Reactions of Oxygenated Radicals in the Gas Phase. Part 7.[1] Reactions of Methylperoxyl Radicals and Alkenes

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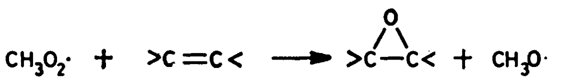
The reactions of methylperoxyl radicals with alkenes have been studied between 373 and 403 K. The peroxyl radicals were generated by the oxidation of di-t-butyl peroxide. Arrhenius parameters for reaction (18) have been



$$CH_3O_2\cdot + {>}C{=}C{<} \longrightarrow {>}\overset{O}{C{-}C}{<} + CH_3O\cdot \qquad (18)$$

determined for 2-methylbut-1-ene, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene. They are $\log(A_{18}/dm^3\,mol^{-1}\,s^{-1}) = 8.60 \pm 0.72, 8.16 \pm 0.49$, and 8.14 ± 0.32, and $E_{18} = 52.8 \pm 5.4, 42.4 \pm 3.6$, and 36.4 ± 2.8 kJ mol^{-1}, respectively.

THERE is still little quantitative experimental information concerning the propagation reactions of alkylperoxyl radicals in the gas phase. In an earlier paper,[2] a technique was described whereby the reaction between methylperoxyl radicals and alkenes could be followed. Essentially, a co-oxidation system is set up, using a mixture of di-t-butyl peroxide and an alkene as the fuels.

In this paper, data for the Arrhenius parameters for the reaction of methylperoxyl radicals and three alkenes of varying structures are given. The results are compared with the corresponding reactions of peracetyl radicals and alkenes.

EXPERIMENTAL

The apparatus has been described.[3] The Pyrex cylindrical reaction vessel had a volume of 228 cm^3 and surface : volume ratio of 1 : 1.1 cm^{-1}. A similar analytical procedure was adopted. The concentration of peroxide was obtained by an iodometric method.[4] The reactants and other products were determined using g.l.c. (Pye 104, equipped with flame ionisation detectors). The column packing materials were Gas Chrom Q (100—120 mesh) on which there was either 10% (w/w) bis-(2-ethylhexyl) sebacate or 20% (w/w) squalane. The identity of the products was confirmed by m.s. (AEI MS30).

Di-t-butyl peroxide (DTBP) (Koch-Light) was purified by passage through activated alumina, and/or preparative g.l.c. [10% (w/w) bis-(2-ethylhexyl) sebacate]. The purity was checked by g.l.c. using flame ionisation and kathrometer detection systems, to ensure that impurities, for example acetone, t-butyl alcohol, t-butyl hydroperoxide, methanol, and water, were absent.

Authentic samples of the epoxides used to calibrate the analytical procedure were prepared from the parent alkene, using either *N*-bromosuccinimide [5] or perbenzoic acid.[6]

RESULTS

DTBP, on oxidation in the gas phase, yields acetone, formaldehyde, methanol, and methyl hydroperoxide.[2,7]

On addition of 2-methylbut-1-ene, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene, the corresponding epoxides are formed (Tables 1—3). On addition of 2-methylbut-2-ene and 2,3-dimethylbut-2-ene, the rates of formation of acetone are increased. On addition of the former, acetaldehyde is also produced. On adding 2-methylbut-1-ene, very small traces of butan-2-one were detected. Small amounts of t-butyl alcohol are also formed on addition of the alkenes.

DISCUSSION

Di-t-butyl peroxide (DTBP), on thermolysis, yields methyl radicals which react rapidly with oxygen [reactions (1)—(3)]. These reactions, and subsequent reactions of methylperoxyl radicals are discussed fully elsewhere.[2,8] (*The numbering of reactions is that used earlier.*[2])

When ethylene,[2] or, as in this study, 2-methylbut-1-ene, is added, the rate of formation of acetone is unaltered. Thus the rate of reaction (2) is much faster than the rate of addition of t-butoxyl radical to the alkene. However, the formation of t-butyl alcohol indicates that an abstraction reaction competes with reaction (2).

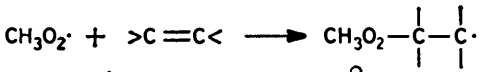
$$DTBP \longrightarrow 2(CH_3)_3CO\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot + M \longrightarrow (CH_3)_2CO + \cdot CH_3 + M \qquad (2)$$

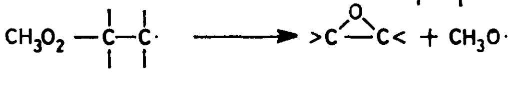
$$\cdot CH_3 + O_2 + M \longrightarrow CH_3O_2\cdot + M \qquad (3)$$

Abstraction reactions play a large part in the early stages of the autoxidation of alkenes in the gas phase.[9,10] Subsequently, as the concentration of oxygenated radicals builds up, addition reactions play the principal role in the propagation chain.[10,11] Addition of hydroxyl and alkoxyl radicals leads to the formation of carbonyl compounds. These compounds are R^1R^2CO and R^3R^4CO from the alkene $R^1R^2C{=}CR^3R^4$.[9-11] On the other hand, addition of $XO_2\cdot$ radicals (whether they be alkenyl-, alkyl-, or acyl-peroxyl) leads to the formation of epoxides.[10-12] The epoxides are formed in much smaller concentrations than the carbonyl compounds in these autoxidation reactions, although the relative proportions change with the structure of the alkene and with the temperature.[9-11] However, in controlled experiments in which high concentrations of acetylperoxyl are formed, the major product is the epoxide,[3,13-15] and indeed conditions can be obtained whereby the alkene can be converted quantitatively into the epoxide.

In this study, with methylperoxyl radicals, large amounts of carbonyl compounds are formed from 2-methylbut-2-ene and 2,3-dimethylbut-2-ene, indicating that epoxidation is not the favoured process, as compared with the reaction between acetylperoxyl radicals and alkenes;[3,14,15] the ratio of products is much more like that obtained during the autoxidation of the hydrocarbons. Indeed, the rate of formation of carbonyl compounds from the alkene increases on passing from 2-methylbut-1-ene to 2-methylbut-2-ene and 2,3-dimethylbut-2-ene as one observes in the autoxidation process,[9-11] *i.e.* as the number of substituent alkyl groups adjacent to the carbon double bond increases.



$$CH_3O_2\cdot + {>}C{=}C{<} \longrightarrow CH_3O_2-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \qquad (18a)$$



(18b)

Table 1

Reaction of methylperoxyl radicals and 2-methylbut-1-ene

Di-t-butyl peroxide 20 Torr; oxygen 5 Torr; total pressure of 500 Torr with nitrogen

T/K	Alkene added/ Torr	Time/min	10^3 Epoxide/ Torr	Acetone/Torr	10^4 Peroxide/Torr
373	30	60	1.75	· · · (0.05 †)	— (— †)
		120	3.13	· · · (0.09 †)	— (— †)
		180	4.30	· · · (0.14 †)	— (— †)
		240	6.30	· · · (0.18 †)	— (— †)
	45	60	2.06	· · · (0.05 †)	— (— †)
		120	4.46	· · · (0.09 †)	— (— †)
		180	6.83	· · · (0.14 †)	— (— †)
		240	8.60	· · · (0.18 †)	— (— †)
	60	60	3.08	· · · (0.05 †)	— (— †)
		120	5.76	· · · (0.09 †)	— (— †)
		180	8.43	· · · (0.14 †)	— (— †)
		240	11.0	· · · (0.18 †)	— (— †)
393	5	30	0.87	0.23 (0.27 †)	1.23 (1.20 †)
		60	1.75	0.51 (0.50 †)	2.21 (1.90 †)
		90	2.55	0.74	3.31
		120	3.50	0.99 (1.12 †)	5.15 (5.40 †)
		150	4.82	1.26	6.13
		180	5.65	1.41 (1.42 †)	6.86
	10	30	1.70	0.23 (0.27 †)	1.23 (1.20 †)
		60	3.63	0.49 (0.50 †)	2.20 (1.90 †)
		90	5.41	0.73	3.43
		120	7.06	0.95 (1.12 †)	5.15 (5.40 †)
		150	9.41	1.25	5.88
		180	10.90	1.39 (1.42 †)	6.86
	15	30	2.75	0.23 (0.27 †)	1.23 (1.20 †)
		60	5.44	0.47 (0.50 †)	1.96 (1.90 †)
		90	8.07	0.74	3.19
		120	10.43	1.04 (1.12 †)	5.02 (5.40 †)
		150	14.05	1.24	5.88
		180	15.93	1.43 (1.42 †)	6.62
403	5	30	2.62	0.88	3.52
		60	4.96	1.63	7.04 (7.50 †)
		90	6.40	2.57	· · ·
		120	9.06	3.27	14.1 (18.0 †)
		150	11.6	4.43	17.8
	10	30	5.49	0.84	3.52
		60	9.07	1.66	7.04 (7.50 †)
		90	13.2	2.51	10.6
		120	17.8	3.30	14.3 (18.0 †)
		150	24.8	4.49	· · ·
	15	30	7.07	0.83	3.27
		60	14.6	1.67	7.04
		90	21.4	2.54	10.3 (7.50 †)
		120	27.5	3.28	· · ·
		150	34.4	4.47	17.6

† Experiments performed with DTBP 20 Torr; oxygen 5 Torr; nitrogen 475 Torr. — Not observable. · · · Experiment not performed.

The addition of methylperoxyl radicals to alkenes is followed by ring closure [reactions (18a and b)]. As has been described, reaction (18b) is considerably faster than the subsequent addition of an oxygen molecule to the peroxyalkyl radical,[2] which agrees with data obtained in solution.[16,17]

The reaction can be described overall as (18). There is little reason to doubt that the epoxide is formed solely by this reaction.[1]

The principal termination reactions for methylperoxyl radicals are (4a and b).[2,8,18,19] One must also take into account reaction (5) of methoxyl radicals with oxygen which competes effectively with the self-reaction (6) and other radical–radical reactions involving methoxyl

(18)

radicals.[2] The effect of oxygen on the relative yields of methyl hydroperoxide, methanol, and formaldehyde is explained by reactions (5) and (7). At low oxygen pressures as described above, the rates of reactions (8) and (9) are much smaller than the rate of reaction (5). Reaction (10) explains the fall-off in the rate of formation of the hydroperoxide as reaction proceeds.

TABLE 2

Reaction of methylperoxyl radicals and 2-methylbut-2-ene

Di-t-butyl peroxide 20 Torr; oxygen 5 Torr; total pressure of 500 Torr with nitrogen

T/K	Alkene added/ Torr	Time/min	10^3 Epoxide/ Torr	Acetone/ Torr	10^2 Acetaldehyde/ Torr	10^4 Peroxide/ Torr
373	5	60	2.60	0.06	—	—
		120	4.78	0.12	0.5	—
		180	7.00	0.18	0.8	—
		240	9.04	0.23	1.0	—
	7.5	60	3.43	0.06	—	—
		120	7.01	0.12	0.5	—
		180	1.08	0.18	1.0	—
		240	1.44	0.24	1.5	—
	10.0	60	4.55	0.06	—	—
		120	9.38	0.12	0.5	—
		180	13.7	0.19	1.0	—
		240	18.6	0.24	1.5	—
393	5	30	6.03	0.34	1.5	1.1
		60	14.3	0.66	2.5	2.2
		90	23.8	0.98	3.5	3.4
		120	30.1	1.30	5.0	5.3
		150	35.7	1.61	7.5	5.9
		180	45.5	1.93	9.0	7.4
	7.5	30	9.76	0.37	2.0	1.0
		60	21.0	0.67	3.8	2.2
		90	33.3	1.01	6.5	3.4
		120	41.6	1.37	9.0	5.1
		150	55.0	1.64	10.0	5.8
		180	69.9	2.06	12.0	7.1
	10	30	15.2	0.38	2.0	1.0
		60	29.4	0.70	4.0	2.1
		90	47.6	1.04	6.5	3.4
		120	60.5	1.41	9.5	5.1
		150	77.3	1.72	11.0	5.6
		180	87.9	2.05	13.5	6.9
403	5	30	1.81	1.26	5.0	3.4
		45	2.57	1.81	7.5	5.0
		60	3.58	2.23	9.5	6.8
		75	4.54	2.96	12.0	8.7
		90	5.40	3.56	14.0	10.7
		105	6.08	4.07	15.5	12.2
	7.5	30	2.81	1.30	5.0	3.0
		45	3.92	1.86	8.5	5.0
		60	5.34	2.36	11.0	. . .
		75	6.74	3.00	13.0	8.5
		90	7.97	3.42	15.5	10.6
		105	9.45	4.16	18.5	12.3
	10	30	3.81	1.30	6.0	3.0
		45	5.40	1.85	9.0	4.9
		60	7.29	2.41	11.0	6.6
		75	9.37	2.95	14.0	8.5
		90	11.2	3.60	16.5	. . .
		105	12.9	4.27	19.5	12.1

— Not observable. ... Experiment not perfomed.

$$2CH_3O_2\cdot \longrightarrow CH_3OH + HCHO + O_2 \qquad (4a)$$

$$2CH_3O_2\cdot \longrightarrow 2CH_3O\cdot + O_2 \qquad (4b)$$

$$CH_3O\cdot + O_2 \longrightarrow HCHO + HO_2\cdot \qquad (5)$$

$$2CH_3O\cdot \longrightarrow CH_3OH + HCHO \qquad (6)$$

$$CH_3O_2\cdot + HO_2\cdot \longrightarrow CH_3O_2H + O_2 \qquad (7)$$

$$CH_3O\cdot + CH_3O\cdot \longrightarrow CH_3O_2H + HCHO \qquad (8)$$

$$HO_2\cdot + CH_3O\cdot \longrightarrow CH_3OH + O_2 \qquad (9)$$

$$CH_3O_2H + CH_3O\cdot \longrightarrow CH_3O_2\cdot + CH_3OH \qquad (10)$$

The assumptions for this argument are set out in an earlier paper.[8] A steady-state treatment of reactions (1)—(10) and (18) gives the relation (A) where R_A, R_E, and R_M are the rates of formation of acetone, epoxide, and methyl hydroperoxide, respectively.

As has been mentioned above, there are two sources of acetone when either 2-methylbut-2-ene or 2,3-dimethylbut-2-ene are added, namely di-t-butyl peroxide and the alkene. Thus, the rate of formation of acetone used in the calculation, R_A, is the rate of acetone produced by the peroxide. This has been determined in four different sets of experiments, with peroxide and inert gas, with peroxide and oxygen,[2] with peroxide, oxygen, and ethylene,[2] and with peroxide, oxygen, and 2-methylbut-1-ene. The rate of formation of acetone from peroxide, R_A, is independent

$$\frac{k_{18}}{[2(k_{4a} + k_{4b})]^{\frac{1}{2}}} = \frac{R_E}{(R_A - R_E - R_M)^{\frac{1}{2}}[\text{Alkene}]} \qquad (A)$$

of these additives and there is no reason why either 2-methylbut-2-ene or 2,3-dimethylbut-2-ene should affect it.

Acetaldehyde, formed from 2-methylbut-2-ene, may react further in this system, to yield peracetyl radicals which undergo rapid reaction with alkenes.[14,15] However, peracetic acid was never observed as a product during the reaction and thus it is most probable that, at the small extents of reaction studied, the further oxidation products of acetaldehyde play a minimal role in the reaction.

In the last few years, the first direct studies of the self-reactions of methylperoxyl radicals have been reported.[18-24] Although methylperoxyl radicals have been generated by different methods, all the studies use

$$CH_3O_2\cdot + CH_3O_2\cdot \longrightarrow \text{products} \qquad (4)$$

u.v. absorbance of the peroxyl radical to determine the rate constant [reaction (4)]. The values obtained, on following the rate of consumption of methylperoxyl radicals, are remarkably self-consistent, being 3.3 $(\pm 0.7) \times 10^8$,[19] $(2.3 \pm 0.3) \times 10^8$,[20] $(2.7 \pm 0.6) \times 10^8$,[21,22] $(2.2 \pm 0.2) \times 10^8$,[23] and $(2.5 \pm 0.3) \times 10^8$ dm^3 mol^{-1} s^{-1}.[24]

As Parkes,[18,19] and later Kan *et al.*,[24] have pointed out, the rate constants above are not true values of k_4 for they

TABLE 3

Reaction of methylperoxyl radicals and 2,3-dimethylbut-2-ene

Di-t-butyl peroxide 20 Torr; oxygen 5 Torr; total pressure of 500 Torr with nitrogen

T/K	Alkene added/ Torr	Time/min	10^2 Epoxide/ Torr	Acetone/ Torr	10^4 Peroxide/ Torr
373	2.5	30	0.3	0.06	—
		60	0.7	0.12	—
		90	1.0	0.17	—
		120	1.4	0.23	—
		150	1.7	0.30	—
	5	30	0.7	0.08	—
		60	1.4	0.14	—
		90	2.0	0.22	—
		120	2.7	0.31	—
		150	3.5	0.38	—
	7.5	30	1.1	0.09	—
		60	2.0	0.17	—
		90	2.8	0.27	—
		120	3.7	0.36	—
		150	4.9	0.44	—
393	3	30	2.6	0.66	1.0
		60	4.9	1.22	2.0
		90	7.0	1.84	. . .
		120	10.1	2.23	4.9
		150	12.4	2.91	5.9
	5	30	4.3	0.71	0.7
		60	8.2	1.34	2.0
		90	12.1	2.08	2.9
		120	15.4	2.61	4.7
		150	19.7	3.41	5.9
	7.5	30	5.6	0.73	0.7
		60	11.9	1.42	1.6
		90	17.3	2.20	2.2
		120	23.0	2.91	3.9
		150	29.2	3.56	5.6
	10	30	7.6	0.81	0.7
		60	14.5	1.56	1.4
		90	22.5	2.47	2.5
		120	30.1	3.23	3.4
		150	35.7	3.87	5.2
403	5	15	6.0	1.30	1.5
		30	10.1	2.51	3.3
		45	16.4	3.74	4.7
		60	21.4	4.88	6.5
		75	27.0	5.99	. . .
	7.5	15	7.8	1.32	1.3
		30	15.4	2.60	3.0
		45	23.0	3.90	. . .
		60	29.5	4.97	6.0
		75	37.5	6.40	8.4
	10	15	10.7	1.33	1.3
		30	19.1	2.75	2.8
		45	28.5	4.03	4.3
		60	38.9	5.33	6.3
		75	49.7	6.66	8.0

— Not observable. ... Experiment not performed.

incorporate side-reactions of methylperoxyl radicals, principally with methoxyl and hydroperoxyl radicals. In detailed argument, Parkes[18] has shown that these reactions lead the values obtained above to be 1.2 ± 0.1

$$2CH_3O_2\cdot \longrightarrow CH_3OH + HCHO + O_2 \qquad (4a)$$

$$2CH_3O_2\cdot \longrightarrow 2CH_3O\cdot + O_2 \qquad (4b)$$

$$2CH_3O_2\cdot \longrightarrow CH_3O_2CH_3 + O_2 \qquad (4c)$$

too large. Thus, the true value of k_4 obtained from his study[19] is $(2.8 \pm 0.7) \times 10^8$ dm^3 mol^{-1} s^{-1} at room temperature. Broadly similar arguments lead Kan *et al.*[24] to give a value for k_4 of $(2.4 \pm 0.1) \times 10^8$ dm^3 mol^{-1} s^{-1}. Further, Parkes[18] has separated k_4 into two components ($k_{4a} + k_{4c}$) and k_{4b}. Using his revised value of k_4,[19] ($k_{4a} + k_{4c}$) is 1.8×10^8 dm^3 mol^{-1} s^{-1} and k_{4b} is 1.0×10^8 dm^3 mol^{-1} s^{-1} at room temperature.

Unfortunately, detailed results for the effect of temperature on k_4 have not been published, but the energy of activation is reported to be close to zero.[22,25] In a recent study in our laboratories,[2] it was shown that k_{4a}/k_{4b} varies with temperature and that $(E_{4b} - E_{4a})$ is 9 ± 1 kJ mol^{-1}. (Dimethyl peroxide was not observed.) Thus, we have reported values of the ratio for $k_{18}/[2(k_{4a} + k_{4b})]^{\frac{1}{2}}$ and for k_{18}, where values of k_{4a} and k_{4b} were calculated using Parkes' results, with E_{4a} and E_{4b} being given values of 0 and 9 kJ mol^{-1} (Table 4).

TABLE 4

Rate constants for the addition reaction between methylperoxyl radicals and alkenes

Alkene	T/K	$k_{18}/[2(k_{4a} + k_{4b})]^{\frac{1}{2}}$/dm$^{3/2}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$	k_{18}/dm^3 mol^{-1} s^{-1}
2-Methylbut-1-ene	373	5.77×10^{-4}	$(1.60 \pm 0.14) \times 10^1$
	393	5.79×10^{-3}	$(1.67 \pm 0.10) \times 10^2$
	403	3.50×10^{-2}	$(1.03 \pm 0.03) \times 10^3$
2-Methylbut-2-ene	373	1.49×10^{-3}	$(4.15 \pm 0.24) \times 10^1$
	393	1.23×10^{-2}	$(3.57 \pm 0.18) \times 10^2$
	403	7.24×10^{-2}	$(2.13 \pm 0.28) \times 10^3$
2,3-Dimethylbut-2-ene	373	1.99×10^{-3}	$(5.54 \pm 0.58) \times 10^1$
	393	1.57×10^{-2}	(4.55 ● 0.26) $\times 10^2$
	403	9.15×10^{-2}	$(2.69 \pm 0.27) \times 10^3$

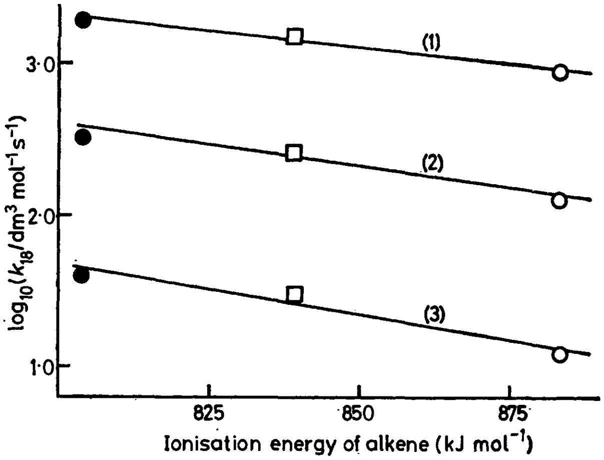
Table 4 gives the rate constants and Table 5 the Arrhenius parameters for reaction (18) for the three alkenes studied. The rate of addition depends on the structure. As the ionisation energy of the alkene decreases (*i.e.* as substitution at the carbon double bond increases), the rate of epoxidation increases. Similar behaviour has been observed for the addition of difluoroamino,[26] trifluoromethyl,[27,28] and peracetyl[15] radicals, oxygen(^3P)[29,30] atoms, and peracetic acid[15] in the gas phase. There is a similar linear relationship for log k for the reaction of methylperoxyl radicals and alkenes and the ionisation energy of the alkenes[31,32] (Figure), the slope being negative. The electrophilic nature of the methylperoxyl radicals is thus shown and suggests that the transition state for reaction (18a) can be described as $>\dot{C}-\overset{+}{C}<{}^{-}O_2CH_3$.

TABLE 5

Arrhenius parameters for the addition reaction between methylperoxyl radicals and alkenes

Alkene	$\log_{10}(A_{18}$/dm^3 mol^{-1} s^{-1})	E_{18}/kJ mol^{-1}
2-Methylbut-1-ene	8.60 ± 0.72	52.8 ± 5.4
2-Methylbut-2-ene	8.16 ± 0.49	42.4 ± 3.6
2,3-Dimethylbut-2-ene	8.14 ± 0.32	36.4 ± 2.8

The reactions are much slower, by several orders of magnitude, than the corresponding reactions with peracetyl radicals. Thus, while methylperoxyl radicals are electrophilic, their electrophilicity is much lower than in peracetyl due to the presence of the carbonyl group in the latter. This can readily be seen from the data presented in the Figure. The rate constants for reaction (18) increase as an alkyl group replaces a hydrogen atom on a carbon atom of the double bond, but not to the same extent as the corresponding reactions between peracetyl radicals and alkenes.[15] Nevertheless, the behaviour is in contrast say to the addition reaction between methyl radicals and alkenes.[33]



The relationship between the rate constant for reaction (18) and the ionisation energy of the alkene at (1), 403 K; (2), 393 K; (3), 373 K. ○, 2-Methylbut-1-ene; ☐, 2-methylbut-2-ene; ●, 2,3-dimethylbut-2-ene

The importance of peracyl radicals in hydrocarbon oxidation systems cannot be overemphasised. If acetaldehyde or a higher aldehyde is formed during the reaction under conditions which then yield peracyl radicals, a co-oxidation system is produced in which the aldehyde is likely to play the major role in controlling the rate of reaction. Subsequent papers will compare the rates of reaction of other alkylperoxyl radicals where the alkyl group is ethyl, isopropyl, and t-butyl, and, together, compared with reactions between peracyl radicals.

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