J. Chem. Soc., Faraday Trans. 1, 1984, **80**, 3481–3489

Relative Rate Study of the Addition of HO_2 Radicals to Ethylene and to Tetramethylethylene

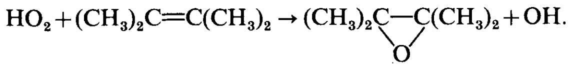
By Roy R. Baldwin, David R. Stout and Raymond W. Walker*

Department of Chemistry, The University, Hull, North Humberside HU6 7RX

Received 19*th April*, 1984

Studies of the competitive oxidation of ethylene and tetramethylethylene in the presence and absence of tetramethylbutane as a source of HO_2 radicals have been carried out between 400 and 500 °C over a range of mixture composition and total pressure using aged boric-acid-coated Pyrex vessels. From measurements of the initial relative yields of oxirane and tetramethyloxirane, values of $\log_{10}(A_7/A_5) = -0.77 \pm 0.09$ and $E_5 - E_7 = 36.5 \pm 0.9$ kJ mol^{-1} have been obtained:

$$HO_2 + C_2H_4 \rightarrow C_2H_4O + OH \qquad (5)$$



$$HO_2 + (CH_3)_2C{=}C(CH_3)_2 \rightarrow (CH_3)_2C{-}C(CH_3)_2(O) + OH. \qquad (7)$$

Use of the published values of the Arrhenius parameters for reaction (5) gives $\log_{10}(A_7/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 9.24 \pm 0.29$ and $E_7 = 40.0 \pm 4.5$ kJ mol^{-1}. No other values are available in the literature, but the present results are consistent with the very limited data available for the addition of HO_2 radicals to ethylene, propene and i-butene. Trends in the variation of the values of the rate constant and of the activation energy for HO_2 addition with structure of the alkene are very similar to those observed for the addition of CH_3O_2 and i-$C_3H_7O_2$ radicals. The relative rate of addition of i-$C_3H_7O_2$, CH_3O_2 and HO_2 radicals to any alkene at 130 °C is *ca.* 1:4:30.

At temperatures above *ca.* 300 °C, alkenes are major initial products in the oxidation of alkanes with yields often exceeding 50%[1,2] and, in the case of ethane, rising to 99%.[3] Conjugate alkenes are formed together with the HO_2 radical in the relatively rapid ($k = 10^7$–10^8 dm^3 mol^{-1} s^{-1} at 400 °C) reaction:

$$C_nH_{2n+1} + O_2 \rightarrow C_nH_{2n} + HO_2. \qquad (A)$$

Lower alkenes are also formed above *ca.* 400 °C through C—C homolysis, as shown for example by the butyl radical in the reaction $C_4H_9 \rightarrow C_2H_4 + C_2H_5$, the ethyl radical then reacting as in reaction (A). Consequently, it is not surprising that oxiranes formed in reaction (B) are major secondary products in the oxidation of alkanes:

$$HO_2 + C_nH_{2n} \rightarrow C_nH_{2n}O + OH. \qquad (B)$$

In common with many other reactions of HO_2 radicals, very few rate constants are available for reactions of type (B), despite their importance, mainly because of the difficulties experienced in finding a suitable source of HO_2.

Recently, it has been established that the decomposition of tetramethylbutane (TMB) in the presence of O_2 in both aged boric-acid-coated Pyrex vessels[4] and

KCl-coated vessels[5] is a very reliable source of HO_2 radicals over the temperature range 380–540 °C. The basic mechanism comprising reactions (1)–(4) is simple:

$$\mathrm{TMB} \longrightarrow 2\text{t-}C_4H_9 \tag{1}$$

$$\text{t-}C_4H_9 + O_2 \longrightarrow \text{i-}C_4H_8 + HO_2 \tag{2}$$

$$HO_2 \xrightarrow{\text{surface}} \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 \tag{3}$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2. \tag{4}$$

This mechanism is only slightly complicated by chain contributions to the removal of TMB through attack by HO_2 radicals, and by OH radicals formed mainly in the decomposition of H_2O_2. By working mainly at pressures below 60 Torr, the importance of OH reactions may be minimised.

From studies of the separate addition of ethylene[6] and of propene[7] to $\mathrm{TMB} + O_2$ mixtures, and measurement of yields of oxirane and of methyloxirane relative to those of i-butene (formed in 99% yield from TMB), reliable Arrhenius parameters have been determined for the first time for the reactions

$$HO_2 + C_2H_4 \rightarrow C_2H_4O + OH \tag{5}$$

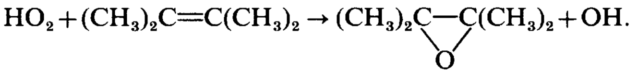
$$HO_2 + C_3H_6 \rightarrow C_3H_6O + OH. \tag{6}$$

Although, as confirmed by computer analysis, the decomposition of TMB is the major source of HO_2, the concentration of HO_2 is perturbed significantly when alkene is added to the $\mathrm{TMB} + O_2$ mixtures. In consequence, a detailed product analysis is required for each mixture used in order to establish the mechanism of alkene oxidation so that $[HO_2]$ can be calculated accurately. Considerable effort is thus required to determine Arrhenius parameters such as E_5 and E_6, although additional information is obtained on other reactions involving the alkene, for example rate constants for OH + alkene.[6,7]

Studies of the addition of ethylene[6] and of propene[7] to the $\mathrm{TMB} + O_2$ system have established that the oxirane is formed only through the addition of HO_2 radicals to the alkene at temperatures above 380 °C. At lower temperatures, Waddington and coworkers[8–12] have shown that oxiranes may be formed through addition of acylperoxy and alkylperoxy radicals. If HO_2 addition is the sole source of oxiranes at the higher temperatures, then the simplest and most reliable method of determining Arrhenius parameters for any particular alkene is to carry out competitive reactions using either reaction (5) or reaction (6) as the reference reaction. Hence for the two alkenes A and B giving the two oxiranes AO and BO with rate constants k_A and k_B, respectively, then the ratio k_A/k_B may be obtained from eqn (i) with no knowledge of $[HO_2]$ necessary:

$$d[AO]/d[BO] = k_A[A]/k_B[B]. \tag{i}$$

This paper describes the use of the approach to obtain the ratio k_5/k_7, the relative rate of reaction of HO_2 radicals with ethylene and with TME to give the respective oxiranes. TME was chosen because the studies of Osborne and Waddington[10] of CH_3O_2 addition to alkenes suggest that HO_2 addition to TME should be considerably faster than to ethylene:



$$HO_2 + (CH_3)_2C{=}C(CH_3)_2 \rightarrow (CH_3)_2C{-}C(CH_3)_2 + OH. \tag{7}$$

A value of 2.4×10^4 dm^3 mol^{-1} s^{-1} at 300 K is given for the rate constant for the unspecified reaction of HO_2 radicals with TME by Graham *et al.*,[13] who used the decomposition of HO_2NO_2 as the source of HO_2 radicals. However, owing to several uncertainties in the mechanism of the system, they were forced to consider the value only as an upper limit.

EXPERIMENTAL

Reactions were carried out in a conventional static vacuum apparatus, using Pyrex vessels coated with boric acid and aged by repeated runs with H_2+O_2 mixtures at 500 °C. Pressure changes and absolute pressures below 50 Torr were measured by use of a Southern Electronics pressure transducer, capable of an output of 1 mV for a pressure change of 1 Torr in the reaction vessel. A microprocessor-controlled timing unit, coupled to solenoid valves, was used both to admit gases to the vessel and to take samples at pre-set times. The response of the valves was *ca.* 0.1 s, so that very precise admission and sampling times could be achieved, even at the highest temperature used where reaction times varied between 2 and 15 s. Gas chromatography was used for the analysis of products. N_2 was used as a diluent, and independent variation of TMB, TME, ethylene and O_2 pressures at a fixed total pressure could be achieved by interchange with N_2.

RESULTS

Co-oxidation of TME and ethylene in the presence and absence of TMB showed that both the rate of consumption of the two alkenes and the value of the relative amounts of oxirane and tetramethyloxirane (TMO) formed were virtually unaffected by the presence of TMB. These observations are caused by the high rate of oxidation of TME, even in the absence of TMB, and because the oxidation of both alkenes produces HO_2 radicals faster than the decomposition of TMB. After preliminary experiments to establish that this pertained over all the conditions used, the yields of the oxiranes were determined in the absence of TMB.

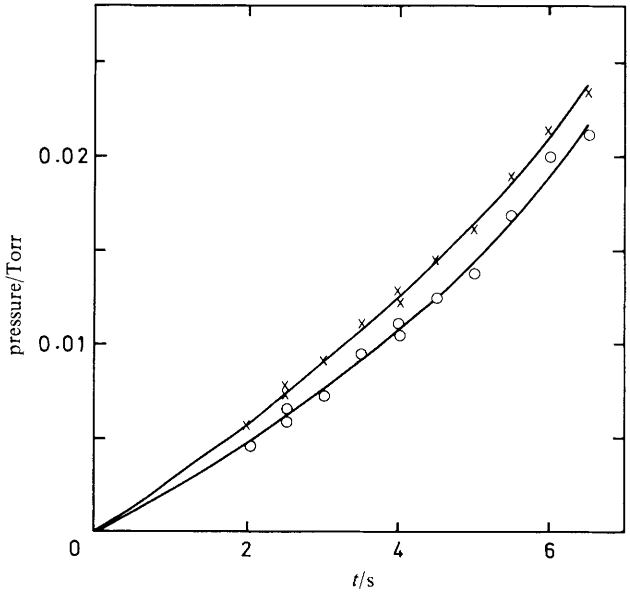


Fig. 1. Yields of oxirane and TMO at 480 °C (TME = 0.5, C_2H_4 = 20, O_2 = 5, N_2 = 34.5 Torr): ×, TMO; ○, oxirane.

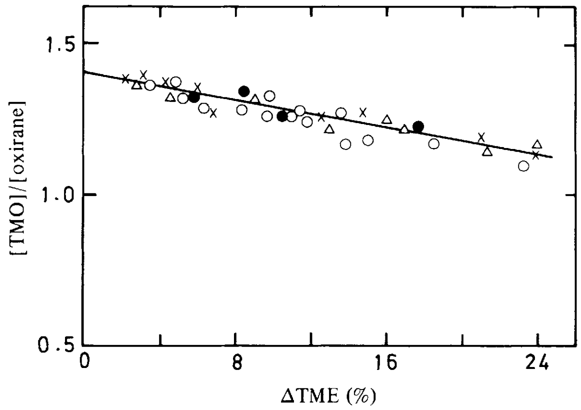


Fig. 2. Variation of [TMO]/[oxirane] with extent of reaction and mixture composition (pressures in Torr).

symbol	TMB	TME	C_2H_4	O_2	N_2
○	0	0.5	20	5	34.5
●	2	0.5	20	5	32.5
×	0	0.5	20	30	9.5
△	0	0.5	20	9.5	0

Table 1. Initial values of [TMO]/[oxirane]

	mixture composition/Torr				total	[TMO]	
T/°C	C_2H_4	TME	O_2	N_2	pressure/Torr	[oxirane]	k_7/k_5
380	20	0.5	5	34.5	60	3.48	139
	20	0.5	20	19.5	60	3.55	142
	20	0.5	5	374.5	400	3.90	156
440	20	0.5	9.5	0	30	2.00	80
	20	0.5	5	34.5	60	2.03	81
	20	0.5	20	19.5	60	2.04	81.5
	5	0.5	20	34.5	60	7.9	79
	20	2.0	20	18	60	8.2	82
	20	0.5	5	374.5	400	2.21	88.5
480	20	0.5	9.5	0	30	1.44	57.5
	20	0.5	5	34.5	60	1.40	56
	20	0.5	20	19.5	60	1.40	56
	20	0.5	5	374.5	400	1.75	70
500	20	0.5	9.5	0	30	1.28	51
	20	0.5	5	34.5	60	1.21	48.5
	20	0.5	20	19.5	60	1.24	49.5
	20	0.5	5	374.5	400	1.35	54

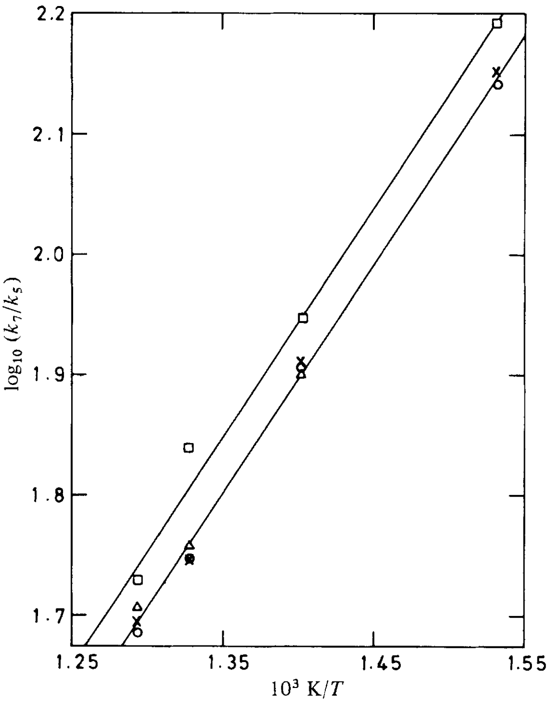
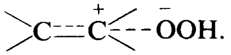


Fig. 3. Arrhenius plot for k_7/k_5 (TME = 0.5, C_2H_4 = 20 Torr): ○, O_2 = 5, N_2 = 34.5 Torr; ×, O_2 = 30, N_2 = 9.5 Torr; △, O_2 = 9.5, N_2 = 0 Torr; □, O_2 = 5, N_2 = 374.5 Torr.

Fig. 1 shows the absolute yields of oxirane and TMO as a function of time for the mixture containing 0.5, 20, 5 and 34.5 Torr of TME, ethylene, O_2 and N_2, respectively, at 480 °C. The curves illustrate the good reproducibility of the results and show that both products are formed in primary processes. The high ratio of ethylene to TME was maintained throughout the study to obtain similar yields of oxirane and TMO. Fig. 2 shows a plot of the product ratio as a function of extent of reaction (loss of TME). The slight fall in the product ratio with extent of reaction is typical of most mixtures at all temperatures studied, and is probably caused by the relatively high consumption of TME. As fig. 2 shows, variation of O_2 pressure and the presence of TMB do not noticeably change the product ratio. Variation between 30 and 60 Torr total pressure has no significant effect, but slightly higher values of [TMO]/[oxirane] are observed when the total pressure is increased to 400 Torr. At 400 Torr, the decrease in the ratio with extent of reaction tends to be slightly greater than observed at the lower pressures, the highest decrease being found at 380 °C where the ratio falls from 151 to 125 between 1 and 5% consumption of TME. In all cases initial values of the ratio were determined by extrapolation to zero extent of reaction, the accuracy of the low-pressure values being better than 5%.

Table 1 summarises the values of k_7/k_5 obtained from eqn (i) for the various mixtures used at each temperature. The values are independent of O_2 pressure, variation in the $[TME]/[C_2H_4]$ ratio, and are in good agreement at 30 and 60 Torr total pressure, as predicted by eqn (i). However, the values obtained at 400 Torr are consistently 10–20% higher than at the lower pressures, and there is no obvious explanation for this observation. If reaction (5) is slightly dependent on pressure owing to a third-body effect, as was suggested as a possibility recently,[6] then the values of k_7/k_5 should be lower at 400 Torr than at 30 and 60 Torr. One contributory factor may be that the observed values of [TMO]/[oxirane] fall more rapidly with extent of reaction at 400 Torr than at the lower pressures, so that extrapolation to zero extent of reaction is less reliable. Fig. 3 shows that an Arrhenius plot of $\log_{10}(k_7/k_5)$ against $1/T$ gives two good straight lines of effectively the same gradient. At 400 Torr, $\log_{10}(A_7/A_5) = -0.72 \pm 0.09$ and $E_5 - E_7 = 36.4 \pm 0.9$ kJ mol^{-1}, whereas all the other mixtures give a common line with $\log_{10}(A_7/A_5) = -0.77 \pm 0.09$ and $E_5 - E_7 = 36.5 \pm 0.9$ kJ mol^{-1}. As suggested above, the results at 30 and 60 Torr are probably more reliable, and thus the latter parameters are recommended.

DISCUSSION

The large difference in the activation energies for the addition of HO_2 radicals to ethylene and to TME is similar to that observed[14, 15] for the addition of NF_2 radicals ($\Delta E = 30$ kJ mol^{-1}) and to that calculated for the addition of CH_3O_2 radicals of 27 ± 5 kJ mol^{-1}, obtained from $k_{C_2H_4} = 1.2 \pm 0.7$ dm^3 mol^{-1} s^{-1} at 410 K, $A_{TME} = 10^{8.14 \pm 0.32}$ dm^3 mol^{-1} s^{-1} and $E_{TME} = 36.4 \pm 2.8$ kJ mol^{-1}, both given by Waddington and coworkers,[9, 10] it being assumed in the calculation that $A_7/A_5 = A_{TME}/A_{C_2H_4}$. This large dependence on the alkene structure is typical of electrophilic radicals.[14] As the ionisation energy of the alkene decreases, the rate of radical addition increases. Such behaviour is observed for the addition of CH_3CO_3,[8] CH_3O_2,[10] i-$C_3H_7O_2$,[12] NF_2[15] and CF_3[16] radicals and of O atoms[17] to double bonds. All these systems show a linear decrease in log k with increase in ionisation energy at any particular temperature. As HO_2 radicals appear to fit the general pattern, the transition state for the addition is likely to involve a contribution from 

Absolute Arrhenius parameters for reaction (7) may be obtained by use of $\log_{10}(A_5/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}) = 10.01 \pm 0.25$ and $E_5 = 76.5 \pm 4.0$ kJ mol^{-1}, obtained from studies of the addition of ethylene to mixtures of TMB + O_2 between 400 and 500 °C,[6] so that $\log_{10}(A_7/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}) = 9.24 \pm 0.29$ and $E_7 = 40.0 \pm 4.5$ kJ mol^{-1}. No other reliable values are available for k_7, but table 2 summarises the limited data available for the addition of HO_2 radicals to alkenes. The Arrhenius parameters for i-butene are calculated from the single rate constant determination[18] at 470 °C on the assumption of equal A factors for addition to i-butene and to propene. The activation energy falls uniformly as the ionisation energy decreases, as observed for CH_3O_2 and i-$C_3H_7O_2$ radicals (table 2). Further, for the three radicals the activation energies for the addition to a particular alkene are very similar, as are the variations of activation energy with ionisation energy. This is shown in fig. 4, which also shows points for the addition of NF_2[15, 16] and CH_3CO_3[8] radicals. Within experimental error, the NF_2 points fit on the line drawn through the HO_2 and CH_3O_2 data. Although the activation energies for CH_3CO_3 addition are clearly lower, a good line of similar gradient may be drawn through the points. Clearly patterns do exist, and when more reliable data are available it should be possible to formulate the variation in activation energy in terms of ionisation energy of the alkene, electrophilicity of the radical and the enthalpy change on addition. However, even at this stage it is concluded from the general consistency of the data that the values of the rate constants probably refer to the actual addition step.

Table 2. Comparison of Arrhenius parameters for addition of peroxy radicals to alkenes[a]

alkene	ionisation energy[b]	HO_2 + alkene[6, 7, 18]			CH_3O_2 + alkene[9, 10]			i-$C_3H_7O_2$ + alkene[11, 12]		
		$\log_{10}A$	E	T/°C	$\log_{10}A$	E	T/°C	$\log_{10}A$	E	T/°C
C_2H_4	1013	10.01 ± 0.25	76.5 ± 4	400–500	$\log_{10}k = 0.08 \pm 0.30$		137	—	—	—
C_3H_6	939	9.02 ± 0.30	59.4 ± 5	400–500	—	—	—	8.92 ± 0.36	67.7 ± 2.5	100–135
i-C_4H_8	891	9.02 ± 0.30	52.9 ± 5	470[c]	—	—	—	8.59 ± 0.19	62.7 ± 2.2	100–135
2-methylbut-1-ene	880	—	—	—	8.60 ± 0.72	52.8 ± 5.4	100–130	8.30 ± 0.07	54.9 ± 0.6	90–135
2-methylbut-2-ene	837	—	—	—	8.16 ± 0.49	42.4 ± 3.6	100–130	8.03 ± 0.35	48.2 ± 1.7	30–90
2,3-dimethylbut-2-ene	801	9.24 ± 0.29	40.0 ± 4.5	380–500	8.14 ± 0.32	36.4 ± 2.8	100–130	7.96 ± 0.50	40.9 ± 1.8	30–90

[a] Units: A, $dm^3\ mol^{-1}\ s^{-1}$; energy, $kJ\ mol^{-1}$. [b] Ionisation energies from *C.R.C. Handbook of Chemistry and Physics*, ed. R. C. Weast (C.R.C. Press, Florida, 62nd edn, 1982), p. E.72. [c] Arrhenius parameters calculated from single value of $\log k = 5.30$ at 470 °C[18] on the assumption that A is the same as for $HO_2 + C_3H_6$.

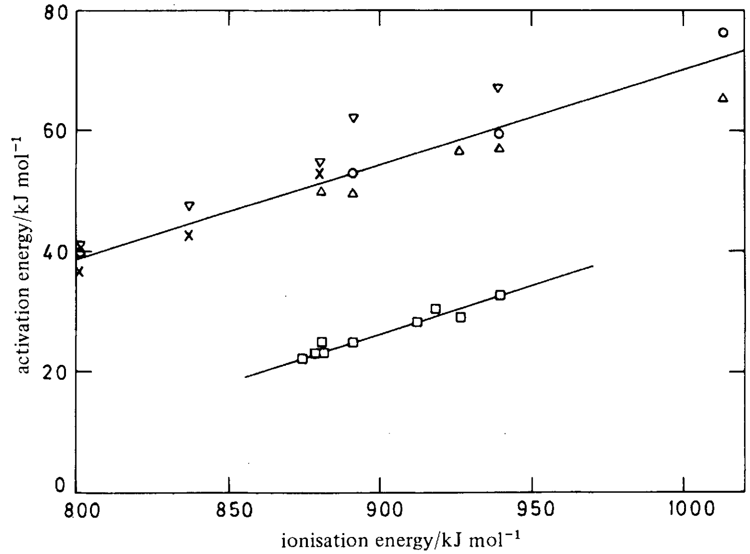


Fig. 4. Plots of activation energy for radical addition to alkenes against ionisation energy of alkene: ○, HO_2: ×, CH_3O_2: ▽, i-PrO_2; △, NF_2; □, CH_3CO_3.

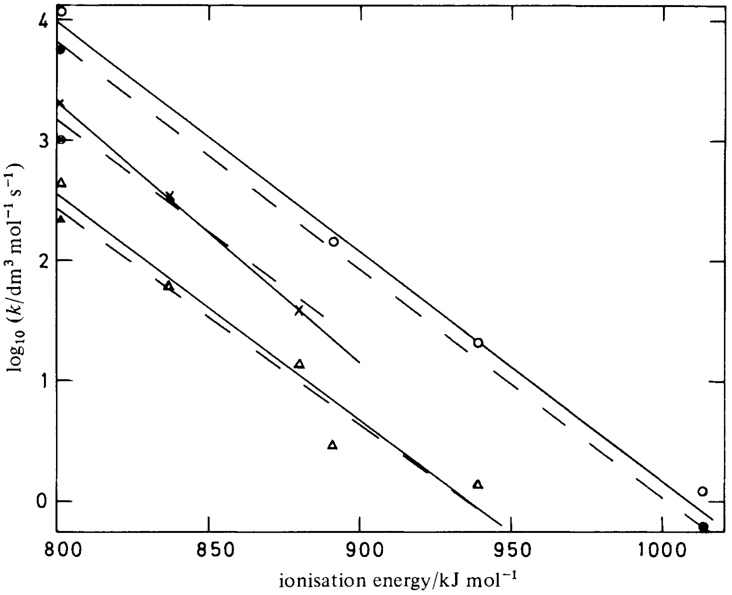


Fig. 5. Plots of $\log_{10}k$ for radical addition to alkenes against ionisation energy of alkene: ○, ●, HO_2; ×, ⊗, CH_3O_2; △, ▲, i-PrO_2. ●, ⊗, ▲ and dashed lines allow for path degeneracy.

Direct comparison of the relative rates of addition of the peroxy species is difficult because of the large difference in the temperatures used for the studies, particularly as the CH_3O_2 additions were studied over a 30 K range only. Fig. 5 shows plots of log k against ionisation energy for the three peroxy radicals at 130 °C, the HO_2 values being extrapolated from the studies in the temperature range used of 400–500 °C. The good line for HO_2 confirms that at least the activation-energy differences for HO_2 addition to the alkenes are accurate. The dashed lines represent the best relationships between the points when, in the cases of ethylene and TME, the rate constants are halved to allow for the path degeneracy of 2 in the symmetrical alkenes. Within the limits of experimental accuracy the lines (full or dashed) for each radical are almost parallel and indicate that the rate constants for the addition of i-$C_3H_7O_2$, CH_3O_2 and HO_2 to any alkene at 130 °C are in the approximate ratio 1:4:30. Addition reactions of HO_2 radicals to alkenes are thus likely to be important even at quite low temperatures (*ca.* 150 °C), although under typical atmospheric conditions reactions of alkenes with OH radicals are likely to be dominant.[13]

---

[1] R. T. Pollard, in *Comprehensive Chemical Kinetics*, ed. C. H. Bamford and C. F. H. Tipper (Elsevier, Amsterdam, 1977), vol. 17, p. 249.

[2] R. W. Walker, in *Reaction Kinetics* (Specialist Periodical Report, The Chemical Society, London, 1975), vol. 1, p. 161.

[3] R. R. Baldwin, I. A. Pickering and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2374.

[4] R. R. Baldwin, M. W. M. Hisham, A. Keen, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1165.

[5] G. M. Atri, R. R. Baldwin, G. A. Evans and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 366.

[6] R. R. Baldwin, D. G. Malcolm and R. W. Walker, paper presented at the second International Specialists Meeting of the Combustion Institute on Oxidation, Budapest, August 1982; to be published in *Oxidation Communications*.

[7] R. R. Baldwin, M. W. M. Hisham and R. W. Walker, paper to be presented at the 20th International Symposium on Combustion, University of Michigan, Ann Arbor, August 1984; to be published in the symposium proceedings in 1985.

[8] R. Ruiz Diaz, K. Selby and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1977, 360.

[9] K. Selby and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1980, 65.

[10] D. A. Osborne and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1980, 925.

[11] M. I. Sway and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1982, 999.

[12] M. I. Sway and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1983, 139.

[13] R. A. Graham, A. M. Winer, R. Atkinson and J. N. Pitts, *J. Phys. Chem.*, 1979, **83**, 1563.

[14] J. A. Kerr and M. J. Parsonage, *Evaluated Kinetic Data on Gas Phase Addition Reactions* (Butterworths, London, 1972).

[15] A. J. Dijkstra, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 1967, 105.

[16] *C.R.C. Handbook of Bimolecular and Termolecular Gas Reactions*, ed. J. A. Kerr (C.R.C. Press, Florida, 1981), vol. 2.

[17] S. Furuyama, R. Atkinson, A. J. Colussi and R. J. Cvetanovic, *Int. J. Chem. Kinet.*, 1974, **6**, 741.

[18] R. R. Baldwin, D. G. Malcolm and R. W. Walker, unpublished work.

(PAPER 4/650)