J. R., BENSON, S. W., and GOLDEN, D. M., 1977, *Int. J. chem. Kinet.*, **9**, 31.
- BATT, L., 1967, *J. chem. Phys.*, **47**, 3674.
- BATT, L., 1969, *J. phys. Chem.*, **73**, 2091.
- BATT, L., 1979, *Int. J. chem. Kinet.*, **11**, 977.
- BATT, L., 1982, *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*, edited by S. Patai (Chichester: Wiley).
- BATT, L., ALVARADO, G., REID, I. A. B., and SMITH, D. B., 1982, *19th Int. Symp. Combust.*, 81.
- BATT, L., and BENSON, S. W., 1962, *J. chem. Phys.*, **36**, 895.
- BATT, L., BURROWS, J. P., and ROBINSON, G. N., 1981, *Chem. Phys. Lett.*, **78**, 467.
- BATT, L., ISLAM, T. S. A., and RATTRAY, G. N., 1978 a, *Int. J. chem. Kinet.*, **10**, 931.
- BATT, L., ISLAM, T. S. A., and SCOTT, H., 1978 b, *Int. J. chem. Kinet.*, **10**, 1195.
- BATT, L., and LIU, M. T. H., 1984, *The Chemistry of Peroxides*, edited by S. Patai (Chichester: J. Wiley).
- BATT, L., and MCCULLOCH, R. D., 1976 a, *Int. J. chem. Kinet.*, **8**, 911.
- BATT, L., and MCCULLOCH, R. D., 1976 b, *Int. J. chem. Kinet.*, **8**, 491.
- BATT, L., MCCULLOCH, R. D., and MILNE, R. T., 1975, *Int. Symp. Gas Kinetics*, *Int. J. chem. Kinet.*, 141.
- BATT, L., and MILNE, R. T., 1976, *Int. J. chem. Kinet.*, **8**, 59.
- BATT, L., and MILNE, R. T., 1977 a, *Int. J. chem. Kinet.*, **9**, 141.
- BATT, L., and MILNE, R. T., 1977 b, *Int. J. chem. Kinet.*, **9**, 549.
- BATT, L., MILNE, R. T., and MCCULLOCH, R. D., 1977, *Int. J. chem. Kinet.*, **9**, 567.
- BATT, L., and RATTRAY, G. N., 1979, *Int. J. chem. Kinet.*, **11**, 1183.
- BATT, L., and ROBINSON, G. N., 1979, *Int. J. chem. Kinet.*, **11**, 1045.
- BATT, L., and ROBINSON, G. N., 1981, *Int. J. chem. Kinet.*, **14**, 1653.
- BATT, L., and ROBINSON, G. N., 1982 a, *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*, edited by S. Patai (Chichester: J. Wiley).
- BATT, L., and ROBINSON, G. N., 1982 b, *Int. J. chem. Kinet.*, **14**, 1053.
- BATT, L., and WALSH, R., 1982, *Int. J. chem. Kinet.*, **14**, 933.
- BATT, L., and WALSH, R., 1983, *Int. J. chem. Kinet.*, **15**, 605.
- BAYES, K. D., and SELZER, E. A., 1983, *J. Phys. Chem.*, **87**, 392.
- BENSON, S. W., 1960, *Foundations of Chemical Kinetics* (New York: McGraw-Hill).
- BENSON, S. W., 1965, *J. Am. chem. Soc.*, **87**, 972.
- BENSON, S. W., 1976, *Thermochemical Kinetics*, Second edition (New York: Wiley).
- BENSON, S. W., and CHOO, K. Y., 1981, *Int. J. chem. Kinet.*, **13**, 833.
- BENSON, S. W., CRUICKSHANK, F. R., GOLDEND, M., HAVGEN, G. R., O'NEAL, H. E., RODGERS, A. S., SHAW, R., and WALSH, R., 1969, *Chem. Rev.*, **69**, 279.
- BENSON, S. W., GOLDEN, D. M., and MENDENHALL, G. D., 1975, *Int. J. chem. Kinet.*, **7**, 725.
- BENSON, S. W., and O'NEAL, H. E., 1969, *Int. J. chem. Kinet.*, **1**, 221.
- BENSON, S. W., and O'NEAL, H. E., 1970, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS-NBS21, Washington D.C.
- BENSON, S. W., and SHAW, R., 1968, *Oxidation of Organic Compounds*, Volume 1, *Adv. Chem. Ser.* No. 75 (Washington: American Chemical Society), p. 288.
- BENSON, S. W., and SHAW, R., 1970, *Organic Peroxides*. Volume 1, edited by D. Swern (New York: Wiley-Interscience).
- BENT, G. D., ADAMS, G. F., BARTRAM, R. H., PURVIS, G. D., and BARTLETT, R. J., 1982, *J. chem. Phys.*, **76**, 4144.
- BOGAN, D. J., CELII, F., SHEINSON, R. S., and COVELESKIE, R. A., 1984, *J. Photochem.*, **25**, 409.
- CALLEAR, A. B., and WOOD, P. M., 1971, *Trans. Faraday Soc.*, **67**, 3399.
- CALVERT, J. G., and DEVER, D. F., 1962, *J. Am. chem. Soc.*, **84**, 1362.
- CALVERT, J. G., and PITTS, J. N. JR., 1966, *Photochemistry* (New York: Wiley).
- CARALP, F., and LESCLAUX, R., 1983, *Chem. Phys. Lett.*, **102**, 54.
- CARTER, W. P. L., DARWELL, K. R., LLOYD, A. C., WINER, A. M., and PITTS, J. N. JR., 1976, *Chem. Phys. Lett.*, **12**, 22.
- CHOO, K. Y., and BENSON, S. W., 1981, *Int. J. chem. Kinet.*, **13**, 833.
- CHRISTIE, K. O., and PILIPOVICH, D., 1971, *J. Am. chem. Soc.*, **51**, 923.
- COWLEY, L. T., WADDINGTON, D. J., and WOOLLEY, A., 1982, *J. chem. Soc. Faraday Trans. I*, **75**, 2535.

- COX, R. A., DERWENT, R. G., HOLT, P. M., and KERR, J. A., 1976, *J. chem. Soc. Trans. Faraday I*, **72**, 2061.
- COX, R. A., DERWENT, R. G., KEARSEY, S. V., BATT, L., and PATRICK, K. G., 1980, *J. Photochem.*, **13**, 149.
- COX, D. L., LIVERMORE, R. A., and PHILLIPS, L., 1966, *J. chem. Soc.*, 245.
- COX, R. A., and TYNDALL, G. S., 1979, *Chem. Phys. Lett.*, **65**, 357.
- COX, R. A., and TYNDALL, G. S., 1980, *J. chem. Soc. Faraday Trans II*, **76**, 153.
- DESCAMPS, B., and FORST, W., 1976, *J. phys. Chem.*, **80**, 933.
- DORER, F. H., and JOHNSTON, S. N., 1971, *J. phys. Chem.*, **75**, 3651.
- DULCEY, C. S., and HUDGEONS, J. W., 1983, *J. phys. Chem.*, **87**, 2296.
- DUPUIS, M., WENDOLSKI, J. J., and LESTER, W. A., 1982, *J. chem. Phys.*, **76**, 488.
- EMANUEL, N. M., DENISOV, E. T., and MAIZUS, Z. K., 1967, *Liquid Phase Oxidation of Hydrocarbons* (New York: Plenum).
- ENDO, Y., SAITO, S., and HIROTA, E., 1982, *Int. Symp. Chem. Kinet. Atmos. Chem.*, **62**.
- EUSUF, M., and LAIDLER, K. J., 1964, *Can. J. Chem.*, **42**, 1851.
- GRAY, P., SHAW, R., and THYNNE, J. C. J., 1967, *Progress in Reaction Kinetics* Volume 4, edited by G. Porter (Oxford: Pergamon), p. 63.
- GRIFFITHS, J. F., and SKIRROW, G., 1968, *Oxidation and Combustion Reviews*. Volume 3, edited by C. F. H. Tipper (New York: Elsevier), p. 47.
- GUNNING, H. E., and KNIGHT, A. R., 1961, *Can. J. Chem.*, **39**, 1231, 2251.
- GUNNING, H. E., and KNIGHT, A. R., 1962, *Can. J. Chem.*, **40**, 1134.
- GUNNING, H. E., and KNIGHT, A. R., 1963, *Can. J. Chem.*, **41**, 763, 2849.
- GUTMAN, D., SANDERS, N., and BUTLER, J. E., 1982, *J. phys. Chem.*, **86**, 66.
- HEICKLEN, J., 1968, *Oxidation of Organic Compounds*, Volume 2, *Advances in Chemistry Ser.* (Washington: American Chemical Society), p. 23.
- HEICKLEN, J., and JOHNSTON, H. S., 1962, *J. Am. chem. Soc.*, **84**, 4030.
- HENDRY, D. G., and KENLEY, R. A., 1977, *J. Am. chem. Soc.*, **99**, 3198.
- HENEGHAN, S. P., and BENSON, S. W., 1983, *Int. J. chem. Kinet.*, **15**, 815.
- HENEGHAN, S. P., KNOOT, P. A., and BENSON, S. W., 1981, *Int. J. chem. Kinet.*, **13**, 677.
- HERCHENSON, H., and BENSON, S. W., 1962, *J. chem. Phys.*, **37**, 1889.
- HOCHANADEL, C. J., GHORMLEY, J. A., BOYLE, J. W., and OGREN, P. J., 1977, *J. phys. Chem.*, **81**, 3.
- HOLMES, J. L., and LOSSING, F. P., 1985, *Int. J. Mass Spec. Ion. Phys.*, (in the press).
- HUNZIKER, H. E., KNEPPE, H., and WEND, T. H. R., 1981, *J. Photochem.*, **17**, 377.
- INOUE, G., and AKIMOTO, H., 1981, *J. chem. Phys.*, **74**, 425.
- INOUE, G., AKIMOTO, H., and OKUDA, M., 1979, *Chem. Phys. Lett.*, **63**, 213.
- INOUE, G., AKIMOTO, H., and OKUDA, M., 1980, *J. chem. Phys.*, **72**, 1769.
- INOUE, G., AKIMOTO, H., and OKUDA, M., 1981, *J. chem. Phys.*, **75**, 2060.
- ISLAM, T. S. A., 1977, Thesis, Aberdeen.
- KAN, C. W., CALVERT, J. G., and SHAW, J. H., 1981, *J. phys. Chem.*, **85**, 1126.
- KAN, C. S., MCQUIGG, R. D., WHITBECK, H. R., and CALVERT, J. G., 1979, *Int. J. chem. Kinet.*, **11**, 921.
- KAUFMAN, M., and SHERWELL, J., 1983, *Progress in Reaction Kinetics*. Volume 12, edited by K. R. Jennings, R. B. Cundall and D. W. Margerom (Oxford: Pergamon), p. 1.
- KEBARLE, P., and LOSSING, F. P., 1959, *Can. J. Chem.*, **37**, 389.
- KENNEDY, R. C., and LEVY, J. B., 1972, *J. phys. Chem.*, **76**, 3480.
- KHACHATRYAN, L. A., NIAZYAN, O. M., MANTASHYAN, A. A., VEDENEV, V. I., and TEITEL'BOIM, M. A., 1982, *Int. J. chem. Kinet.*, **14**, 1231.
- KIJEWSKI, H., and TROE, J., 1972, *Helv. chim. Acta*, **55**, 205.
- KIRSCH, L. J., PARKES, D. A., WADDINGTON, D. J., and WOOLLEY, A., 1978, *J. chem. Soc. Faraday Trans. I*, **74**, 2293.
- KIRSCH, L. J., PARKES, D. A., WADDINGTON, D. J., and WOOLLEY, A., 1979, *J. Chem. Soc. Faraday Trans. I*, **75**, 2678.
- KNIGHT, A. R., and GUNNING, H. E., 1961 a, *Can. J. Chem.*, **39**, 1231.
- KNIGHT, A. R., and GUNNING, H. E., 1961 b, *Can. J. Chem.*, **39**, 2466.
- KNIGHT, A. R., and GUNNING, H. E., 1962, *Can. J. Chem.*, **40**, 1134.
- KNIGHT, A. R., and GUNNING, H. E., 1963, *Can. J. Chem.*, **41**, 2849.
- KONDO, O., and BENSON, S. W., 1984, *J. phys. Chem.*, **88**, 6675.
- LAIDLER, K. J., and LIU, M. T. H., 1967, *Proc. R. Soc. A*, **297**, 365.
- LEGETT, C., and THYNNE, J. C. J., 1967, *Trans. Faraday Soc.*, **63**, 2504.

- LESCLAUX, R., 1983 (Private communication).
- LONGORIA, R., 1983, Thesis, Aberdeen.
- LONGORIA, R., and BATT, L., 1983 (unpublished work).
- LORENZ, K., RHASA, D., and ZELLNER, R., 1984, *Third European Symp. Pollution* (Dordrecht: Reidel).
- LUR'E, B. A., and SVETLOV, B. S., 1976, *Russ. J. phys. Chem.*, **50**, 1344.
- MCGRATH, W. D., and MCGARVEY, J. J., 1964, *Nature*, **201**, 991.
- MICHEL, K. W., and RABINOVITCH, B. S., 1959, *J. Am. chem. Soc.*, **81**, 5065.
- MORGAN, C. A., PILLING, M. J., TULLOCH, J. M., RUIZ, R. P., and BAYES, K. D., 1982, *J. chem. Soc. Faraday Trans. II*, **78**, 1323.
- MOZURKEWICH, M., and BENSON, S. W., 1985, *Int. J. chem. Kinet.*, **17**, 787.
- NANGIA, P. S., and BENSON, S. W., 1979, *J. phys. Chem.*, **83**, 1138.
- NANGIA, P. S., and BENSON, S. W., 1980 a, *Int. J. chem. Kinet.*, **12**, 29.
- NANGIA, P. S., and BENSON, S. W., 1980 b, *Int. J. chem. Kinet.*, **12**, 43.
- NIKI, H., MAKER, P. D., SAVAGE, C. M., and BREITENBACH, L. P., 1978, *Chem. Phys. Lett.*, **55**, 289.
- NIKI, H., MAKER, P. D., SAVAGE, C. M., and BREITENBACH, L. P., 1981, *J. phys. Chem.*, **85**, 877.
- NIKI, H., MAKER, P. D., SAVAGE, C. M., and BREITENBACH, L. P., 1983, *J. phys. Chem.*, **87**, 2190.
- OHBAYASHI, K., AKIMOTO, H., and TANAKA, I., 1977, *J. phys. Chem.*, **81**, 798.
- OREF, I., and RABINOVITCH, B. S., 1968, *J. phys. Chem.*, **72**, 4488.
- PARK, C. R., SONG, S. A., LEE, Y. E., and CHOO, Y. C., 1982, *J. Am. chem. Soc.*, **104**, 6445.
- PARKES, D. A., 1977, *Int. J. chem. Kinet.*, **9**, 451.
- PARKES, D. A., and DONOVAN, R. J., 1975, *Chem. Phys. Lett.*, **36**, 211.
- PARKES, D. A., PAUL, D. M., QUINN, C. P., and ROBSON, R. C., 1973, *Chem. Phys. Lett.*, **23**, 425.
- PERONA, M. J., and GOLDEN, D. M., 1973, *Int. J. chem. Kinet.*, **5**, 55.
- PLUMB, I. C., RYAN, K. R., STEVEN, J. R., and MULCAHY, M. F. R., 1979, *Chem. Phys. Lett.*, **63**, 255.
- PLUMB, I. C., RYAN, K. R., STEVEN, J. R., and MULCAHY, M. F. R., 1982, *Int. J. chem. Kinet.*, **14**, 183.
- POTTIE, R. F., and LOSSING, F. P., 1961, *Can. J. Chem.*, **39**, 1900.
- PURNELL, J. H., and QUINN, C. P., 1964, *J. chem. Soc.*, 4049.
- RADFORD, H. E., 1980, *Chem. Phys. Lett.*, **71**, 195.
- RADFORD, H. E., and RUSSELL, D. K., 1977, *J. chem. Phys.*, **66**, 2222.
- RALEY, J. H., PORTER, L. M., RUSS, F. F., and VAUGHAN, W. E., 1951, *J. Am. chem. Soc.*, **73**, 11.
- RAVISHANKARA, A. A., EISELE, F. L., KREUTTER, N. M., and WINE, P. H., 1981, *J. chem. Phys.*, **74**, 2267.
- REED, K. S., and BRAUMAN, J. I., 1975, *J. Am. chem. Soc.*, **97**, 1625.
- RUIZ, R. P., BAYES, K. D., MACPHERSON, M. T., and PILLING, M. J., 1981, *J. phys. Chem.*, **85**, 1622.
- RUSSELL, G. A., 1957, *J. Am. chem. Soc.*, **79**, 3871.
- SAEBO, S., RADOM, L., and SCHAEFER, H. F. III, 1983, *J. chem. Phys.*, **78**, 845.
- SAHETCHIAN, K. A., HESS, A., and RIGNY, R., 1982, *Can. J. Chem.*, **60**, 2896.
- SANDER, S. P., and WATSON, R. T., 1980, *J. phys. Chem.*, **84**, 1664.
- SANDER, J. P., and WATSON, R. T., 1981 a, *Chem. Phys. Lett.*, **77**, 473.
- SANDER, S. P., and WATSON, R. T., 1981 b, *J. phys. Chem.*, **85**, 2960.
- SANDERS, N., BUTLER, J. E., PASTERNAK, L. R., and McDONALD, J. R., 1980, *Chem. Phys. Lett.*, **46**, 203.
- SAHETCHIAN, K. A., RIGNY, R., HEISS, A., and BEN-AIM, R. I., 1982, *Chem. Phys. Lett.*, **87**, 333.
- SANHUEZA, E., SIMONAITIS, R., and HEICKLEN, J., 1979, *Int. J. chem. Kinet.*, **11**, 907.
- SCHAEFER, H. F. III, 1979, *Accs. Chem. Res.*, **12**, 288.
- SELZER, E. A., and BAYES, K. D., 1983, *J. phys. Chem.*, **87**, 392.
- SIMONAITIS, R., GLAVAS, S., and HEICKLEN, J., 1979, *Geophys. Res. Lett.*, **6**, 385.
- SIMONAITIS, R., and HEICKLEN, J., 1979, *Chem. Phys. Lett.*, **62**, 473.
- SIMONAITIS, R., and HEICKLEN, J., 1981, *J. phys. Chem.*, **85**, 2946.
- SLAGLE, I. R., RATAJCZAK, E., and GUTMAN, D., 1986, *J. phys. Chem.*, **90** (in the press).
- SLAGLE, I. R., RATAJCZAK, E., HEAVEN, M. C., GUTMAN, D., and WAGNER, A. F., 1985, *J. Am. chem. Soc.*, **107**, 1838.
- SPICER, C. W., VILLA, A., WIEBE, H. A., and HEICKLEN, J., 1973, *J. Am. Chem. Soc.*, **95**, 13.
- STULL, D. R., and PROPHET, H., et al. 1970, *JANAF Thermochemical Tables*, NSRDS-NBS 37, Washington, D.C.
- STYLE, D. W. G., and WARD, J. C., 1953, *Trans. Faraday Soc.*, **49**, 999.

- SUTCH, M., WASHIDA, N., AKIMOTO, H., NAKAMURA, M., and OKUDA, M., 1980, *J. chem. Phys.*, **73**, 591.
- TAKACS, G. A., and HOWARD, C. J., 1986, *J. chem. Phys.* (in press).
- TAKESAKI, Y., and TAKEUCHI, C., 1954, *J. chem. Phys.*, **22**, 1527.
- TROE, J., 1969, *Ber. Bunsenges, phys. Chem.*, **73**, 946.
- TROE, J., 1983, *Ber. Bunsenges, phys. Chem.*, **87**, 161.
- TROTMAN-DICKENSON, A. F., 1953, *Gas Kinetics* (London: Butterworths).
- VAN DEN BERGH, H. E., and CALLEAR, A. B., 1971, **67**, 2017.
- VEYRET, B., RAYEZ, J.-C., and LESCLAUX, R., 1982, *J. phys. Chem.*, **86**, 3424.
- WENDT, H. R., and HUNZIGER, H. E., 1979, *J. chem. Phys.*, **71**, 5202.
- WIJNEN, M. J. H., 1958, *J. chem. Phys.*, **28**, 271.
- WIJNEN, M. J. H., 1960, *J. Am. chem. Soc.*, **82**, 3034.
- YARKONY, D. R., SCHAEFER, H. F. III, and ROTHENBERG, S., 1974, *J. Am. chem. Soc.*, **96**, 656.
- YEE QUEE, M. J., and THYNNE, J. C. J., 1968, *J. phys. Chem.*, **72**, 2824.