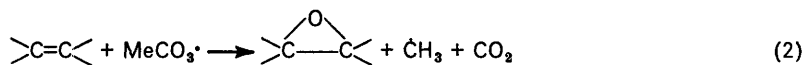
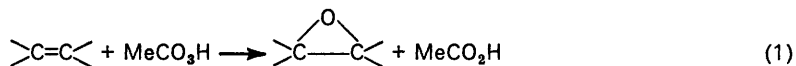


Reactions of Oxygenated Radicals in the Gas Phase. Part 3.¹ Reactions of Peracetyl Radicals with Alkenes

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Rate constants for the addition reactions of peracetic acid and peracetyl radicals with alkenes have been determined at 393 K [reactions (1) and (2)]. The alkenes studied were propene, 3-methylbut-1-ene, *cis*- and *trans*-pent-2-ene,

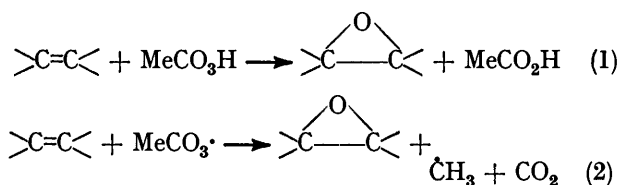


2-methylbut-1-ene, 2-methylbut-2-ene, and hex-1-ene. Arrhenius parameters for the reactions with 2-methylbut-2-ene have been determined as follows:

$$\log_{10} (k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (8.23 \pm 0.33) - [(61\,600 \pm 2\,420) \text{ J mol}^{-1}/2.3RT]$$

$$\log_{10} (k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (8.08 \pm 0.12) - [(16\,340 \pm 910) \text{ J mol}^{-1}/2.3RT].$$

By studying the gas-phase co-oxidation of acetaldehyde and alkenes, it is possible to determine the rates of the addition reactions of peracetic acid and peracetyl radicals with alkenes [reactions (1) and (2)].² Rate data have



been obtained for the addition reactions of peracetic acid and peracetyl radicals with the four isomeric butenes.^{1,2} The rates of addition are markedly dependent on the structure of the alkene, and are considerably larger than both the rates of abstraction of hydrogen by peracetyl radicals from the alkene and the corresponding addition reactions of alkylperoxy radicals in solution.³

The reactions of peracetic acid and peracetyl radicals with alkenes in the gas-phase have now been studied further by altering the structure of the hydrocarbon.

EXPERIMENTAL

The apparatus has been described in ref. 2; a similar analytical method was adopted, in particular, the method by which the rates of formation of epoxides from the alkenes and peracetic acid from acetaldehyde are determined by g.l.c.-mass spectrometry.^{2,4}

RESULTS AND DISCUSSION

All the alkenes studied retard the oxidation of acetaldehyde (Figure 1); the results for but-1-ene and 2-methylpropene¹ are given for comparison. The products from the co-oxidation of alkenes and acetaldehyde are those obtained in the oxidation of acetaldehyde itself

under the conditions used in this study,² together with the epoxide from the corresponding alkene. Indeed, except for the epoxide, no other oxidation products from the alkenes were detected. The amounts of epoxides formed during the reaction are given in Tables 1 and 2.

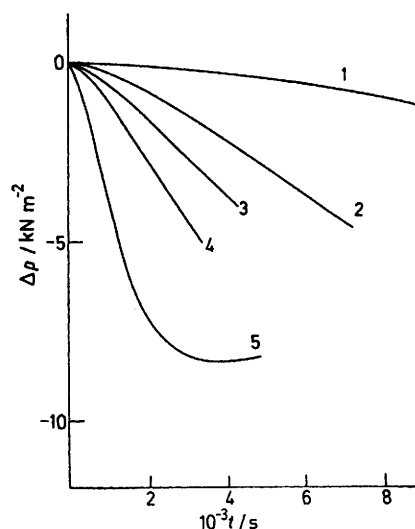


FIGURE 1 Co-oxidation of acetaldehyde and alkenes at 393 K; $p(\text{acetaldehyde})$ 13.33 kN m⁻²; $p(\text{oxygen})$ 13.33 kN m⁻²: 1, 2-methylbut-2-ene (1.33 kN m⁻²) added; 2, 2-methylpropene (1.33 kN m⁻²) added; 3, but-1-ene (2.66 kN m⁻²) added; 4, propene (2.66 kN m⁻²) added; 5, no alkene added

Under the conditions of the experiments, the principal propagation reactions for the oxidation of acetaldehyde are considered to be reactions (3) and (4).⁵ Peracetic acid and peracetyl radical react with alkenes to form epoxides [reactions (1) and (2)], there being a growth of both epoxidising agents during the reaction, albeit at unequal rates. However, it is possible to calculate both

¹ Part 2, K. Selby and D. J. Waddington, *J.C.S. Perkin II*, 1975, 1715.

² R. Ruiz Diaz, K. Selby, and D. J. Waddington, *J.C.S. Perkin II*, 1975, 758.

³ P. Koelewiyn, *Rec. Trav. chim.*, 1972, **91**, 759.

⁴ G. T. Cairns, R. Ruiz Diaz, K. Selby, and D. J. Waddington, *J. Chromatography*, 1975, **103**, 381.

⁵ J. F. Griffiths and G. Skirrow, *Oxidation and Combustion Rev.*, 1968, **3**, 47.

k_1 and k_2 ,² and rate constants for the reactions of peracetic acid and peracetyl radicals with alkenes at 393 K are given in Table 3.



The results in Table 1 are from two reaction vessels (RV1 and RV2). The oxidation of acetaldehyde in

TABLE 1

Co-oxidation of acetaldehyde and alkenes; formation of epoxides; p (acetaldehyde) 13.3 kN m⁻²; p (oxygen) 13.3 kN m⁻²; 393 K

$p(\text{alkene})/$ kN m ⁻²	$10^{-3} t/s$	Pressure change ($\Delta p/$ kN m ⁻²)	$p(\text{epoxide})/$ kN m ⁻²	Radical epoxidation (%)
2.66	0.990	0.66	0.004	>95
	1.488	1.33	0.012	93.6
	2.220	2.66	0.024	88.0
	2.880	3.99	0.040	83.7
	3.840	5.32	0.065	77.2
(b) 3-Methylbut-1-ene (RV 1) †				
6.66	1.950	2.66	0.137	60.1
	1.986	2.66	0.129	60.1
	2.478	3.32	0.185	55.4
	2.970	3.99	0.202	51.7
(c) <i>cis</i> - and <i>trans</i> -Pent-2-ene (RV 1) †				
1.33	0.588	1.33	0.124	94.1
	0.616	1.59	0.130	93.1
	0.876	1.99	0.178	91.7
	1.170	2.66	0.230	89.7
	1.746	3.99	0.315	86.2
(d) 2-Methylbut-1-ene (RV 1) †				
1.33	1.008	1.99	0.187	88.0
	1.344	2.66	0.268	85.2
	1.548	3.06	0.308	83.7
	1.674	3.32	0.328	82.7
	2.016	3.99	0.400	80.6
(e) Hex-1-ene (RV 1) †				
5.32	1.002	1.33	0.010	75.7
	1.986	2.66	0.231	62.5
	2.574	3.46	0.352	57.2

† The rate of oxidation of acetaldehyde in one reaction vessel (RV 1) is about twice that in the other (RV 2).

RV1 is about twice that in RV2, although, except for the vessel itself, the conditions and method of operation were identical. The vessels, of similar dimensions, were treated identically before being used. The difference in rates is presumably due to the initiation, chain branching, and termination reactions in the oxidation of acetaldehyde being, at least in part, heterogeneous.⁵⁻⁷ However, the co-oxidation of acetaldehyde and but-1-ene was studied in both vessels and the data for k_1 and k_2 were consistent. For example, the values for k_2 were (1.12 ± 0.07) and $(1.06 \pm 0.10) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for RV1⁸ and RV2¹ at 393 K. Thus, the concentrations of

⁶ D. J. Dixon, G. Skirrow, and C. F. H. Tipper, 'Combustion Institute European Symposium,' ed. F. J. Weinberg, Academic Press, London, 1973, p. 94.

⁷ D. J. Dixon, G. Skirrow, and C. F. H. Tipper, *J.C.S. Faraday I*, 1974, **70**, 1090.

⁸ R. Ruiz Diaz, D.Phil. Thesis, University of York, 1974.

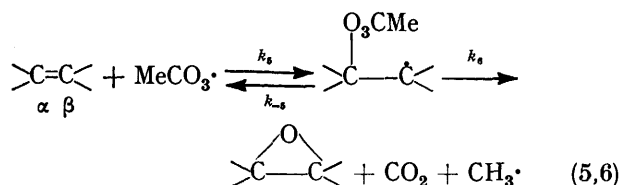
peracetyl radicals in the co-oxidation studies must be significantly different in the two vessels, showing that reaction (2) is homogeneous.

TABLE 2

Co-oxidation of acetaldehyde and alkenes; formation of 2,3-epoxy-2-methylbutane from 2-methylbut-2-ene (RV 2); p (2-methylbut-2-ene) 1.33 kN m⁻²; p (acetaldehyde) 13.3 kN m⁻²; p (oxygen) 13.3 kN m⁻²

T/K	$10^{-3} t/s$	Pressure change ($\Delta p/$ kN m ⁻²)	$p(\text{epoxide})/$ kN m ⁻²	$p(\text{peracetic}$ acid)/ kN m ⁻²
370	10.02	0.20	0.15	0.035
	14.82	0.40	0.23	0.052
	16.20	0.47	0.26	0.055
375	5.52	0.13	0.07	0.017
	12.12	0.29	0.20	0.027
	12.48	0.33	0.21	0.048
	17.40	0.53	0.30	0.068
	18.00	0.53	0.29	0.061
	20.10	0.73	0.39	0.065
	21.60	0.80	0.36	0.076
393	4.50	0.36	0.23	0.093
	6.30	0.67	0.43	0.226
	7.20	0.80	0.49	0.279
410	8.16	1.06	0.65	0.346
	9.00	1.33	0.77	0.412
	1.25	0.27	0.14	0.077
	1.74	0.56	0.31	0.132
	2.16	0.41	0.27	0.172
	2.22	0.80	0.34	0.182
	2.70	1.06	0.57	0.355
	3.30	1.20	0.79	0.379
	3.42	1.33	0.72	0.463
	3.72	1.46	0.75	0.270

From the evidence gained in earlier work,^{1,2,9,10} it appears that the reaction between the alkene and the radical involves the formation of a radical adduct, followed by ring closure. Thus, reaction (2) could be described as in reactions (5) and (6). Analogous radical



adducts in solution have been observed recently by e.s.r. techniques, and rate constants (k_6) in the range 10^4 – 10^5 s^{-1} at 298 K have been observed.¹¹ This is considerably higher than one would expect for k_5 under these conditions. For example, it has been estimated¹² that ΔH° for the reaction between alkylperoxyl radicals and an alkene is *ca.* -50 kJ mol^{-1} , a value which will be no smaller for the addition reaction of peracetyl and an alkene. Thus, if ΔH_5° is -50 kJ mol^{-1} , the minimum value for E_{-5} will be *ca.* 85 kJ mol^{-1} .¹² Given A_{-5} as *ca.*

⁹ D. J. M. Ray and D. J. Waddington, *J. Phys. Chem.*, 1972, **76**, 3319.

¹⁰ R. Ruiz Diaz and D. J. Waddington, *Archivum procesów spalania*, 1974, **5**, 399.

¹¹ A. J. Bloodworth, A. G. Davies, I. M. Griffin, B. Muggleston, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1974, **96**, 7599.

¹² S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87**, 972.

10^{13} s^{-1} , it can be seen that $k_6 \gg k_5$, and therefore k_2 can be identified with k_5 .

Values of $\log(A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ for reactions (1) and (2) for 2-methylbut-2-ene (obtained from values of rate constants in Table 3) are 8.23 ± 0.33 and 8.08 ± 0.12 . These may be compared with corresponding values of 8.68 ± 1.40 and 7.94 ± 0.48 , and 7.63 ± 1.83 and

another. Values of k_1 and k_2 for 2-methylbut-2-ene are considerably larger than those for any other alkene studied.

Taking an average value of $\log_{10}(A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, approximate values of the energies of activation E_1 and E_2 can be calculated (Table 4). For each methyl group added to the carbon atom adjacent to the double bond,

TABLE 3

	$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	T/K	Ref.
Propene	$(2.32 \pm 0.86) \times 10^{-3}$	$(6.40 \pm 0.36) \times 10^3$	393	This work
But-1-ene	$(3.75 \pm 2.30) \times 10^{-3}$	$(1.06 \pm 0.10) \times 10^4$	393	1
	$(8.09 \pm 1.25) \times 10^{-3}$	$(1.12 \pm 0.07) \times 10^4$	393	8
<i>trans</i> -But-2-ene	$(3.44 \pm 0.82) \times 10^{-2}$	$(1.20 \pm 0.07) \times 10^5$	393	2
<i>cis</i> -But-2-ene	$(3.45 \pm 1.24) \times 10^{-2}$	$(7.53 \pm 0.92) \times 10^4$	393	2
2-Methylpropene	$(4.34 \pm 1.68) \times 10^{-2}$	$(9.19 \pm 1.32) \times 10^4$	393	1
3-Methylbut-1-ene	$(9.97 \pm 2.10) \times 10^{-3}$	$(1.25 \pm 0.62) \times 10^4$	393	This work
<i>cis</i> -Pent-2-ene	$(4.28 \pm 1.70) \times 10^{-2}$	$(1.41 \pm 0.84) \times 10^5$	393	This work
<i>trans</i> -Pent-2-ene	$(4.28 \pm 1.70) \times 10^{-2}$	$(1.41 \pm 0.84) \times 10^5$	393	This work
2-Methylbut-1-ene	$(6.03 \pm 2.16) \times 10^{-2}$	$(1.52 \pm 0.08) \times 10^5$	393	This work
2-Methylbut-2-ene	$(3.50 \pm 0.80) \times 10^{-1}$	$(5.92 \pm 0.47) \times 10^5$	370	This work
	$(4.90 \pm 1.90) \times 10^{-1}$	$(6.48 \pm 0.18) \times 10^5$	375	This work
	(1.24 ± 0.15)	$(8.38 \pm 0.84) \times 10^5$	393	This work
	(2.48 ± 0.06)	$(9.92 \pm 0.61) \times 10^5$	410	This work
Hex-1-ene	$(2.13 \pm 1.20) \times 10^{-2}$	$(2.24 \pm 0.83) \times 10^4$	393	This work

8.29 ± 0.16 , for but-1-ene and 2-methylpropene (Table 4). These results show that the radical reactions are

TABLE 4

	Arrhenius parameters for reactions (1) and (2)		
	But-1-ene	2-Methylpropene	2-Methylbut-2-ene
$\log_{10}(A_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	8.68 ± 1.40	7.63 ± 1.83	8.23 ± 0.33
$E_1/\text{kJ mol}^{-1}$	82.43 ± 10.32	66.00 ± 13.54	61.60 ± 2.42
$\log_{10}(A_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	7.94 ± 0.48	8.29 ± 0.16	8.08 ± 0.12
$E_2/\text{kJ mol}^{-1}$	28.93 ± 3.51	25.04 ± 1.17	16.34 ± 0.91
Ref.	†	†	This work

isentrope and that the trend in reactivity is determined principally by differences in the activation energy, which is in contrast with the addition of alkyl,¹³ halogenoalkyl,¹⁴ and difluoroamino¹⁵ radicals to alkenes and substituted alkenes.

The values for k_1 and k_2 fall into three groups (Table 3). The alkenes studied with structure $\text{RR}'\text{CH}-\text{CH}=\text{CH}_2$ (propene, but-1-ene, 3-methylbut-1-ene, and hex-1-ene) have similar rate constants, and both k_1 and k_2 increase as the alkyl group is either lengthened or branched. Rate constants k_1 and k_2 for alkenes with structures $\text{RHC}=\text{CHR}'$ (the geometric isomers of but-2-ene and pent-2-ene) and $\text{RR}'\text{C}=\text{CH}_2$ (2-methylpropene and 2-methylbut-1-ene) are considerably larger than those in the first group but lie within a relatively small range of one

¹³ R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.*, 1957, *A*, **240**, 396.

¹⁴ For example, J. P. Sloan, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1975, 1841, 1846.

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

¹⁶ J. Böseken and J. Stuurman, *Rec. Trav. chim.*, 1937, **56**, 1034; D. Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692; *Chem. Rev.*, 1949, **45**, 1.

there is a decrease of *ca.* -9.0 and -7.3 kJ mol^{-1} in E_1 and E_2 , respectively.

The negative value for the change in E_2 fulfils an important criterion for confirming that the peracetyl radical is an electrophile, as indeed peracetic acid is too.¹⁶ The differences in the changes in E_1 and E_2 as methyl groups are added to the double bond are to be

TABLE 5

Activation energies for the addition reactions (1) and (2) of peracetic acid and peracetyl radicals with alkenes

	$E_1/\text{kJ mol}^{-1}$	$E_2/\text{kJ mol}^{-1}$
C_3 alkenes		
Propene	83.1	32.6
C_4 alkenes		
But-1-ene	82.4 †	28.9 †
2-Methylpropene	66.0 †	25.0 †
<i>trans</i> -But-2-ene	74.2	24.7
<i>cis</i> -But-2-ene	74.2	23.0
C_5 alkenes		
<i>trans</i> -Pent-2-ene	73.5	22.6
<i>cis</i> -Pent-2-ene	73.5	22.6
2-Methylbut-1-ene	72.4	22.2
3-Methylbut-1-ene	78.3	30.5
2-Methylbut-2-ene	61.6 †	16.3 †
C_6 alkenes		
Hex-1-ene	75.8	28.4

† From Table 3; other values calculated by taking $\log_{10}(A_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ as 8.36 and $\log_{10}(A_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ as 8.11.

compared with values of -8.0 , -1.7 , and $+3.4 \text{ kJ mol}^{-1}$ for the addition of difluoroamino,¹⁵ trifluoromethyl,¹⁷ and cyclopropyl¹⁸ radicals to alkenes. As with the addition of difluoroamino¹⁵ and trifluoromethyl^{17,19}

¹⁷ A. P. Stefani, L. Herk, and M. Szwarc, *J. Amer. Chem. Soc.*, 1961, **83**, 4732.

¹⁸ A. P. Stefani, L.-Y. Y. Chuang, and H. E. Todd, *J. Amer. Chem. Soc.*, 1970, **92**, 4168.

¹⁹ I. M. Whittemore, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, 1962, **84**, 3799.

radicals and oxygen (3P) atoms^{20,21} to alkenes, there is a linear relationship between $\log_{10} k_2$ and the ionization energy²² of the substrate, the slope being negative (Figure 2). This suggests that the polar structure $\text{>}\overset{\ominus}{\text{C}}\text{-}\overset{\oplus}{\text{C}}\text{<}-\text{O}_3\text{CMe}$ is important in describing the transition state in the addition reaction.

The linear relationship between $\log k_2$ and the ionization energy of the alkene is not obtained for the addition of methyl radicals to alkenes in solution. For example,

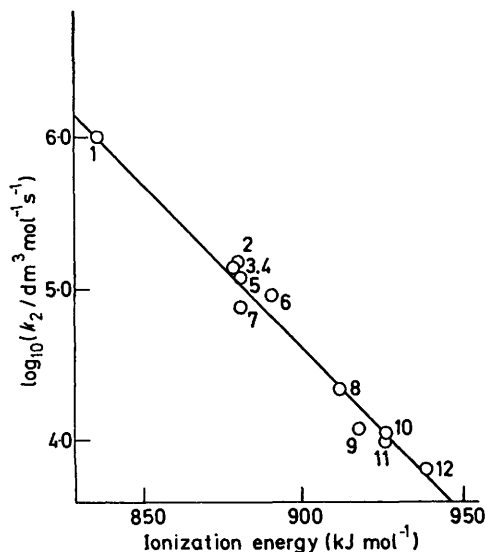


FIGURE 2 Co-oxidation of acetaldehyde and alkenes; plot of $\log_{10}(k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ against ionization energy of the alkene; 1, 2-methylbut-2-ene (RV 2); 2, 2-methylbut-1-ene (RV 1); 3, *trans*-pent-2-ene (RV 1); 4, *cis*-pent-2-ene (RV 1); 5, *trans*-but-2-ene (RV 2); 6, 2-methylpropene (RV 2); 7, *cis*-but-2-ene (RV 2); 8, hex-1-ene (RV 1); 9, 3-methylbut-1-ene (RV 1); 10, but-1-ene (RV 1); 11, but-1-ene (RV 2); 12, propene (RV 2)

the energy of activation increases on passing from 2-methylpropene through ethylene and propene to the isomers of but-2-ene,¹³ suggesting that the methyl groups at the double bond hinder sterically the addition of the incoming radical. The results in the present study suggest that such behaviour is subordinate to the electronic effect when a strong electrophile is adding to the alkene, although there is a significant difference in the values for k_2 between *trans*- and *cis*-but-2-ene.²

²⁰ R. E. Huie, J. T. Herron, and D. D. Davis, *J. Phys. Chem.*, 1971, **75**, 3902; M. J. Kurylo, *Chem. Phys. Letters*, 1972, **14**, 117; D. D. Davis, R. E. Huie, J. T. Herron, M. J. Kurylo, and W. Braun, *J. Chem. Phys.*, 1972, **56**, 4868; D. D. Davis, R. E. Huie, and J. T. Herron, *ibid.*, 1973, **59**, 628.

²¹ R. Atkinson and R. J. Cvetanovic, *J. Chem. Phys.*, 1971, **55**, 659; 1972, **56**, 432; S. Furuyama, R. Atkinson, A. J. Colussi, and R. J. Cvetanovic, *Internat. J. Chem. Kinetics*, 1974, **6**, 741.

As far as we are aware, there are no data for molecular reactions in the gas phase corresponding to reaction (1). Further, kinetic data for the reaction between simple aliphatic alkenes and peracetic acid in solution were reported some forty years ago.¹⁶ Of the compounds in our study, Arrhenius parameters for only 2-methylbut-2-ene are available, and even these must be calculated from results at two temperatures. By using these data, the parameters $\log_{10}(A_1/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = 8.4$ and $E_1 = 58.1 \text{ kJ mol}^{-1}$ are obtained. In this earlier work,¹⁶ rate constants were also found for pent-1-ene at two temperatures, and the parameters $\log_{10}(A_1/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = 8.6$ and $E_1 = 73.5 \text{ kJ mol}^{-1}$ may be calculated, and compared with the values we obtained for but-1-ene (Table 4).

Given that the parameters are calculated from limited data, there is a remarkable similarity to those obtained in the gas phase in the present study (Table 4), suggesting that the mechanisms in the liquid and gas phases are alike.

It has already been noted that the proportion of molecular epoxidation grows with time during a given reaction,^{1,2} showing that the concentration of peracetic acid grows faster than that of the peracetyl radicals. However, the results in this paper also show that the relative importance of molecular epoxidation changes with changing structure of the alkene (Table 3). Direct comparison cannot be made with liquid-phase co-oxidation studies with benzaldehyde as relative proportions of epoxides formed by reactions (1) and (2) with time have not been reported.²³

It is also not possible to compare directly the rates of reaction of various types of oxygenated radicals with the alkenes in the gas phase. In the study with hydroxyl radicals and alkenes the consumption of alkene was used as the parameter to determine the rate of reaction; thus no distinction was made between the addition and abstraction reactions.²⁴ However, we are studying at present the reaction of methylperoxy and other peroxy radicals with alkenes to determine whether the reduced electrophilicity of the radicals does affect the rate of addition in the gas phase.

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[6/1228 Received, 24th June, 1976]

²² F. H. Field and J. L. Franklin, 'Electron Impact Phenomena,' Academic Press, New York, 1957.

²³ A. D. Vreugdenhil and H. Reit, *Rec. Trav. chim.*, 1972, **91**, 237.

²⁴ E. D. Morris and H. Niki, *J. Phys. Chem.*, 1971, **75**, 3640.