Reactions of Oxygenated Radicals in the Gas Phase. Part I. Reaction of Peracetyl Radicals and But-2-ene

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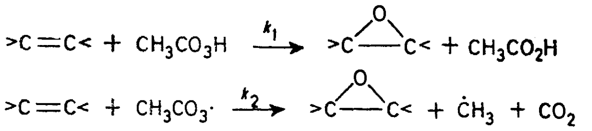
In the co-oxidation of acetaldehyde and but-2-ene at 393 K, both peracetyl radicals and peracetic acid react with the alkene to form 2,3-epoxybutanes [reactions (1) and (2)]. The proportion of *cis*- and *trans*-epoxides



$$>C{=}C< + CH_3CO_3H \xrightarrow{k_1} >C\overset{O}{\text{—}}C< + CH_3CO_2H \quad (1)$$

$$>C{=}C< + CH_3CO_3\cdot \xrightarrow{k_2} >C\overset{O}{\text{—}}C< + \dot{C}H_3 + CO_2 \quad (2)$$

formed varies with time, the reaction between the alkene and peracetic acid being stereospecific. Two methods of calculating k_1 are used. In one, values of $(3{\cdot}0 \pm 0{\cdot}7) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, in the other, values of $(3{\cdot}4 \pm 1{\cdot}0) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, are obtained for both alkenes. k_2 Is found to be $(1{\cdot}2 \pm 0{\cdot}1) \times 10^5$ and $(7{\cdot}5 \pm 0{\cdot}1) \times 10^4$ dm^3 mol^{-1} s^{-1} for *trans*- and *cis*-but-2-ene, respectively.

IN order to understand fully the phenomena that occur in the gas-phase oxidation of hydrocarbons (such as the occurrence of cool flames, the negative temperature coefficient, and the significant changes in product distribution as the temperature of reaction is increased) it is necessary to have data for the rates of reactions occurring in these complex systems.

There is a considerable amount of data for the reactions between hydrocarbons and atoms, alkyl radicals, and hydroxyl radicals. In comparison, there is relatively little information, obtained experimentally, for the gas-phase reactions of alkylperoxyl and α-oxoalkylperoxyl radicals, although in recent years, Baldwin, Walker, and their co-workers have been obtaining significant rate data for the reactions of hydroperoxyl radicals with hydrocarbons and aldehydes. Baldwin and Walker have generally used a technique of co-oxidising the substrate with hydrogen [1-3] or with formaldehyde,[4-6] and have obtained data for the abstraction reactions between hydroperoxyl and ethane,[1,4,6] propane,[2,4,6] butane,[2] 2-methylpropane,[2,4,6] formaldehyde,[3,4] and for the addition reaction with ethylene.[6] Furthermore, they have estimated Arrhenius parameters for the abstraction reactions between hydroperoxyl and hydrogen atoms in different types of C–H bond in alkanes.[5,6]

These data are undoubtedly of great importance in the elucidation of the mechanism of the high temperature (*ca.* 650 K and above) oxidation of hydrocarbons. However, data for the reactions between alkylperoxyl and α-oxoalkylperoxyl radicals with hydrocarbons are also necessary when considering the low-temperature oxidation region. Alkylperoxyl radicals which are formed from the parent hydrocarbons, $RH \xrightarrow{X\cdot} R\cdot \xrightarrow{O_2} RO_2\cdot$ where X· is a chain carrier, yield carbonyl compounds.[6] These, in turn, yield α-oxoalkylperoxyl radicals, which are often more reactive than the precursor radicals, $RO_2\cdot \longrightarrow R'CHO \xrightarrow{X\cdot} R'CO\cdot \xrightarrow{O_2} R'CO_3\cdot$. In particular, the formation of acetaldehyde, as an intermediate, has a profound effect on the oxidation of many hydrocarbons. For example, the aldehyde is the principal product in the early stages of the gas-phase oxidation of but-2-ene, and, after a very short time, it controls the subsequent pattern of the reaction.[7]

Preliminary results for the addition reaction between peracetyl radicals and but-2-ene indicate that the reaction is very rapid [8,9] and these have been followed by data for the abstraction reaction between peracetyl and formaldehyde.[10] Calculations leading to both sets of results depend on values for the rate of reaction between the radical and acetaldehyde.[11,12]

In this paper, a method to obtain rate data for the addition reaction between peracetyl and alkenes to form the corresponding epoxide is described. A complicating feature is that peracetic acid is formed from acetaldehyde and is also involved in the formation of the epoxide. However, it is shown how, in the treat-

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[2] R. R. Baker, R. R. Baldwin, and R. W. Walker, *Trans. Faraday Soc.*, 1970, **66**, 2812.

[3] R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, *J.C.S. Faraday I*, 1972, 1362.

[4] R. R. Baldwin, D. H. Langford, M. J. Matchan, R. W. Walker, and D. A. Yorke, 13th Internat. Combustion Symp., The Combustion Institute, Pittsburgh, 1971, p. 251.

[5] R. R. Baldwin and R. W. Walker, 14th Internat. Combustion Symp., The Combustion Institute, Pittsburgh, 1973, p. 241.

[6] R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, Combustion Institute European Symp., ed. F. J. Weinberg, Academic Press, London, 1973, p. 70.

[7] D. J. M. Ray, R. Ruiz Diaz, and D. J. Waddington, 14th Internat. Combustion Symp., The Combustion Institute, Pittsburgh, 1973, p. 259.

[8] D. J. M. Ray and D. J. Waddington, *J. Phys. Chem.*, 1972, **76**, 3319.

[9] F. McKeon, D. J. M. Ray, A. Redfearn, R. Ruiz Diaz, and D. J. Waddington, Combustion Institute European Symp., ed. F. J. Weinberg, Academic Press, London, 1973, p. 88.

[10] D. J. Dixon, G. Skirrow, and C. F. H. Tipper, *J.C.S. Faraday I*, 1974, 1090.

[11] J. F. Griffiths, G. Skirrow, and C. F. H. Tipper, *Combustion and Flame*, 1968, **12**, 360.

[12] J. F. Griffiths and G. Skirrow, *Oxidation Combustion Rev.*, 1968, **3**, 47.

ment, it is possible to obtain relative rates of formation of the epoxide, from the alkene, by the radical (peracetyl) and molecular (peracetic acid) mechanisms. Rate data for the molecular reaction (known, in solution, as the Prilezhaev reaction) in the gas phase are therefore also obtained.

The experiments involve the co-oxidation of an aldehyde and an alkene, a method that has been used in the liquid phase,[13] much of the detailed work being done with benzaldehyde,[14-17] acetaldehyde,[18-20] and 2-methylpropanal.[21] The calculations in this paper, however, allow for a continuous variation of the concentrations of peracetyl radicals and peracetic acid with time.

EXPERIMENTAL

Apparatus.—A static vacuum apparatus (Pyrex) was used. A cylindrical reaction vessel (13·5 cm long; 5·9 cm diameter; surface : volume ratio, 1 : 1·04 cm^{-1}) was suspended in an electric furnace, the temperature being controlled to within ±0·1°. The line from the reaction vessel led to gas chromatographs (Pye 104 models, with flame ionization and thermal conductivity detectors), which in turn could be linked to a mass spectrometer (A.E.I. MS 12; 70 eV electron energy; 100 μA trap current; 8 kV accelerating potential; source temperature 378 K). Pressure measurements were made with a transducer (Consolidated Electrodynamics).

Analysis.—Reactants and products were determined by gas chromatography, their identity being confirmed from their mass spectra. Oxygen and carbon dioxide were determined on silica gel (60—85 mesh; column 1·5 m long, 4 mm i.d.; 323 K; hydrogen as carrier gas). Acetaldehyde, methanol, but-2-ene, and the 2,3-epoxybutanes were determined using Porapak Q (100—120 mesh; column 3 m long, 4 mm i.d.; 408 K; nitrogen as carrier gas) and peracetic and acetic acids using GasChrom Q (100—120 mesh)–20% (w/w) dinonylphthalate [22] (column 1·5 m long, 4 mm i.d.; 323 K; nitrogen as carrier gas).

Concentrations of reactants and products were obtained from a knowledge of the response of standard amounts of each compound, following experiments to ensure that there was no interaction between reactants and products during sampling and analysis.

Reagents.—Acetaldehyde, acetic acid, methanol, and the 2,3-epoxybutanes (Fluka A.G.) were purified by fractional distillation until impurities could not be detected by gas chromatography and were degassed before use. The purity of the hydrocarbons (Cambrian Chemicals Ltd.) was tested by gas chromatography; the gases were over 99·5% pure. The purest available commercial samples of oxygen, nitrogen, and carbon dioxide were dried and used without further treatment.

A sample of peracetic acid dissolved in acetic acid was supplied by Laporte Industries Ltd.

RESULTS

(a) *Oxidation of Acetaldehyde at* 393 K.—Under the conditions used there was a period during which the pressure decreased and peracetic acid was the principal product (Figure 1). The concentration of the peracid increased to a maximum beyond which the pressure began

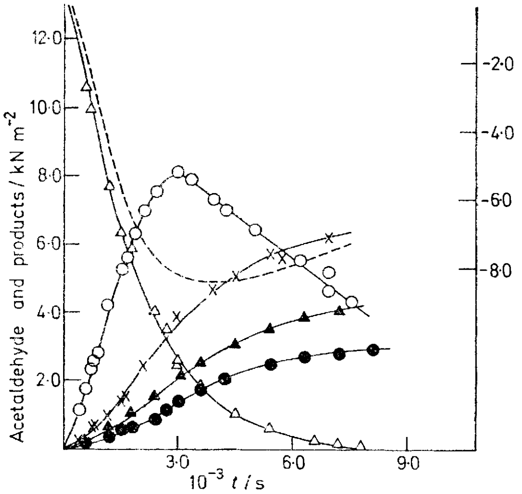

FIGURE 1 Oxidation of acetaldehyde at 393 K. Acetaldehyde 13·33 kN m^{-2}; oxygen 13·33 kN m^{-2}. △, Acetaldehyde; ×, acetic acid; ▲, carbon dioxide; ●, methanol; ○, peracetic acid; — — — —, pressure change

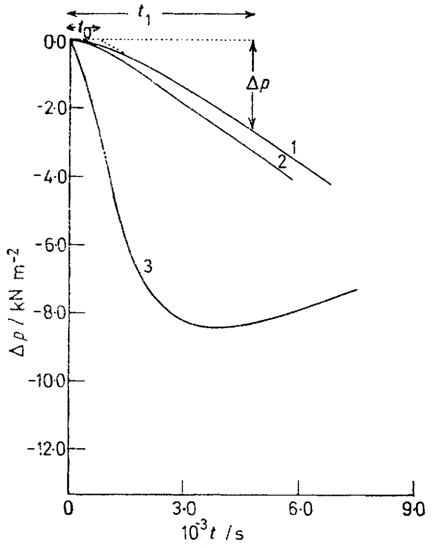

FIGURE 2 Co-oxidation of acetaldehyde and but-2-ene at 393 K. Acetaldehyde 13·33 kN m^{-2}; oxygen 13·33 kN m^{-2}. 1, 1·33 kN m^{-2} *trans*-But-2-ene added; 2, 1·33 kN m^{-2} *cis*-but-2-ene added; 3, no alkene added

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[13] D. I. Metelitsa, *Russian Chem. Rev.*, 1972, **41**, 807.

[14] T. Ikawa, T. Fukushima, M. Muto, and T. Yanagihara, *Canad. J. Chem.*, 1966, **44**, 1817.

[15] T. Ikawa, H. Tomizawa, and T. Yanagihara, *Canad. J. Chem.*, 1967, **45**, 1900.

[16] F. Tsuchiya and T. Ikawa, *Canad. J. Chem.*, 1969, **47**, 3191.

[17] A. D. Vreugdenhil and H. Reit, *Rec. Trav. chim.*, 1972, **91**, 237.

[18] P. I. Valov, E. A. Blyumberg, and N. M. Emanuel, *Bull. Acad. Sci. U.S.S.R.*, 1966, 1283; 1969, 718.

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[20] A. A. Andriyanov, V. I. Chernak, and R. V. Kucher, *Ukrain. Khim. Zhur.*, 1970, **36**, 1136.

[21] G. Montorsi, G. Caprara, G. Pregaglia, and G. Messina, *Internat. J. Chem. Kinetics*, 1973, **5**, 777.

[22] G. T. Cairns, R. Ruiz Diaz, K. Selby, and D. J. Waddington, *J. Chromatography*, 1975, **103**, 381.

to rise and the proportion of acetic acid, methanol, and carbon dioxide to peracetic acid increased markedly.

(b) *Co-oxidation of Acetaldehyde and* cis- *and* trans-*But-2-ene at* 393 K.—The first series of experiments was made with but-2-ene, acetaldehyde, and oxygen in the proportions of (1 : 10 : 10), added in that order, to a total pressure of 27·99 kN m^{-2}. Both *cis*- and *trans*-but-2-ene retard the oxidation of acetaldehyde, the *trans*-isomer being more effective (Figure 2).

Similar products to those in the oxidation of acetaldehyde are observed; the only products formed from the alkenes appear to be the 2,3-epoxybutanes. The concentrations of geometric isomers are formed in different ratios from the two alkenes. The ratio varies with time, proportionately more epoxide being formed per unit pressure change from the *trans*-alkene (Table 1).

TABLE 1

Co-oxidation of acetaldehyde and but-2-ene at 393 K. The formation of *trans*- and *cis*-2,3-epoxybutanes. But-2-ene, 1·33 kN m^{-2}; acetaldehyde 13·33 kN m^{-2}; oxygen 13·33 kN m^{-2}

		Epoxybutanes formed			
t/s	Δp/ kN m^{-2}	*trans*/ kN m^{-2}	*cis*/ kN m^{-2}	Total/ kN m^{-2}	Mole fraction of *trans*
		trans-But-2-ene			
1770	0·67	0·08	0·02	0·10	0·80
2910	1·33	0·14	0·03	0·17	0·81
3870	2·00	0·19	0·04	0·23	0·83
4770	2·66	0·25	0·05	0·30	0·80
6600	3·99	0·30	0·07	0·37	0·80
		cis-But-2-ene			
1440	0·67	0·05	0·02	0·07	0·71
2310	1·33	0·08	0·04	0·12	0·67
3240	2·00	0·11	0·06	0·17	0·65
4080	2·66	0·13	0·10	0·23	0·60
5850	3·99	0·19	0·12	0·31	0·61

A second series of experiments was made by adding 6·67 kN m^{-2} of alkene to an acetaldehyde–oxygen mixture (13·33 kN m^{-2} each) at the pressure minimum [at 65 min (Figure 2)], and analyses were performed at various times following addition. No difference in the rate of pressure change, compared with acetaldehyde–oxygen mixture, was observed (as would be expected if the principal reaction of the alkene is with peracetic acid). The *trans*-epoxide, with <0·2% of the *cis*-isomer, was formed on addition of *trans*-but-2-ene, while the *cis*-epoxide was overwhelmingly the predominant product from the *cis*-alkene.

CALCULATIONS

(a) *Calculation of the Rate Constant for the Reaction between Peracetic Acid and But-*2*-ene at* 393 K.—On addition of alkene at the pressure minimum that occurred in the acetaldehyde–oxygen system, the only observable product from the alkene was the epoxide with the same configuration as the parent hydrocarbon. This shows that the epoxide has not been formed by radical attack,[23] but has been produced by reaction between the alkene and peracetic acid, which is said to be stereospecific.[13] (Experiments have been conducted in this laboratory in which the alkenes were passed through a solution of peracetic acid in acetic acid. The epoxide was formed in small amounts, stereospecifically.[24])

$$>C{=}C< + CH_3CO_3H \xrightarrow{k_1} >C\overset{O}{—}C< + CH_3CO_2H \qquad (1)$$

Under the conditions used in the gas-phase studies, the concentration of the alkene, A, remains sensibly constant. Peracetic acid, PA, is decomposing at a constant rate (to methanol, carbon dioxide, acetic acid). Thus, the rate of formation of epoxide, E, is given by equation (i) where

$$d[E]/dt = k_1[A]_i([PA]_i - at) \qquad (i)$$

$[A]_i$ and $[PA]_i$ are the concentrations of alkene and peracetic acid on addition of the alkene and a is a constant. Thus, the epoxide concentration, at time t, $[E]_t$ is given by equation (ii). a, Determined from values of the concentration of peracetic acid at different times, is 8·0 × 10^{-4} kN m^{-2} s^{-1}, equation (ii) being plotted in Figure 3.

$$[E]_t = k_1[A]_i([PA]_i - at/2)t \qquad (ii)$$

Using a least mean squares programme, k_1 for both *cis*- and *trans*-but-2-ene is (3·0 ± 0·7) × 10^{-2} dm^3 mol^{-1} s^{-1}. Using this value, the predicted $[E]_t$ against time curve is shown in Figure 4.

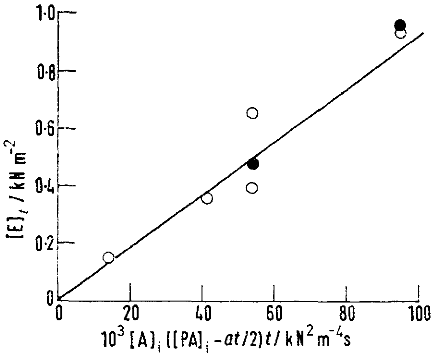
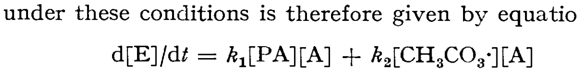


FIGURE 3 Co-oxidation of acetaldehyde and but-2-ene at 393 K. Plot of equation (ii): acetaldehyde 13·33 kN m^{-2}; oxygen 13·33 kN m^{-2}; but-2-ene 1·33 kN m^{-2} added at 65 min. ●, Epoxide formed from *cis*-but-2-ene; ○, epoxide formed from *trans*-but-2-ene

(b) *Calculation of the Rate Constant for the Reaction between Peracetyl Radicals and But-*2*-ene at* 393 K.—When an alkene is added at the start of the reaction between aldehyde and oxygen at 393 K, the epoxide is formed not only *via* reaction (1) but, probably, more importantly, by reaction between the alkene and peracetyl radicals [7–9,23] [reaction (2)]. The overall rate of formation of epoxide under these conditions is therefore given by equation (iii)



$$>C{=}C< + CH_3CO_3\cdot \xrightarrow{k_2} >C\overset{O}{—}C< + \dot{C}H_3 + CO_2 \qquad (2)$$

$$d[E]/dt = k_1[PA][A] + k_2[CH_3CO_3\cdot][A] \qquad (iii)$$

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[23] D. J. M. Ray and D. J. Waddington, 13th Internat. Combustion Symp., The Combustion Institute, Pittsburgh, 1971, p. 261.

[24] K. Selby, unpublished results.

The concentrations of peracetic acid and peracetyl vary with time. The concentration of peracetic acid, formed *via* reaction (3), increases uniformly during the major part of the pressure decrease observed. In order to determine

$$CH_3CO_3\cdot + CH_3CHO \longrightarrow CH_3CO_3H + CH_3\dot{C}O \quad (3)$$

the peracetyl concentration, several assumptions are made. As the rate of pressure change, ΔP, is constant, after a short time, the reaction time, t, is assumed to be equal to $(t_1 - t_0)$ (Figure 2). Thus, at time t, $[PA]_t = at$; $[E]_t = bt$; $[A]_t = [A]_i - bt$ where a and b are constants.

Equation (iii) can now be written as (iv). As the peracid

$$d[E]/dt = k_1(at)([A]_i - bt) + k_2[CH_3CO_3\cdot]_t([A]_i - bt) \quad (iv)$$

is formed at a constant rate, $k_2[CH_3CO_3\cdot]_t$ may be written in the form $k'(1 + ct)$ where k' incorporates k_2 and the initial pseudo-stationary concentration of peracetyl, and c is a constant. Thus, substitution and integration of equation (iv) gives (v) where $x = ([A]_i/2 - [E]_t/3)$. c Is

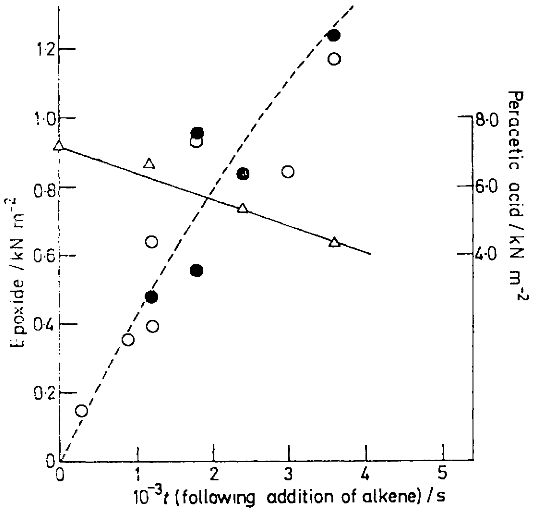

FIGURE 4 Co-oxidation of acetaldehyde and but-2-ene at 393 K. Acetaldehyde 13·33 kN m^{-2}; but-2-ene 6·67 kN m^{-2}; oxygen 13·33 kN m^{-2}. ●, Epoxide formed from *cis*-but-2-ene; ○, epoxide formed from *trans*-but-2-ene; △, peracetic acid; — — — —, predicted concentration of epoxide formed

$$[E]_t = k_1t[PA]_t x + k't([A]_i - [E]_t/2 + ctx) \quad (v)$$

found on examining the rate of formation of peracetic acid [reaction (3)] for the concentrations of the peracid (and its decomposition products) and acetaldehyde have been determined through the reaction. k_1 And k' are then calculated by substituting values for $[E]_t$, $[PA]_t$, and t into equation (v), solving the simultaneous equations using a computer program.

The proportion of epoxide formed by radical attack at different times, $[E]_{t,RAD}$, can now be calculated. As there is competition through the reaction between the alkene and acetaldehyde for peracetyl radicals,[8,9] such that $d[E]_{RAD}/d[PA] = k_2[\text{Alkene}]_t/k_3[\text{Acetaldehyde}]_t$, k_2 can also be calculated. The value of k_3 used was calculated from data obtained by McDowell and Sharples.[25] From the average of six solutions, the following values of k_1 and k_2 at 393 K for the reaction between but-2-ene and peracetic acid and peracetyl respectively are: *trans*-but-2-ene, $k_1 = (3·4 \pm 1·0) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k_2 = (1·2 \pm 0·1) \times 10^5$ dm^3 mol^{-1} s^{-1}; *cis*-but-2-ene, $k_1 = (3·4 \pm 1·0) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k_2 = (7·5 \pm 0·1) \times 10^4$ dm^3 mol^{-1} s^{-1}.

DISCUSSION

Two methods were used to calculate k_1, the rate constant for the reaction between but-2-ene and peracetic acid. In one, the alkene was added when the parent fuel, acetaldehyde, had been consumed. At this time, the concentration of peracetyl radicals was low, this being confirmed by the retention of configuration on epoxidising the alkene. A value of $(3·0 \pm 0·7) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} is obtained. The second value is found by a more circuitous route in which the alkene is added at the start of reaction between acetaldehyde and oxygen and there is competition for the alkene between peracetyl radicals and peracetic acid, and a value of $k_1 = (3·4 \pm 1·0) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} is obtained. Thus, these values are within experimental error of each other and, further, are consistent with the rate constant quoted by Swern[26] for the reaction in solution at 299 K, $k_1 = 1·6 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. These results give confidence to the values of k_2 obtained for the radical reaction between peracetyl and alkene. The values for k_1 and k_2 have been used to calculate the total concentrations of epoxides formed and, on comparing them with the experimental values (Table 2), good agreement is obtained.

TABLE 2

Co-oxidation of acetaldehyde and but-2-ene at 393 K. A comparison of yields of *trans*- and *cis*-2,3-epoxybutanes as determined experimentally and theoretically. But-2-ene 1·33 kN m^{-2}; acetaldehyde 13·33 kN m^{-2}; oxygen 13·33 kN m^{-2}

	Epoxides formed/ kN m^{-2}		Epoxides calculated/ kN m^{-2}		% Radical
t/s	*trans*	*cis*	*trans*	*cis*	epoxidation
		trans-But-2-ene			
1770	0·08	0·02	0·08	0·02	90·3
2910	0·14	0·03	0·14	0·03	86·0
3870	0·19	0·04	0·20	0·04	82·5
4770	0·25	0·05	0·25	0·05	79·4
6600	0·30	0·07	0·31	0·06	77·1
		cis-But-2-ene			
1440	0·05	0·02	0·05	0·02	86·0
2310	0·08	0·04	0·08	0·04	80·2
3240	0·11	0·06	0·10	0·06	75·6
4080	0·13	0·10	0·13	0·10	72·6
5850	0·19	0·12	0·18	0·13	69·5

The alkenes do not appear to react under these conditions in any other way than by epoxidation. This is consistent with previous co-oxidation studies. For example, in the preliminary gas-phase studies in the co-oxidation of acetaldehyde and alkenes at 453 K,[9,23]

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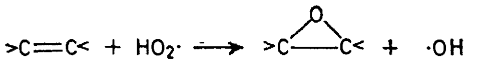
[25] C. A. McDowell and L. K. Sharples, *Canad. J. Chem.*, 1958, **36**, 251, 258, 268.

[26] D. Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692; *Chem. Rev.*, 1949, **45**, 1.

unsaturated carbonyl compounds or alcohols were not observed, and their absence was also noted in the co-oxidation of benzaldehyde and but-2-ene in solution.[16]

The relative proportions of epoxidation by the peracetyl radical and peracetic acid alters through the reaction. Under the conditions studied, the radical accounts for *ca.* 90% of the epoxide in the early stages of reaction and even when high concentrations of peracetic acid are present (a pressure of 2—4 kN m^{-2}), the proportion of epoxidation by the radical is still over 70% (Table 2). It is only when the acetaldehyde has been virtually consumed that peracetic acid becomes the dominant epoxidising agent of but-2-ene. Similar results are obtained in the liquid-phase co-oxidation of benzaldehyde and but-2-ene,[16] and Emanuel and his co-workers found that, in the co-oxidation of acetaldehyde and propene, a slightly higher proportion of the epoxidation was *via* the radical.[18] Interestingly, Vreugdenhil and Reit, in their co-oxidation studies with benzaldehyde and oct-1-ene and oct-2-ene, found that there was a large difference in the percentage radical epoxidation for the two alkenes, that for oct-1-ene being only *ca.* 15% while that for oct-2-ene is 45%.[17] It is not possible to compare these results with those in this study for we have followed the reaction while the relative concentrations of peracetyl radicals and peracetic acid alter markedly. On the other hand, we have already observed how the structure of the alkene, in the gas-phase co-oxidation studies, significantly alters the ratio between k_1 and k_2.[8,23]

There are, as yet, no results under conditions similar to those used in this study for the reaction between alkenes and either $RO_2\cdot$ and $HO_2\cdot$ radicals. In solution, values of 0·6 and 0·8 $dm^3\ mol^{-1}\ s^{-1}$ at 393 K have been obtained for the addition reaction of t-butylperoxyl radicals and two terminal alkenes, propene and hex-1-ene.[27] A value of $1{\cdot}7 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ has been obtained for the rate constant for the reaction between ethylene and $HO_2\cdot$ radicals [reaction (4)] at 773 K.[6]

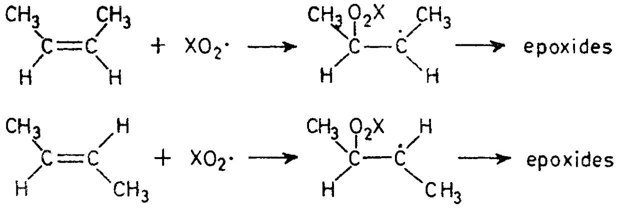


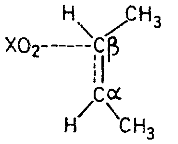
(4)

Benson has suggested[28] that reactions of the nature of (4) have A factors of *ca.* $10^8\ dm^3\ mol^{-1}\ s^{-1}$. k_4 At 393 K would therefore be *ca.* $3{\cdot}0\ dm^3\ mol^{-1}\ s^{-1}$. (This calculation does not agree with a preferred value of *ca.* $10^4\ dm^3\ mol^{-1}\ s^{-1}$, subject to significant error, suggested by Lloyd,[29] and based on work by Avramenko *et al.*[30]) Nevertheless, there does appear to be a general trend, in which one observes that the rate of addition to alkenes decreases on passing from peracetyl to hydroperoxyl to t-butylperoxyl.

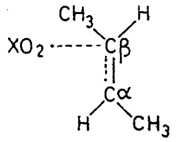
It would be unwise to comment at present too deeply on these comparisons. However, parallel series of experiments are being undertaken, one in which the structure of the alkene is altered and the other in which the structure of the radical $XO_2\cdot$ is varied. Alkenes are known to be particularly susceptible to attack, by addition, by electrophilic reagents, and the rate of reaction is dependent on the structure of the alkene. Thus, in comparing the results above, one must bear in mind that but-2-ene reacts *ca.* 500 times more rapidly than ethylene with peracetic acid in solution,[26] while addition of oxygen atoms is over 20 times[31,32] and hydroxyl radicals *ca.* 40 times[33] faster on the substituted alkene. Further, in comparing the reactivity of the radical $XO_2\cdot$ one must take into account the electron density of the radical site. In the series X = Bu^t, H, CH_3CO, the density will decrease and hence the energy needed to form the transition state will be lower.

A further interesting point is the higher reactivity of *trans*-but-2-ene towards peracetyl radicals compared with the *cis*-isomer. This type of behaviour has been observed in the addition of methyl[32,34,35] and hydroxyl[33] radicals, and oxygen [O(^3P)][31] and hydrogen[36,37] atoms (data are summarised in Table 3) but the results have not been previously discussed. The behaviour which has also been noted for the effect of alkenes on the rate of photo-oxidation of nitric oxide,[38] cannot be rationalized simply in terms of electron densities since both alkenes have two methyl groups adjacent to the C–C double bond, but it may be rationalized in terms of steric effects. Consider, for example, the passage of the butene and an attacking radical species $XO_2\cdot$ into the transition states (A) and (B). On entering the





cis
(A)



trans
(B)

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TABLE 3

Reactions of atoms and radicals with *trans*- and *cis*-but-2-ene

	$\dot{C}H_3$	$\dot{C}H_3$	$\cdot OH$	$O(^3P)$	H	H	$CH_3CO_3\cdot$
Reference	**34**	**35**	**33**	**31**	**36**	**37**	This work
T/K	338	403	298	298	290	290	393
Ratio of rate of reaction with *trans*- and *cis*-but-2-ene	2·01	1·48	1·17	1·19	1·25	1·11	1·60

transition state, the carbon atom of the alkene to which the $XO_2\cdot$ radical is to be bonded to form the radical adduct becomes more sp^3 in character. This creates a greater degree of steric hindrance between the two methyl groups (and H atoms) on the α- and β-carbon atoms in the radical adduct than in the parent sp^2 hybridized alkene, since the distance between them is reduced. This effect, which may be referred to as steric compression, will be greater for radical adduct formed from the *cis*-alkene, since the distance between the methyl groups is shorter in this isomer.

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