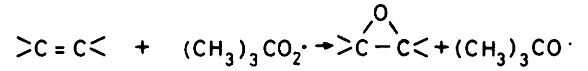
Reactions of Oxygenated Radicals in the Gas Phase. Part 15.[1] Reactions of t-Butylperoxyl Radicals with Alkenes

Morag E. Morgan, David A. Osborne, and David J. Waddington*
Department of Chemistry, University of York, York YO1 5DD

The photo-oxidation of mixtures of *trans*-2,2′-azoisobutane and some aliphatic alkenes has been studied between 313 and 393 K. Rate constants for the reaction between t-butylperoxyl radicals with ethene, 2-methylpropene, 2-methylbut-1-ene, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene have been determined at 393 K. Arrhenius parameters for the reaction (22) have been determined for 2-methylbut-



$$>C=C< \;+\; (CH_3)_3CO_2\cdot \rightarrow >\overset{O}{C-C}< + (CH_3)_3CO\cdot \qquad (22)$$

2-ene and 2,3-dimethylbut-2-ene. They are log (A_{22}/dm^3 mol^{-1} s^{-1}) of 8.16 ± 0.38 and 8.58 ± 0.61, and E_{22}/kJ mol^{-1} of 56.6 ± 2.4 and 48.7 ± 4.1, respectively. The data obtained in this work are compared with that obtained for the series hydroperoxyl, methylperoxyl, and isopropylperoxyl radicals, and with rate data obtained for the addition reaction between alkenes and peracetyl radicals.

In this series, several papers have reported rate data for the self-reactions of three alkylperoxyl radicals in the gas phase between 300 and 450 K, namely ethylperoxyl,[2] isopropylperoxyl,[3–5] and t-butylperoxyl.[1] We have also shown that such systems allow rates of radical–molecule reactions, such as the addition reaction between alkylperoxyl radicals and alkenes, to be determined. The first examples described were the reactions of isopropylperoxyl radicals with a series of related aliphatic alkenes.[6,7]

In this paper, rate data are reported for the reactions of t-butylperoxyl radicals and alkenes, and these are compared with data obtained for the corresponding reactions with hydroperoxyl,[8,9] methylperoxyl,[10] isopropylperoxyl,[6,7] and peracetyl[11–13] radicals.

Experimental

The apparatus and methods of analysis of reactants and products were described in the previous paper.[1] *trans*-2,2′-Azoisobutane was prepared from t-butylamine[14] and purified to over 99% by preparative g.c.[1] Samples of 2-methyl-2,3-epoxybutane and 2,3-dimethyl-2,3-epoxybutane were prepared by reaction of their parent alkenes with perbenzoic acid.[15] 2-Methyl-1,2-epoxybutane was prepared from the corresponding alkene *via* the bromohydrin.[16] Other samples of the epoxides used in this work were obtained commercially.

Results

Five alkenes were added, separately, to mixtures of *trans*-2,2′-azoisobutane, nitrogen, and oxygen. Of these, ethene, 2-methylpropene, 2-methylbut-1-ene, and 2-methylbut-2-ene had no effect on the yields of products from the photo-oxidation of *trans*-2,2′-azoisobutane. Examples of results are presented in Table 1.

The only product formed from the alkene is the corresponding epoxide.

The effect of varying temperature on the formation of the

Table 1. Photo-oxidation of *trans*-2,2′-azoisobutane: effect of addition of alkenes at 393 K

trans-2,2′-Azoisobutane, 5 Torr; alkene, 5 Torr; oxygen, 20 Torr; total pressure (made up with nitrogen), 200 Torr

Alkene	*t*/min	*p*(Acetone)/ Torr	*p*(t-Butyl alcohol)/ Torr	*p*(Formaldehyde)/ Torr	10^3 *p*(Epoxide)/ Torr
	30	0.52 (0.56)	0.10 (0.09)	0.39 (0.40)	
	60	1.10 (1.11)	0.20 (0.21)	0.65 (0.71)	
	90	1.70 (1.60)	0.30 (0.34)	0.81 (0.95)	
	120	2.24 (2.05)	0.40 (0.47)	0.88 (1.14)	
Ethene	30	0.54 (0.56)	0.09 (0.09)	0.39 (0.40)	3.2 (3.3)
	60	1.09 (1.11)	0.19 (0.21)	0.64 (0.71)	6.4 (6.5)
	90	1.64 (1.60)	0.30 (0.34)	0.79 (0.95)	10.2 (9.7)
	120	2.25 (2.05)	0.39 (0.47)	0.87 (1.14)	12.4 (12.8)
2-Methylpropene	15	0.27 (0.28)	0.05 (0.04)	0.23 (0.22)	1.9 (1.8)
	30	0.56 (0.56)	0.09 (0.09)	0.38 (0.40)	3.6 (3.6)
	60	1.15 (1.11)	0.20 (0.21)	0.69 (0.71)	7.2 (7.2)
	90	1.74 (1.60)	0.30 (0.34)	0.81 (0.95)	10.6 (10.6)
	120	2.34 (2.05)	0.41 (0.47)	0.95 (1.14)	13.2 (14.0)
	150	2.90 (2.47)	0.50 (0.61)	1.10 (1.30)	17.9 (17.2)
2-Methylbut-1-ene	30	0.54 (0.56)	0.09 (0.09)	0.26 (0.40)	4.7 (4.7)
	60	1.14 (1.16)	0.17 (0.21)	0.55 (0.71)	9.8 (9.4)
	90	1.63 (1.60)	0.26 (0.34)	0.69 (0.95)	13.0 (14.0)
	120	2.14 (2.05)	0.38 (0.47)	0.86 (1.14)	18.8 (18.4)

(Simulated values are given in parentheses).

Table 2. Photo-oxidation of *trans*-2,2′-azoisobutane: effect of addition of 2-methylbut-2-ene

AIB, 5 Torr; alkene, 20 Torr; oxygen, 20 Torr; nitrogen 155 Torr

T/K	t/min	p(Acetone)/ Torr	p(t-Butyl alcohol)/ Torr	p(Formaldehyde)/ Torr	10^3 p(Epoxide)/ Torr
313	30	0.25 (0.47)		0.16 (0.32)	2.5 (2.8)
	60	0.47 (0.83)		0.28 (0.51)	5.2 (5.4)
	90	0.70 (1.14)	0.58 (1.19)	0.38 (0.63)	6.8 (7.8)
	120	0.99 (1.39)	0.82 (1.59)	0.44 (0.72)	10.1 (10.1)
	150	1.16 (1.62)	1.02 (1.97)	0.50 (0.78)	13.3 (12.2)
328	30	0.31 (0.58)		0.17 (0.35)	4.8 (5.5)
	60	0.60 (1.07)		0.34 (0.57)	10.0 (10.7)
	90	0.91 (1.49)	0.54 (0.74)	0.44 (0.72)	14.4 (15.5)
	120	1.18 (1.86)	0.73 (1.03)	0.53 (0.83)	20.3 (20.1)
	150	1.44 (2.19)	0.88 (1.31)	0.58 (0.90)	25.9 (24.5)
343	30	0.35 (0.53)		0.22 (0.38)	9.6 (10.7)
	60	0.72 (0.97)		0.37 (0.65)	19.0 (20.9)
	90	1.10 (1.36)	0.44 (0.79)	0.49 (0.84)	31.3 (30.4)
	120	1.45 (1.69)	0.58 (1.09)	0.58 (0.99)	39.6 (39.5)
	150	1.79 (1.99)	0.72 (1.38)	0.61 (1.11)	50.4 (48.0)

(Simulated values are given in parentheses).

Table 3. Photo-oxidation of *trans*-2,2′-azoisobutane: effect of addition of 2,3-dimethylbut-2-ene

AIB, 5 Torr; alkene, 5 Torr; oxygen, 20 Torr; nitrogen, 170 Torr

T/K	t/min	p(Acetone)/ Torr	p(t-Butyl alcohol)/ Torr	p(Formaldehyde)/ Torr	p(Epoxide)/ Torr
313	15	0.19 (0.25)	0.22 (0.14)	0.19 (0.19)	0.01 (0.01)
	30	0.40 (0.47)	0.43 (0.34)	0.35 (0.32)	0.02 (0.02)
	60	0.83 (0.83)	0.88 (0.76)	0.51 (0.51)	0.04 (0.04)
	90	1.28 (1.14)	1.38 (1.19)	0.61 (0.63)	0.07 (0.07)
	120	1.64 (1.39)	1.81 (1.59)	0.66 (0.72)	0.09 (0.08)
343	15	0.44 (0.27)	0.13 (0.08)	0.21 (0.21)	0.02 (0.02)
	30	0.94 (0.53)	0.26 (0.20)	0.41 (0.38)	0.04 (0.04)
	60	1.96 (0.97)	0.53 (0.48)	0.68 (0.65)	0.07 (0.08)
	90	2.79 (1.36)	0.83 (0.79)	0.83 (0.84)	0.11 (0.12)
	120	3.75 (1.69)	1.11 (1.09)	0.92 (0.99)	0.16 (0.15)
393	15	0.74 (0.28)	0.05 (0.03)	0.17 (0.22)	0.09 (0.09)
	30	1.36 (0.56)	0.10 (0.08)	0.34 (0.40)	0.19 (0.18)
	45	2.18 (0.84)	0.16 (0.13)	0.42 (0.56)	0.27 (0.27)
	60	2.77 (1.11)	0.22 (0.19)	0.49 (0.70)	0.35 (0.36)
	75	3.38 (1.36)	0.26 (0.25)	0.58 (0.83)	0.44 (0.45)
	90	3.89 (1.60)	0.30 (0.31)	0.65 (0.94)	0.50 (0.53)
	120	5.08 (2.05)	0.41 (0.44)	0.34 (1.12)	0.68 (0.68)

(Simulated values are given in parentheses).

Table 4. Photo-oxidation of *trans*-2,2′-azoisobutane: effect of oxygen pressure on the co-oxidation of 2,3-dimethylbut-2-ene

AIB, 5 Torr; 2,3-dimethylbut-2-ene, 5 Torr; oxygen and nitrogen added to a total of 200 Torr, photolysis time, 30 min

T/K	p(Oxygen)/ Torr	p(Acetone)/ Torr	p(t-Butyl alcohol)/ Torr	p(t-Butyl hydroperoxide)/Torr	p(Formaldehyde)/ Torr	p(Epoxide)/ Torr
343	5	0.91 (0.55)	0.21 (0.20)	0.16 (0.14)	0.39 (0.37)	0.04 (0.04)
	20	0.94 (0.53)	0.20 (0.20)	0.15 (0.16)	0.41 (0.38)	0.04 (0.04)
	80	0.93 (0.52)	0.20 (0.20)	0.16 (0.17)	0.40 (0.39)	0.05 (0.04)
	160	0.92 (0.51)	0.21 (0.20)	0.15 (0.18)	0.41 (0.39)	0.04 (0.04)
393	5	1.32 (0.62)	0.09 (0.08)	0.21 (0.19)	0.32 (0.35)	0.19 (0.19)
	10	1.36 (0.59)	0.08 (0.08)	0.21 (0.22)	0.31 (0.38)	0.18 (0.19)
	20	1.37 (0.56)	0.08 (0.08)	0.22 (0.25)	0.34 (0.40)	0.18 (0.18)
	40	1.34 (0.55)	0.07 (0.08)	0.24 (0.27)	0.33 (0.41)	0.16 (0.18)
	80	1.35 (0.54)	0.07 (0.08)	0.26 (0.28)	0.34 (0.42)	0.16 (0.18)
	160	1.34 (0.53)	0.06 (0.07)	0.27 (0.28)	0.36 (0.42)	0.15 (0.18)

(Simulated values are given in parentheses).

Table 5. Photo-oxidation of *trans*-2,2′-azoisobutane: effect of alkene pressure on the co-oxidation of 2,3-dimethylbut-2-ene at 393 K

AIB, 5 Torr; oxygen, 20 Torr; 2,3-dimethylbut-2-ene and nitrogen to a total of 200 Torr, photolysis time, 30 min

p(Alkene)/ Torr	*p*(Acetone)/ Torr	*p*(t-Butyl alcohol)/ Torr	*p*(t-Butyl hydroperoxide)/Torr	*p*(Formaldehyde)/ Torr	*p*(Epoxide)/ Torr
0	0.58 (0.57)	0.09 (0.09)	0.21 (0.23)	0.38 (0.40)	0.00 (—)
1	0.84 (0.57)	0.08 (0.09)		0.36 (0.40)	0.04 (0.04)
2	1.05 (0.57)	0.08 (0.08)		0.37 (0.40)	0.06 (0.08)
3	1.28 (0.57)	0.08 (0.08)		0.43 (0.40)	0.11 (0.12)
5	1.40 (0.56)	0.08 (0.08)	0.21 (0.25)	0.34 (0.40)	0.16 (0.18)
10	1.51 (0.56)	0.08 (0.07)	0.21 (0.26)	0.37 (0.40)	0.27 (0.33)
15	1.46 (0.56)	0.08 (0.06)		0.40 (0.40)	0.37 (0.45)
20	1.51 (0.56)	0.08 (0.06)	0.21 (0.28)	0.40 (0.40)	0.44 (0.55)
30	1.49 (0.55)	0.08 (0.05)	0.19 (0.29)	0.39 (0.40)	0.54 (0.70)
40	1.50 (0.55)	0.09 (0.04)	0.23 (0.30)	0.40 (0.40)	0.61 (0.80)
50	1.51 (0.55)	0.09 (0.04)	0.21 (0.30)		0.58 (0.86)

(Simulated values are given in parentheses).

Table 6. Rate constants* used in the simulation of the photo-oxidation of *trans*-2,2′-azoisobutane

Reaction†		313 K	328 K	343 K	393 K
(2)	$Bu^t\cdot + O_2 \rightarrow Bu^tO_2\cdot$	3.1×10^8	3.1×10^8	3.1×10^8	3.1×10^8
(3)	$2Bu^tO_2\cdot \rightarrow 2Bu^tO\cdot + O_2$	2.4×10^4	4.8×10^4	9.0×10^4	5.3×10^5
(6)	$Bu^tO_2\cdot + HO_2\cdot \rightarrow Bu^tO_2H + O_2$	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(8)	$Bu^tO\cdot + Bu^tO_2H \rightarrow Bu^tOH + Bu^tO_2\cdot$	7.5×10^6	9.3×10^6	1.1×10^7	2.0×10^7
(9)	$Bu^tO\cdot + HO_2\cdot \rightarrow Bu^tOH + O_2$	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(10)	$2HO_2\cdot \rightarrow H_2O_2 + O_2$	2.2×10^9	2.2×10^9	2.2×10^9	2.2×10^9
(11)	$Bu^tO\cdot(+M)\cdot \rightarrow Me_2CO + Me\cdot\ (+M)$	6.5×10^1	1.7×10^2	4.2×10^2	5.0×10^3
(12)	$Me\cdot + O_2\ (+M) \rightarrow MeO_2\cdot\ (+M)$	3.1×10^8	3.1×10^8	3.1×10^8	3.1×10^8
(13a)	$2MeO_2\cdot \rightarrow 2MeO\cdot + O_2$	1.3×10^8	1.5×10^8	1.7×10^8	2.5×10^8
(13b)	$2MeO_2\cdot \rightarrow MeOH + HCHO + O_2$	1.8×10^8	1.8×10^8	1.8×10^8	1.8×10^8
(14a)	$MeO_2\cdot + Bu^tO_2\cdot \rightarrow MeO\cdot + Bu^tO\cdot + O_2$	3.8×10^5	5.6×10^5	7.9×10^5	2.0×10^6
(14b)	$MeO_2\cdot + Bu^tO_2\cdot \rightarrow Bu^tOH + HCHO + O_2$	2.0×10^6	2.3×10^6	2.7×10^6	4.0×10^6
(15)	$MeO\cdot + Bu^tO_2\cdot \rightarrow Bu^tO_2H + HCHO$	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(16)	$MeO\cdot + O_2 \rightarrow HCHO + HO_2\cdot$	9.6×10^5	1.2×10^6	1.4×10^6	2.2×10^6
(18)	$MeO\cdot + Bu^tO_2H \rightarrow MeOH + Bu^tO_2\cdot$	1.5×10^7	1.9×10^7	2.3×10^7	4.0×10^7
(21)	$MeO_2\cdot + HO_2\cdot \rightarrow MeO_2H + O_2$	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(23)	$2Bu^tO_2\cdot \rightarrow Bu^tO_2Bu^t + O_2$		see ref. 1		
(24)	$MeO\cdot + MeO_2\cdot \rightarrow MeO_2H + HCHO$	9.2×10^8	9.2×10^8	9.2×10^8	9.2×10^8
(25)	$Bu^tO\cdot + HCHO \rightarrow Bu^tOH + \dot{C}HO$	9.0×10^5	1.5×10^6	2.5×10^6	1.0×10^7
(26)	$MeO\cdot + HCHO \rightarrow MeOH + \dot{C}HO$	9.0×10^5	1.5×10^6	2.5×10^6	1.0×10^7
(27)	$\dot{C}HO + O_2 \rightarrow CO + HO_2\cdot$	3.8×10^5	5.6×10^5	7.1×10^5	1.6×10^6

* Units $dm^3\ mol^{-1}\ s^{-1}$ except for reaction (11) which are s^{-1}.

† Numbering corresponds to corresponding reactions in the azoethane[2] and 2,2′-azoisopropane[3–5] systems.

epoxide was studied using 2-methylbut-2-ene (Table 2) and 2,3-dimethylbut-2-ene (Table 3). When 2,3-dimethylbut-2-ene was added, significantly larger yields of acetone were produced (compare results in Tables 1—3).

Varying the initial pressure of oxygen had little effect on the overall pattern of product yields at 343 K, but at 393 K the yield of t-butyl hydroperoxide increased at the expense of t-butyl alcohol (Table 4).

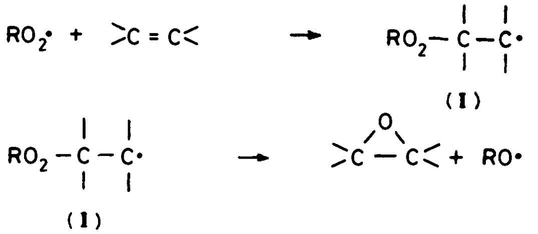
On increasing the initial concentration of 2,3-dimethylbut-2-ene at 393 K, the yield of acetone (but not the other products from the oxidation of *trans*-2,2′-azoisobutane) increased while that of the epoxide increased to a limiting value (Table 5).

Discussion

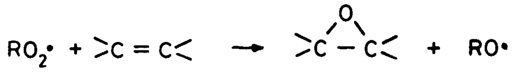
The reaction mechanism for the photo-oxidation of *trans*-2,2′-azoisobutane has been discussed in considerable detail in the preceding paper[1] and is in broad agreement with that proposed by Kirsch and Parkes.[17]

The reaction was simulated using the procedure outlined in earlier papers[2,4,5] and the same rate parameters were used. Individual rate constants used at different temperatures in these calculations are given in Table 6.

Except for 2,3-dimethylbut-2-ene, which will be discussed separately, the alkenes, on addition to the reaction system, only yielded the corresponding epoxide. Epoxides are formed in the autoxidation of alkenes by the mechanism in Scheme 1.[11–13,18,19] The overall reaction can be described as (22). The



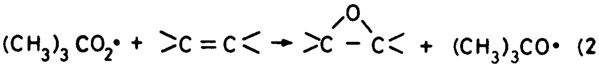
Scheme 1.

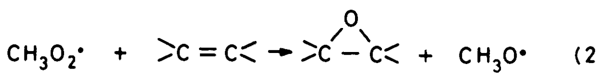


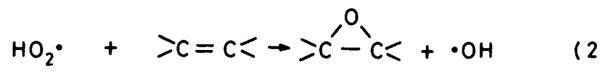
$$RO_2\cdot + {>}C{=}C{<} \rightarrow {>}\overset{O}{C{-}C}{<} + RO\cdot \qquad (22)$$

adduct radical (I) may, in theory, undergo either cyclisation or decompose to reform the alkene; ring closure to form the epoxide is easily the most favourable route.[13,18]

There are three possible candidates for the role of $RO_2\cdot$ in the present system, t-butylperoxyl, methylperoxyl, and hydroperoxyl radicals, and thus we have introduced reactions (22a—c) into the mechanism.


(22a)


(22b)


(22c)

Introducing these reactions into the simulations had no effect on the predicted yields of acetone, t-butyl alcohol, t-butyl hydroperoxide, or formaldehyde, nor on the ratios of the concentrations of oxygenated radicals. By using the rate constant for reaction (22b) obtained in earlier work,[10] and the relative concentrations of t-butylperoxyl and methylperoxyl radicals obtained in the simulations, it was found that both methylperoxyl and t-butylperoxyl radicals play an important part in the epoxidation reactions. On the other hand, the concentration of hydroperoxyl radicals is low and these radicals play a minor role in the system.

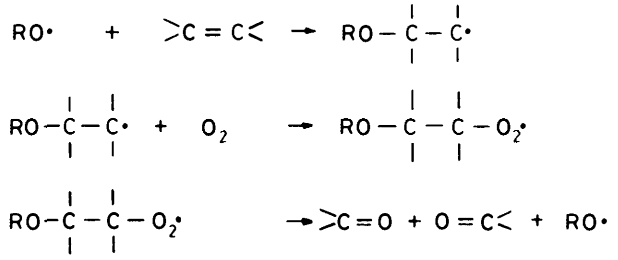
As described above, only the corresponding epoxide is obtained on addition of the alkene to the system. Thus the alkene undergoes addition reactions in preference to abstraction reactions with, for example, alkoxyl radicals. Alkoxyl radicals appear to react preferentially with products, such as formaldehyde [reactions (25) and (26)], in line with the corresponding rate data.[20,21] If reaction between alkoxyl radicals and alkenes had been significant, there would be enhanced yields of t-butyl alcohol and one would also expect to see unsaturated oxygenated compounds amongst the products as obtained in the gas-phase autoxidation of alkenes.[19,23]

Table 7. Rate constants for the reaction between t-butylperoxyl radicals and alkenes

	T/K	k_{22a}/dm^3 mol^{-1} s^{-1}
Ethene	393	3.36
2-Methylpropene	393	2.6
2-Methylbut-1-ene	393	3.6
2-Methylbut-2-ene	313	0.06
	328	0.11
	343	0.38
2,3-Dimethylbut-2-ene	313	3.48
	343	10.9
	393	148

Examples of simulations are given in Tables 1 and 2 and a selection of results for the formation of epoxides under a wide range of conditions. It will be seen that the predicted yields of acetone, formaldehyde, and t-butyl alcohol are indeed reasonably similar to the experimentally determined values.

For the most reactive alkene, 2,3-dimethylbut-2-ene, the experimentally determined yield of acetone was considerably larger than that found on simulation (Tables 3—5). It is probable that this is due to an addition reaction between the alkene and an alkoxyl radical (either t-butoxyl or methoxyl). The adduct can then add an oxygen molecule rapidly and decompose *via* a six-membered transition state yielding acetone and regenerating the alkoxyl radical (Scheme 2).[22,23] Indeed, experimental results from an earlier study involving [^{18}O]-2,3-dimethylbutan-2-ol have verified that such species do yield carbonyl compounds.[24]



Scheme 2.

Although the yield of acetone is larger than expected, the simulated yields of the other products are similar to those obtained experimentally. This confirms that the 'excess' of acetone is coming from the alkene and not from a promoted reaction of *trans*-2,2′-azoisobutane. Further, the variation of initial oxygen (Table 4) and initial alkene (Table 5) pressures are simulated in accord with the experimentally determined values, including the interesting fall-off in yield of epoxide on adding excess of oxygen (Table 4) and the lack of effect of adding alkene on the yield of epoxide beyond a limiting concentration (Table 5).

Using rate constants listed in Table 7, and obtained by the simulation procedure, Arrhenius parameters for reactions between t-butylperoxyl radicals and of two of the alkenes studied have been determined (Table 8).

We are now in a position to compare the rates of addition reaction between peracyl radicals and alkylperoxyl radicals with alkenes and, secondly, the effect of structure of the alkylperoxyl radicals on the reaction.

The rate of addition of t-butylperoxyl radicals to the alkenes studied (Table 7) increases with increasing substitution about the carbon–carbon double bond. Similar behaviour has been

Table 8. Arrhenius parameters for addition of peracetyl, methylperoxyl, isopropylperoxyl, and t-butylperoxyl radicals to alkenes

	$CH_3CO_3\cdot$[a,b]		$CH_3O_2\cdot$[c]		$(CH_3)_2CHO_2\cdot$[d]		$(CH_3)_3CO_2\cdot$[e]	
Alkene	log A	E	log A	E	log A	E	log A	E
2-Methylpropene	8.29 ± 0.16[a]	25.0 ± 1.2			8.59 ± 0.19	62.7 ± 2.2		
2-Methylbut-1-ene	8.11[b*]	22.2	8.60 ± 0.72	52.8 ± 5.4	8.30 ± 0.07	54.9 ± 0.6		
2-Methylbut-2-ene	8.08 ± 0.12[b]	16.3 ± 0.9	8.16 ± 0.49	42.4 ± 3.6	8.03 ± 0.35	48.2 ± 1.7	8.16 ± 0.38	56.6 ± 2.4
2,3-Dimethylbut-2-ene			8.14 ± 0.32	36.4 ± 2.8	7.96 ± 0.50	40.9 ± 1.8	8.58 ± 0.61	48.7 ± 4.1

Units of A are dm^3 mol^{-1} s^{-1} and E are kJ mol^{-1}.

[*] Assumed A factor.

[a] Ref. 12. [b] Ref. 13. [c] Ref. 10. [d] Ref. 7. [e] This work.

observed for other alkylperoxyl[7,10] and for peracetyl[12,13] radicals. As with the addition of such radicals are difluoroamino[25] and trifluoromethyl,[26,27] the result can be attributed to the electrophilic nature of all the radicals. Indeed, linear plots, with negative slopes, for the logarithm of the rate constants for these reactions with ionisation energies of the alkenes is further evidence. This suggests that polar structures of the form $\mathrm{Bu^tO_2^-}\ {>}\overset{+}{\mathrm{C}}{-}\dot{\mathrm{C}}{<}$ are important in describing the transition state in these addition reactions. The importance of the electrophilicity of the oxygenated radical is further seen when comparing the rates of epoxidation by peracetyl radicals and by alkylperoxyl and hydroperoxyl radicals (Table 8).

For a specific alkene, the rate of epoxidation increases over the peroxyl radical series from hydroperoxyl to t-butylperoxyl. Such variations, although small compared with the change from acetylperoxyl to alkylperoxyl, are rationalised in terms of inductive effects. Thus as the number of methyl groups on the carbon atom near the radical centre increases, so does the rate at which the radical will react with an alkene.

Acknowledgements

We thank the S.E.R.C. for a research studentship (D. A. O.)

References

1 Part 14, D. A. Osborne and D. J. Waddington, preceding paper.
2 C. Anastasi, D. J. Waddington, and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 505.
3 L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2293.
4 L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2678.
5 L. T. Cowley, D. J. Waddington, and A. Woolley, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2535.
6 M. I. Sway and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1982, 999.
7 M. I. Sway and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1983, 139.
8 R. W. Walker, D. Phil. Thesis, University of Hull, 1980.
9 M. W. H. Hisham, D. Phil. Thesis, University of Hull, 1981.
10 D. A. Osborne, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1980, 925.
11 R. Ruiz Diaz, K. Selby, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1975, 758.
12 K. Selby and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1715.
13 R. Ruiz Diaz, K. Selby, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1977, 360.
14 J. C. Stowell, *J. Org. Chem.*, 1967, **32**, 2360.
15 E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, 1960, **82**, 1362.
16 A. T. Bottini, R. L. Van Etten, and A. J. Davidson, *J. Am. Chem. Soc.*, 1965, **87**, 755.
17 L. J. Kirsch and D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, 1981, 77, 293.
18 D. J. M. Ray and D. J. Waddington, *J. Phys. Chem.*, 1972, **76**, 3319.
19 D. J. M. Ray and D. J. Waddington, Thirteenth Symposium (International) on Combustion, The Combustion Institute, 1971, p. 261.
20 N. Y. Al Akeel, K. Selby, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1036.
21 M. I. Sway and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1984, 63.
22 D. J. M. Ray, R. Ruiz Diaz, and D. J. Waddington, Fourteenth Symposium (International) on Combustion, The Combustion Institute, 1973, p. 259.
23 D. J. M. Ray and D. J. Waddington, *Combust. Flame*, 1973, **21**, 327.
24 D. J. M. Ray, A. Redfearn, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1973, 540.
25 A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 1967, 105.
26 A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, 1961, **83**, 4732.
27 I. M. Whittlemore, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, 1962, **84**, 3799.

Received 26*th October* 1983; *Paper* 3/1904