Reactions of Oxygenated Radicals in the Gas Phase. Part II.[1] Reactions of Peracetyl Radicals and Butenes

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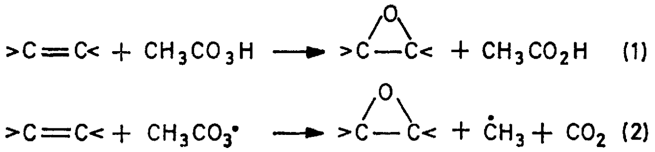
In the co-oxidation of acetaldehyde and alkenes between 356.6 and 410.1 K, peracetic acid and peracetyl radicals (formed from acetaldehyde) react with the hydrocarbon to form the corresponding epoxide [reactions (1) and (2)].


(1)
(2)

The relative proportion of the epoxidising agents changes with time, reaction (2) being predominant in the early stages of reaction. Arrhenius parameters for the reactions of but-1-ene and 2-methylpropene are given in relations (i) and (ii), and (iii) and (iv) respectively.

$$\log_{10}(k_1/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = (8.68 \pm 1.40) - [(82\ 430 \pm 10\ 320)\ \mathrm{J\ mol^{-1}}/2.3RT] \quad \text{(i)}$$

$$\log_{10}(k_2/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = (7.94 \pm 0.48) - [(28\ 930 \pm 3\ 510)\ \mathrm{J\ mol^{-1}}/2.3RT] \quad \text{(ii)}$$

$$\log_{10}(k_1/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = (7.63 \pm 1.83) - [(66\ 000 \pm 13\ 540)\ \mathrm{J\ mol^{-1}}/2.3RT] \quad \text{(iii)}$$

$$\log_{10}(k_2/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = (8.29 \pm 0.16) - [(25\ 040 \pm 1\ 170)\ \mathrm{J\ mol^{-1}}/2.3RT] \quad \text{(iv)}$$

IN recent years, much emphasis has been placed on the subject of co-oxidation reactions in the liquid phase, since the reactions can be used to obtain quantitative data for fundamental processes such as relative reactivities of peroxyl radicals towards hydrocarbons, which are difficult or impossible to obtain by other means.[2]

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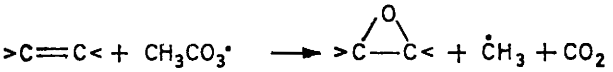
[1] Part I, R. Ruiz Diaz, K. Selby, and D. J. Waddington, *J.C.S. Perkin II*, 1975, 758.

[2] R. A. Sheldon and J. K. Kochi, *Oxidation and Combustion Rev.*, 1973, **5**, 135.

Likewise, rate data, from co-oxidation studies, have been obtained for the gas-phase reactions of hydroperoxyl radicals in the high-temperature oxidation region of hydrocarbons and aldehydes.[3,4] In Part I [1] the importance of obtaining experimental rate data for radical reactions in low-temperature (pre-ignition) gas-phase oxidation systems was stressed and a method was outlined for determining the rates of reaction between peracetic acid and peracetyl radicals with alkenes [reactions (1) and (2)].


(1)


(2)

This paper is concerned with developing the method in two ways. First, the structure of the alkene is altered and rate data for the reactions of but-1-ene and 2-methylpropene are reported and compared with those obtained for their isomers, *cis*- and *trans*-but-2-ene.[1] Secondly, Arrhenius parameters for the reactions are obtained and compared with the values that have been predicted and subsequently used frequently in the literature.

EXPERIMENTAL

The apparatus has been described and a similar analytical method adopted,[1] in particular the method by which the rates of formation of epoxides from the alkene and peracetic acid from acetaldehyde are determined by g.l.c.–m.s.[5]

RESULTS AND DISCUSSION

But-1-ene and 2-methylpropene retard the oxidation of acetaldehyde (Figure), the results for but-2-ene [1] being given for comparison. The products found are those obtained in the oxidation of acetaldehyde itself, under these conditions,[1] together with 1,2-epoxybutane and 1,2-epoxy-2-methylpropane from but-1-ene and 2-methylpropene, respectively (Table 1).

Under the conditions of the experiments, the mechanism for the oxidation of acetaldehyde is considered to consist of reactions (3)—(7).[6] There are thus two species, peracetic acid and peracetyl radicals, which react with alkenes, to form epoxides [reactions (1) and (2)].

$$CH_3CHO + O_2 \longrightarrow CH_3\dot{C}O + HO_2\cdot \qquad (3)$$

$$CH_3\dot{C}O + O_2 \longrightarrow CH_3CO_3\cdot \qquad (4)$$

$$CH_3CO_3\cdot + CH_3CHO \longrightarrow CH_3CO_3H + CH_3\dot{C}O \qquad (5)$$

$$CH_3CO_3H(+\ CH_3CHO) \longrightarrow \text{chain branching} \qquad (6)$$

$$CH_3CO_3\cdot,\ CH_3\dot{C}O \longrightarrow \text{chain termination} \qquad (7)$$

TABLE 1

Co-oxidation of acetaldehyde and alkenes.
Acetaldehyde 100 mmHg; oxygen 100 mmHg

T/K	Pressure of alkene/ mmHg	t/min	Pressure change/ mmHg	Epoxide/ mmHg	Peracetic acid/ mmHg
(a) But-1-ene					
356.6	5.0	90.0	10.0	0.03	6.9
		118.0	15.0	0.04	9.8
		142.0	20.0	0.06	12.3
		162.5	25.0	0.07	14.8
		183.0	30.0	0.09	17.5
369.2	10.0	41.0	10.0	0.05	7.9
		48.0	10.0	0.06	7.9
		61.5	15.0	0.10	11.6
		86.0	20.0	0.16	16.2
		114.0	30.0	0.22	21.7
		117.0	30.0	0.23	20.2
381.0	20.0	37.0	10.0	0.15	8.7
		42.0	12.0	0.18	10.4
		46.0	15.0	0.22	13.9
		62.5	20.0	0.32	15.4
		79.0	30.0	0.53	25.1
		98.0	30.0	0.53	24.6
393.0	20.0	18.5	5.0	0.07	3.3
		29.0	10.0	0.14	6.4
		32.0	10.0	0.15	7.4
		55.0	20.0	0.31	14.5
		77.0	30.0	0.54	21.0
397.5	20.0	15.5	10.0	0.17	9.1
		20.5	15.0	0.29	15.0
		25.0	20.0	0.39	18.8
		31.2	25.0	0.52	24.2
		37.0	30.0	0.66	28.7
410.1	40.0	11.8	10.0	0.45	9.1
		13.0	10.5	0.44	9.6
		16.5	15.0	0.66	13.4
		21.0	20.0	0.97	18.6
		29.0	30.0	1.68	27.5
(b) 2-Methylpropene					
356.6	2.0	137.0	10.0	0.10	5.9
		175.0	15.0	0.17	8.5
		211.0	20.0	0.24	11.3
		242.0	25.0	0.31	13.9
		268.0	30.0	0.37	16.1
369.2	5.0	97.0	10.0	0.30	6.7
		108.5	10.0	0.28	6.8
		137.0	15.0	0.55	10.1
		156.0	20.0	0.66	11.7
		210.0	30.0	1.01	16.2
393.0	10.0	29.0	5.0	0.31	3.4
		45.0	10.0	0.60	6.7
		60.0	15.0	1.09	10.3
		75.0	20.0	1.49	12.5
		90.0	25.0	1.98	16.1
		105.0	30.0	2.44	18.9
		105.0	30.0	2.45	18.8
		122.5	35.0	3.06	21.7
398.2	10.0	27.0	10.0	0.72	8.3
		42.5	21.0	1.73	17.0
		58.5	30.0	2.72	24.5
		75.0	36.5	3.61	27.4
410.1	20.0	23.5	10.0	1.69	7.3
		27.0	15.0	2.64	11.9
		34.0	20.0	3.56	15.7
		45.0	30.0	5.85	22.5

Except for the epoxide, no other oxidation products from the alkenes are obtained under these conditions. Similar behaviour has been found in liquid-phase co-oxidation

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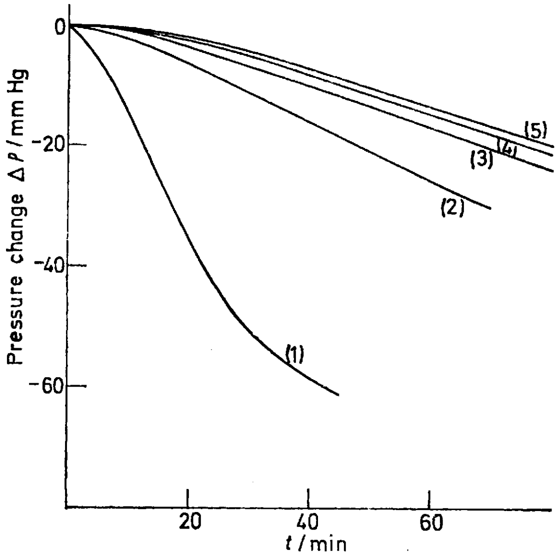
[3] R. R. Baldwin, D. E. Hopkins, and R. W. Walker, *Trans. Faraday Soc.*, 1970, **66**, 189; R. R. Baker, R. R. Baldwin, and R. W. Walker, *ibid.*, p. 2812; R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, *J.C.S. Faraday I*, 1972, 1362; R. R. Baldwin, D. H. Langford, M. J. Matchan, R. W. Walker, and D. A. Yorke, 13th Internat. Combustion Symp., The Combustion Institute, Pittsburgh, 1971, p. *251*; R. R. Baldwin and R. W. Walker, 14th Internat. Combustion Symp., The Combustion Institute, Pittsburgh, 1973, p. 241.

[4] 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.

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

[6] J. F. Griffiths and G. Skirrow, *Oxidation and Combustion Rev.*, 1968, **3**, 47; J. F. Griffiths, G. Skirrow, and C. F. H. Tipper, *Combustion and Flame*, 1968, **12**, 360.

studies involving aldehydes and alkenes.[7,8] However, carbonyl compounds are formed in small amounts from the hydrocarbon in the co-oxidation of acetaldehyde and alkenes at a higher temperature, 457 K.[9] For example, propanal and formaldehyde are formed during the co-oxidation of acetaldehyde and but-1-ene and, under similar conditions, acetone and formaldehyde are formed from 2-methylpropene. The conversion of alkenes into carbonyl compounds has been attributed to the addition of hydroxyl radicals (formed during the chain-branching reactions in the oxidation of acetaldehyde[6]) and oxygen to the alkene, followed by decomposition of the radical.[9,10] At the lower temperatures used in the present study, the concentration of hydroxyl radicals will be considerably lower, particularly in the earlier stages of reaction, and thus reactions (1) and (2) are even more dominant than at 457 K.



Co-oxidation of acetaldehyde and alkenes at 393 K. Acetaldehyde 100 mmHg, oxygen 100 mmHg: (1) no alkene added; (2) but-1-ene (20 mmHg) added; (3) *cis*-but-2-ene (10 mmHg) added; (4) 2-methylpropene (10 mmHg) added; (5) *trans*-but-2-ene (10 mmHg) added

In Part I,[1] the method is given by which k_1 and k_2 may be calculated. The method, which allows both for the growth of peracetyl radicals and peracetic acid and for the varying proportions of the species with time, has been validated using *cis*- and *trans*-but-2-ene as the hydrocarbons. Using the same procedure, k_1 and k_2 for the reactions of but-1-ene and 2-methylpropene have been determined from data in Table 1. The results are summarised in Table 2, and from these the Arrhenius parameters in Table 3 are found. The quoted errors are calculated standard deviations from least mean square Arrhenius plots.

The rate constant for the reaction between peracetyl radicals and but-1-ene, k_2, at 393 K (Table 2) is in close agreement with a value obtained earlier in this laboratory[11] of (1.12 ± 0.07) × 10^4 dm^3 mol^{-1} s^{-1}. Different reaction vessels were used and the oxidation of acetaldehyde itself was about twice as fast as in the present study. That the results for k_2 for but-1-ene correspond so closely indicates the method is reliable, for the concentration of peracetyl radicals must be significantly different in the experiments in the two reaction vessels. There is also good agreement between the calculated and observed concentrations of epoxides in this study. For example, Table 4 gives data for the co-oxidation of acetaldehyde and 2-methylpropene.

TABLE 2

Co-oxidation of acetaldehyde and alkenes. Rate constants for the addition reactions of peracetic acid and peracetyl radicals with alkenes

T/K	k_1/dm^3 mol^{-1} s^{-1} (CH_3CO_3H + alkene)	k_2/dm^3 mol^{-1} s^{-1} ($CH_3CO_3\cdot$ + alkene)
	(a) But-1-ene	
356.6	$(5.64 \pm 3.20) \times 10^{-4}$	$(5.50 \pm 0.19) \times 10^{3}$
369.2	$(1.35 \pm 2.30) \times 10^{-3}$	$(7.77 \pm 0.14) \times 10^{3}$
381.0	$(2.37 \pm 1.90) \times 10^{-3}$	$(9.70 \pm 0.93) \times 10^{3}$
393.0	$(3.75 \pm 2.34) \times 10^{-3}$	$(1.06 \pm 0.10) \times 10^{4}$
397.5	$(7.36 \pm 3.36) \times 10^{-3}$	$(1.59 \pm 0.21) \times 10^{4}$
410.1	$(2.83 \pm 0.10) \times 10^{-2}$	$(2.06 \pm 0.04) \times 10^{4}$
	(b) 2-Methylpropene	
356.6	$(1.41 \pm 1.77) \times 10^{-2}$	$(4.57 \pm 2.02) \times 10^{4}$
369.2	$(1.70 \pm 1.56) \times 10^{-2}$	$(5.82 \pm 1.96) \times 10^{4}$
393.0	$(4.34 \pm 1.68) \times 10^{-2}$	$(9.19 \pm 1.32) \times 10^{4}$
398.2	$(1.36 \pm 0.30) \times 10^{-1}$	$(1.07 \pm 0.34) \times 10^{5}$
410.1	$(2.45 \pm 0.17) \times 10^{-1}$	$(1.38 \pm 0.06) \times 10^{5}$
	(c) *trans*-But-2-ene[1]	
393.0	$(3.40 \pm 1.00) \times 10^{-2}$	$(1.20 \pm 0.10) \times 10^{5}$
	(d) *cis*-But-2-ene[1]	
393.0	$(3.40 \pm 1.00) \times 10^{-2}$	$(7.50 \pm 0.10) \times 10^{4}$

Quoted errors are calculated standard deviations.

TABLE 3

Arrhenius parameters

	But-1-ene	2-Methylpropene
$\log_{10}(A_1$/dm^3 mol^{-1} s$^{-1})$	8.68 ± 1.40	7.63 ± 1.83
E_1/kJ mol^{-1}	82.43 ± 10.32	66.00 ± 13.54
$\log_{10}(A_2$/dm^3 mol^{-1} s$^{-1})$	7.94 ± 0.48	8.29 ± 0.16
E_2/kJ mol^{-1}	28.93 ± 3.51	25.04 ± 1.17

TABLE 4

Co-oxidation of acetaldehyde and 2-methylpropene at 393 K. 2-Methylpropene 10 mmHg; acetaldehyde 100 mmHg; oxygen 100 mmHg

		1,2-Epoxy-2-methylpropane		
t/min	Pressure change/ mmHg	Found/ mmHg	Predicted/ mmHg	Radical epoxidation (%)
45.0	10.0	0.60	0.63	84.7
60.0	15.0	1.09	1.06	78.7
75.0	20.0	1.49	1.50	75.8
90.0	25.0	1.98	2.01	71.4
105.0	30.0	2.45	2.53	68.4

The proportion of epoxide formed by radical attack decreases with time as the concentration of peracetic acid grows (Table 4). This behaviour is seen in the co-oxidation of acetaldehyde and but-2-ene[1] and also in liquid-phase co-oxidation studies.[7] Although the concentration of peracetyl radicals grows during reaction, the growth of peracetic acid is proportionally larger.

The rate constants at 393 K obtained in this study may

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

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

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

[10] D. J. M. Ray, A. Redfearn, and D. J. Waddington, *J.C.S. Perkin II*, 1973, 540.

[11] R. Ruiz Diaz, D.Phil. thesis, University of York, 1974.

be compared with those obtained with but-2-ene[1] (Table 2). They indicate that the rate of both molecular and radical epoxidation increases as the electron density in the carbon double bond increases. Similar behaviour has already been observed in the liquid-phase reaction between peracetic acid and alkenes,[12] and, in the gas-phase, between electrophilic species such as O(^3P) and alkenes.[13] The rate constants obtained for the addition reaction of peracetyl radicals are considerably higher than the corresponding reactions with methyl. For example, the rate constant for the addition of methyl to *cis*-but-2-ene is some 15-fold smaller than the reaction between peracetyl and the alkene.[14] However, the absence of unsaturated oxidation products from the alkenes indicates that the rate of addition of peracetyl to the unsaturated hydrocarbon is considerably larger than the rate of abstraction; such selectivity is not observed with the reaction of methyl and but-2-ene.

On examining the effect of temperature on the but-1-ene and 2-methylpropene systems, it is clear that the relative rates of reaction between the two alkenes is a function of changes in the activation energy of the reactions. The values of the A factor are close to that predicted earlier, $\log_{10}(A/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 8.5$ for the addition of $\mathrm{RO_2\cdot}$[15] to alkenes.

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

[13] R. J. Cvetanović, *J. Chem. Phys.*, 1959, **30**, 19; *Adv. Photochem.*, 1963, **1**, 115; *J. Phys. Chem.*, 1970, **74**, 2732.

[14] N. Yokoyama and R. K. Brinton, *Canad. J. Chem.*, 1969, **47**, 2987.

[15] S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87**, 972.