Reactions of Oxygenated Radicals in the Gas Phase. Part 5.[1] Reactions of Methylperoxyl Radicals and Alkenes

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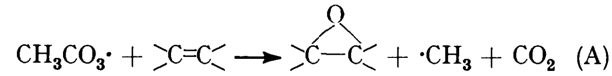
The reactions of methylperoxyl radicals with alkenes have been studied at 410 K. The peroxyl radicals were generated by the oxidation of methyl radicals formed during the thermal oxidation of di-t-butyl peroxide. Rate constants for reaction (18) have been determined: $k_{(18)}$(ethylene) = 1.2 ± 0.7 and $k_{(18)}$ (2-methylpropene) = 9.8 ± 1.6 dm^3

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

mol^{-1} s^{-1} at 410 K. An estimate for an activation energy of the abstraction reaction between t-butoxyl radicals and 2-methylpropene is given.

AMONGST the more important propagation reactions in the oxidation of hydrocarbons in the gas phase is that between alkylperoxyl radicals and an alkene (which might be the original fuel or be formed during the oxidation of an alkane or cycloalkane).

Extensive rate data have been published recently on the reactions of acetylperoxyl radicals and alkenes.[2-4] The reactions are rapid, the activation energies for the reactions lying between 16.3 and 32.6 kJ mol^{-1}, depending on the structure of the alkene [reaction (A)]. However,



$$CH_3CO_3\cdot + >C{=}C< \longrightarrow >C\overset{O}{—}C< + \cdot CH_3 + CO_2 \qquad (A)$$

data for the corresponding reactions with alkylperoxyl radicals are not available and in this study the reactions between methylperoxyl radicals and two alkenes, ethylene and 2-methylpropene, are reported.

TABLE 1

Oxidation of di-t-butyl peroxide. Effect of addition of alkenes at 410 K: DTBP, 20 Torr; oxygen, 5 Torr; total pressure (with argon), 500 Torr [a]

Alkene (Torr)	t/s	Acetone (Torr)	Formaldehyde (Torr)	Methanol (Torr)	Total hydroperoxide (Torr)	t-Butyl alcohol (Torr)	Epoxide (Torr)
No alkene added							
	600	1.03	0.34	0.46	0.05		
	1 200	2.12	0.55	0.98	0.10		
	1 800	3.00	0.70	1.59	0.12		
Ethylene added							
220	1 500	2.59	0.66	1.00	0.09		0.003
250	600	1.06	0.36	0.43	0.01		0.001
250	1 200	2.02	0.68	0.88	0.08		0.002
250	1 800	3.10	0.87	1.42	0.10		0.002
320	600	1.04	0.41	0.47	*b*		0.004
2-Methylpropene added							
200	600	1.26	0.56	0.43	0.03	0.10	0.012
200	1 200	2.51	0.88	0.85	0.10	0.17	0.019
315	600	1.26	0.50	0.82	0.04	0.11	0.016
390	600	1.35	0.61	0.48	*b*	0.13	0.015
430	600	1.33	0.60	0.50	*b*	0.13	0.017
510 [a]	600	1.37	0.61	0.55	*b*	0.14	0.022

[a] Except where indicated. [b] Analyses not performed.

EXPERIMENTAL

The apparatus has been described in an earlier paper and a similar analytical method was adopted.[1] The reactants and products were purified by appropriate means before use, their purity being tested by g.l.c. Di-t-butyl peroxide (DTBP) (Koch–Light) was purified by repeated trap-to-trap distillation on a vacuum line, middle fractions being retained each time. No impurities were detected by g.l.c.

RESULTS

The principal products obtained from the thermal oxidation of DTBP are acetone, formaldehyde, methanol, and methyl hydroperoxide. Addition of ethylene to a mixture of DTBP and oxygen at 410 K does not alter significantly the rate of formation of the products from the peroxide (Table 1). The only extra product is 1,2-epoxyethane. On addition of 2-methylpropene, the total rate of formation of acetone and formaldehyde increases, while relatively large quantities of 1,2-epoxy-2-methylpropane are also formed. t-Butyl alcohol is also formed on addition of 2-methylpropene (Table 1).

DISCUSSION

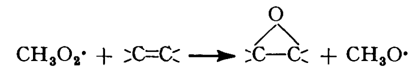
Methylperoxyl radicals are produced from di-t-butyl peroxide [reactions (1)—(3)]. Subsequent reactions of methylperoxyl radicals, under these conditions, are discussed elsewhere,[1,5] and are summarised in Table 2.

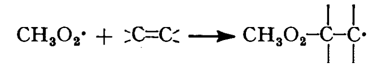
The addition of even large amounts of ethylene to the system does not alter the rate of formation of acetone, showing that reaction (2) is much faster than the rate of addition of t-butoxyl radicals to the alkene. However, the presence of t-butyl alcohol amongst the products on addition of 2-methylpropene shows that the abstraction of allylic hydrogen atoms from 2-methylpropene competes significantly with reaction (2). Further, methoxyl radicals formed during the reaction can also, under the conditions used, undergo both addition and abstraction reactions with alkenes, the rate of the two reactions being approximately equal in solution.[6,7]

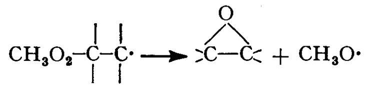
TABLE 2

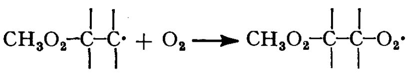
Reactions occurring during the oxidation of di-t-butyl peroxide (refs. 1 and 5)

$\mathrm{DTBP \longrightarrow 2\ (CH_3)_3CO\cdot}$ (1)
$\mathrm{(CH_3)_3CO\cdot + M \longrightarrow \dot{C}H_3 + (CH_3)_2CO + M}$ (2)
$\mathrm{\dot{C}H_3 + O_2 + M \longrightarrow CH_3O_2\cdot + M}$ (3)
$\mathrm{CH_3O_2\cdot + CH_3O_2\cdot \longrightarrow CH_3OH + HCHO + O_2}$ (4a)
$\mathrm{CH_3O_2\cdot + CH_3O_2\cdot \longrightarrow 2\ CH_3O\cdot + O_2}$ (4b)
$\mathrm{CH_3O\cdot + O_2 \longrightarrow HCHO + HO_2\cdot}$ (5)
$\mathrm{2\ CH_3O\cdot \longrightarrow CH_3OH + HCHO}$ (6)
$\mathrm{CH_3O_2\cdot + HO_2\cdot \longrightarrow CH_3O_2H + O_2}$ (7)
$\mathrm{CH_3O_2\cdot + CH_3O\cdot \longrightarrow CH_3O_2H + HCHO}$ (8)
$\mathrm{HO_2\cdot + CH_3O\cdot \longrightarrow CH_3OH + O_2}$ (9)
$\mathrm{CH_3O_2H + CH_3O\cdot \longrightarrow CH_3O_2\cdot + CH_3OH}$ (10)
$\mathrm{CH_3O\cdot + HCHO \longrightarrow \dot{C}HO + CH_3OH}$ (11)
$\mathrm{\dot{C}HO + O_2 \longrightarrow CO + HO_2\cdot}$ (12)
$\mathrm{\dot{C}HO + O_2 \longrightarrow HCO_3\cdot}$ (13)
$\mathrm{CH_3O_2\cdot + HCO_3\cdot \longrightarrow CH_3OH + CO_2 + O_2}$ (14)
$\mathrm{HO_2\cdot + HCO_3\cdot \longrightarrow H_2O + CO_2 + O_2}$ (15)
$\mathrm{CH_3O_2\cdot + HCHO \longrightarrow CH_3O_2H + \dot{C}HO}$ (16)
$\mathrm{(CH_3)_3CO\cdot + HCHO \longrightarrow (CH_3)_3COH + \dot{C}HO}$ (17)


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


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


$\mathrm{CH_3O_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot \longrightarrow {>}\overset{O}{C{-}C}{<} + CH_3O\cdot}$ (18b)


$\mathrm{CH_3O_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot + O_2 \longrightarrow CH_3O_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O_2\cdot}$ (19)

$\mathrm{RO_2\cdot + CH_3CR^1{=}CR^2R^3 \longrightarrow RO_2H + \cdot CH_2CR^1{=}CR^2R^3}$ (20)
$\mathrm{RO\cdot + CH_3CR^1{=}CR^2R^3 \longrightarrow ROH + \cdot CH_2CR^1{=}CR^2R^3}$ (21)
$\mathrm{CH_3O\cdot + CH_3CR^1{=}CR^2R^3 \longrightarrow CH_3OH + \cdot CH_2CR^1{=}CR^2R^3}$ (22)

The proportion of methyl radicals from reaction (2) reacting with alkenes, in the presence of oxygen, using the most recent data,[8] compared with reaction (3) is $<1\%$.

It is immediately noticeable, from the results in Table 1, that the rate of formation of epoxides is much lower than the rate of epoxidation of alkenes by acetylperoxyl radicals.[2-4] In the latter reaction, the alkenes are more or less converted quantitatively into epoxides. As the subsequent discussion evolves, it will be seen that the reactions of methylperoxyl radicals with alkenes play a relatively smaller role in this system.

Just as in the oxidation of alkenes in the gas-phase between 533 and 673 K [9,10] and in the liquid-phase between 323 and 423 K,[11,12] the structure of the carbonyl compounds formed from the alkene $\mathrm{R^1R^2C{=}CR^3R^4}$ on addition to DTBP–oxygen mixtures are $\mathrm{R^1R^2C{=}O}$ and $\mathrm{R^3R^4C{=}O}$. By subtracting the values for the carbonyl compounds obtained in the presence and absence of alkenes (Table 1), it is possible to estimate the amount of formaldehyde formed from ethylene and the amount of acetone and formaldehyde from 2-methylpropene. From these results, it is apparent that, under the conditions of the experiment <0.2 and 3% of the methylperoxyl radicals produced *via* reaction (3) react with ethylene and 2-methylpropene, respectively, to form epoxides.

Epoxides are formed by the addition of the alkylperoxyl radicals to the alkene, followed by ring closure [reactions (18a and b)].[10,13] There is also the possibility that oxygen adds to the adduct radicals [reaction (19)] and the epoxide is formed from the product. The ratio of the rates of reactions (19) and (18b) is given by relationship (B). Rate constants for ring closure of analogous β-peroxyalkyl radicals formed from t-butylperoxyl radicals with ethylene and 2-methylpropene have been determined in the liquid phase;[14] they are $k_{(18b)}$ 2×10^3 and 4×10^4 s^{-1}, respectively at 298 K. Using these data and a value of $A_{(18b)}$ of 3×10^{11} s^{-1},[15] values of $k_{(18b)}$ of 3×10^5 and 3×10^6 for ring closure of the two adduct radicals at 410 K are obtained. $k_{(19)}$ has a maximum value of *ca.* 1×10^9 dm^3 mol^{-1} s^{-1}, corresponding to the generally accepted value for the addition of methyl to oxygen.[16] Ratios of $\mathrm{Rate_{(19)}}/\mathrm{Rate_{(18b)}}$ of *ca.* 0.65 and 0.065 are obtained for ethylene and 2-methylpropene under the conditions of our experiments. Thus ring closure by the adduct radicals leading to epoxides [reaction (18b)] dominates over reaction (19).

$$\frac{\mathrm{Rate_{(19)}}}{\mathrm{Rate_{(18b)}}} = \frac{k_{(19)}\,[\mathrm{O_2}]}{k_{(18b)}} \qquad \text{(B)}$$

This conclusion agrees with the results obtained by Van Sickle *et al.*[11,12] from their studies of the autoxidation of alkenes in solution. Using their data, the percentage of adduct radicals undergoing addition of oxygen varies between 0.8% for 2,3-dimethylbut-2-ene at 323 K, 2.5% for but-2-ene at 333 K, and 3.5% for 2-methylbut-2-ene at 343 K. At higher temperatures, the proportion will decrease further, since the activation energy for the reaction leading to ring closure is higher than that leading to addition of oxygen.

Alkylperoxyl radicals will also undergo allylic hydrogen abstraction reactions with alkenes [reaction (20)]. A value of $k_{(20)}/k_{(18a)} = 0.17$ has been reported for some primary alkylperoxyl radicals reacting with 2-methylpropene in the liquid phase at 343 K.[11] Values of 1.6 and 1.5 have been given for the reaction of t-butylperoxyl radicals, at 393 K, with 2,3-dimethylbut-2-ene and propene, respectively.[17] Even on assuming the maximum values for $k_{(20)}/k_{(18b)}$ for the reactions of methylperoxyl radicals with ethylene and 2-methylpropene at 410 K, estimates show that $<3\%$ of methylperoxyl radicals undergo reaction, by any route, with these alkenes under the conditions of our experiments.

Applications of the steady state treatment to reactions (1)—(22) (Table 2) (for a detailed discussion, see ref. 1) yields equations (C) and (D) where R_E and R_M are the

$$d[(CH_3)_2CO]/dt = R_A = k_{(3)}[\cdot CH_3][O_2][M] \quad (C)$$

$$k_{(3)}[\cdot CH_3][O_2][M] = 2(k_{(4a)} + k_{(4b)})\,[CH_3O_2\cdot]^2 + R_E + R_M \quad (D)$$

rates of formation of the epoxide and methyl hydroperoxide. Thus equation (E) is obtained where $k_{(18)}$ is

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

the overall rate constant for epoxidation. However, since $R_A \gg R_E$ and R_M (Table 1), the terms R_E and R_M were, in effect, neglected in the calculations using relation (E). The ratio of rate constants is $3.7 \pm 2.5 \times 10^{-5}$ and $3.1 \pm 0.5 \times 10^{-4}$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ for ethylene and 2-methylpropene at 410 K. Using a value [18] of $(k_{(4a)} + k_{(4b)})$ of 5×10^8 dm^3 mol^{-1} s^{-1}, values of $k_{(18)} = 1.2 \pm 0.7$ and 9.8 ± 1.6 dm^3 mol^{-1} s^{-1} for ethylene and 2-methylpropene, respectively, are obtained. These values assume that methylperoxyl radicals are solely responsible for the formation of the epoxide.

The only data with which to compare these results are the liquid-phase addition reactions of t-butylperoxyl radicals and two terminal alkenes, propene and hex-1-ene, where values of 0.6 and 0.8 dm^3 mol^{-1} s^{-1} at 383 K were obtained.[17] These are encouragingly similar to the results obtained in the present study.

The value for 2-methylpropene may be compared with the value of 1.38×10^5 dm^3 mol^{-1} s^{-1} for the addition reaction of peracetyl and the alkene at 383 K.[3] The rate constant for the reaction between peracetyl and ethylene has not been obtained but it will be *ca.* 5×10^3 dm^3 mol^{-1} s^{-1} (values for peracetyl addition to propene, but-1-ene, 3-methylbut-1-ene, and hex-1-ene being 6.4×10^3, 1.1×10^4, 1.3×10^4, and 2.2×10^4 dm^3 mol^{-1} s^{-1} at 393 K [4]). The great difference between the rates of addition reaction on alkenes by alkylperoxyl and peracetyl radicals is presumably due to the enchanced electrophilic nature of the peracetyl radicals due to the carbonyl group. The difference can also be noted in the corresponding rates of abstraction reactions by these two radicals,[19] and is of considerable significance in considering the major role played by acetaldehyde formed as a product in the combustion of hydrocarbons.[10,20]

Under the conditions studied, t-butyl alcohol is not detected in the early stage of the oxidation of di-t-butyl peroxide nor is it formed on addition of ethylene. However, significant quantities are formed when 2-methylpropene is present, suggesting that allylic hydrogen-atom abstraction is an important process [reaction (21)]. Unlike the corresponding reactions with methoxyl radicals in solution, where the relative rates of addition and abstraction are equal, the rates of the abstraction reaction are considerably faster for t-butoxyl.[7,21,22] In a subsequent paper we will describe how rate constants for reaction (21) have been determined for several alkenes.

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