Reactions of Oxygenated Radicals in the Gas Phase. Part 4.[1] Reactions of Methylperoxyl and Methoxyl Radicals

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The reactions of methylperoxyl radicals formed during the oxidation of di-t-butyl peroxide have been studied. Particular attention has been paid to the reactions (4a), (4b), and (16). The following rate data have been

$$2CH_3O_2^{\cdot} \longrightarrow CH_3OH + HCHO + O_2 \quad (4a)$$

$$2CH_3O_2^{\cdot} \longrightarrow 2CH_3O^{\cdot} + O_2 \quad (4b)$$

$$CH_3O_2^{\cdot} + HCHO \longrightarrow CH_3O_2H + {}^{\cdot}CHO \quad (30)$$

obtained: $k_{4a}/k_{4b} = 0.69 \pm 0.08$ and $k_{16} = ca.\ 1.2 \times 10^3$ dm^3 mol^{-1} s^{-1} at 410 K. From these results and from those of previous work, $E_{4b} - E_{4a} = 9 \pm 1$ kJ mol^{-1}. Further, the oxidation of methoxyl radicals plays an important role in the overall reaction (5).

$$CH_3O^{\cdot} + O_2 \longrightarrow HCHO + HO_2^{\cdot} \quad (5)$$

THE reactions of methyl radicals with oxygen in the gas phase have been studied extensively.[2-6] At temperatures below 500 K, many of these studies have been concerned with the determination of accurate rate data for reaction (A).

$$CH_3^{\cdot} + O_2 (+M) \longrightarrow CH_3O_2^{\cdot} (+M) \quad (A)$$

The present work is being undertaken for two reasons. The first aim is to clarify some of the aspects of the subsequent reactions of methylperoxyl radicals, for there is uncertainty about their nature, particularly in the range 373—500 K, the region for slow combustion. Secondly, we wish to use this system to generate methylperoxyl radicals and to investigate their reactions with alkanes and alkenes, an important propagation reaction in the slow oxidation of these hydrocarbons.

In the present studies, methyl radicals were generated by thermolysis of di-t-butyl peroxide (DTBP).[7]

EXPERIMENTAL

The apparatus has been described and a similar analytical method adopted,[8] in particular the method by which peroxides are determined by g.l.c.–mass spectrometry.[9] Methyl hydroperoxide was determined iodometrically.[10]

The reactants and products were purified by appropriate means before use, their purity being tested by g.l.c. Di-t-butyl peroxide (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 of the decomposition of di-t-butyl peroxide, in the presence of oxygen, at 410 K are acetone, formaldehyde, methanol, methyl hydroperoxide, carbon monoxide, and carbon dioxide. Traces of hydrogen peroxide were observed at high oxygen concentrations. Methane and ethane were absent in all experiments (Figures 1 and 2).

Detailed analyses were performed to follow rates of formation of products, up to a conversion of 1.7% of the initial concentration of di-t-butyl peroxide, with a variation of the ratio of DTBP to oxygen from 1 : 0.1 to 1 : 14 (Table 1). On increasing the oxygen concentration, the rate of formation of acetone remains constant, that of formaldehyde and methyl hydroperoxide increases, while that of methanol, carbon dioxide, and carbon monoxide decreases. Formaldehyde is always present in greater concentration than methyl hydroperoxide, and carbon monoxide is formed in greater concentration than carbon dioxide.

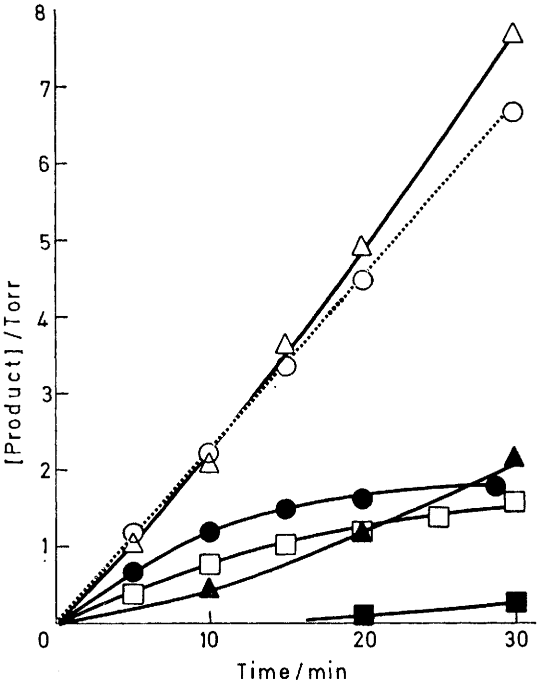

FIGURE 1 Oxidation of di-t-butyl peroxide (DTBP) at 410 K. Initial pressures: DTBP, 70 Torr; oxygen, 20 Torr; argon, 410 Torr. ○, acetone (×½); ■, carbon dioxide; ▲, carbon monoxide; ●, formaldehyde; △, methanol; □, methyl hydroperoxide

Addition of acetone to the DTBP–oxygen system results in a small increase in the rate of formation of methanol, accompanied by a decrease in that of formaldehyde. The rate of formation of methyl hydroperoxide remains constant (Table 2).

Addition of formaldehyde to the system increases the rate of formation of methyl hydroperoxide and, to a small

TABLE 1

Oxidation of di-t-butyl peroxide (DTBP) at 410 K; yields of products after 300 s reaction time. Initial pressure of DTBP, 50 Torr

$P(O_2)$/ Torr	(A) $P[(CH_3)_2CO]$/ Torr	(B) $P(HCHO)$/ Torr	(C) $P(CH_3OH)$/ Torr	(D) $P(CH_3O_2H)$/ Torr	(E) $P(CO)$/ Torr	2(E)/(A)	(B)/[(C) + (D)]	[(B) + (C) + (D) + (E)]/(A)
5.0	1.60	0.45	0.84	0.21	0.20	0.56	0.43	1.06
10.0	1.60	0.50	0.65	0.23	0.13	0.63	0.57	0.91
20.0	1.55	0.62	0.45	0.28	0.11	0.79	0.85	0.92
35.0	1.65	0.71	0.36	0.30	—	0.86	1.08	0.83
50.0	1.65	0.74	0.34	0.37	—	0.90	1.03	0.88
75.0	1.60	0.80	0.25	0.43	—	1.00	1.22	0.91
100.0	1.65	0.81	0.24	0.44	—	0.98	1.20	0.90
150.0	1.60	0.81	0.23	0.49	—	1.01	1.12	0.96
200.0	1.60	0.81	0.22	0.64	—	1.01	0.95	1.04
300.0	1.65	0.81	0.20	0.66	—	0.98	0.95	1.01
430.0	1.60	0.82	0.18	0.65	—	1.03	0.98	1.03
550.0	1.65	0.81	0.18	0.75	—	0.98	0.87	1.05
655.0	1.65	0.82	0.16	0.66	—	0.99	0.99	0.98
700.0	1.65	0.81	0.20	0.75	—	0.98	0.85	1.09

extent, that of methanol. t-Butyl alcohol is also observed; its rate of formation increases with formaldehyde concentration and is accompanied by a decrease in the rate of acetone formation (Table 3).

TABLE 2

Oxidation of DTBP at 410 K; yields of products after 600 s reaction time on addition of acetone. Initial pressures: DTBP, 50 Torr; oxygen, 5 Torr; argon, 445 Torr

$P[(CH_3)_2CO]$/ Torr	$P(CH_3OH)$/ Torr	$P(HCHO)$/ Torr	$P(CH_3O_2H)$/ Torr
—	1.72	0.89	0.38
50	2.01	0.80	0.42
80	2.64	0.74	0.40

DISCUSSION

The rate of formation of acetone, and thus methyl radicals, is essentially independent of the concentration of oxygen [reactions (1) and (2)]. k_1 was determined from

$$(CH_3)_3CO{\cdot}OC(CH_3)_3 \longrightarrow 2(CH_3)_3CO^{\cdot} \qquad (1)$$

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

22 experiments (in the presence of oxygen) as $5.30 \pm 0.04 \times 10^{-5}\ s^{-1}$ at 410 K based on the rate of formation of acetone. This compares with values obtained from previously determined rate data for the reaction in the absence of oxygen of $4.70 \times 10^{-5}\ s^{-1}$ (ref. 11) and $4.53 \times 10^{-5}\ s^{-1}$ (ref. 12).

Overwhelmingly the most important reaction of methyl radicals, under the conditions of this study, is that of addition to oxygen [reaction (3)]. The reaction

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

leading to formaldehyde and hydroxyl radicals is of insignificant importance.[5,13]

The termination reactions of alkylperoxyl radicals in solution yield molecular products [reaction (4a)]. However, under the conditions of our experiments, a striking

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

feature is the marked dependence of the relative rates of formation of methanol and formaldehyde on the initial concentration of oxygen. This has not been noted by earlier workers[7] but is of great importance to the interpretation of the results. For example, the methanol yield expressed as a fraction of acetone yield decreases from 0.57 to 0.13 and the relative yields of methanol and formaldehyde change from 1.9 to 0.25 on altering the DTBP : oxygen ratio from 10 : 1 to 1 : 4. The results suggest that an alternative pathway for the reaction of methylperoxyl radicals is crucial to our understanding

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

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

of the mechanism. Thus an alternative route for methylperoxyl radicals is reaction (4b). Reaction (5)

TABLE 3

Oxidation of DTBP at 410 K; yields of products after 600 s reaction time on addition of formaldehyde. Initial pressures: DTBP, 50 Torr; oxygen, 20 Torr; argon, 430 Torr

$P(HCHO)$/ Torr	$P[(CH_3)_2CO]$/ Torr	$P[(CH_3)_3COH]$/ Torr	$P(CH_3OH)$/ Torr	$P(H_2O_2)$/ Torr	$P(CH_3O_2H)$/ Torr
—	3.14	*a*	1.25	<0.1	0.45
—	3.34	*a*	1.31	<0.1	0.50
—	3.42	*a*	1.25	<0.1	0.54
20	2.95	0.27	1.55	<0.1	0.62
30	2.81	*a*	1.48	<0.1	0.75
50	2.80	0.55	1.42	0.22	0.80
50	2.85	*a*	1.46	*a*	0.82
80	2.73	0.62	1.40	0.28	0.89
80	2.79	0.66	1.47	0.26	0.91
100	2.60	*a*	1.30	0.30	0.93
120	2.57	*a*	1.30	0.30	0.95
120	2.54	*a*	1.26	*a*	0.91

[a] Analyses not performed.

competes with the self-reaction (6) or other radical–radical reactions involving methoxyl radicals

$$2CH_3O^{\bullet} \longrightarrow CH_3OH + HCHO \qquad (6)$$

Using accepted data for the standard enthalpies of formation at 298 K for $CH_3O^{\bullet}$, HCHO, and $HO_2^{\bullet}$ of 8.4,[14] −115.8,[15] and 21.0[16] kJ mol^{-1}, the standard enthalpy of reaction (5) is −103.2 kJ mol^{-1}. Recent estimates for k_5 are 2×10^6 dm^3 mol^{-1} s^{-1} at 410 K[17] and 1.2×10^6 dm^3 mol^{-1} s^{-1} at 373 K.[18] In simulating the reaction, we use the former value.[19] Similar reactions for ethoxyl,[20] propoxyl,[21] and isopropoxyl[22-24] have been shown to be important in hydrocarbon oxidation in general, affording a route by which alkoxyl radicals are replaced by relatively inactive hydroperoxyl radicals.

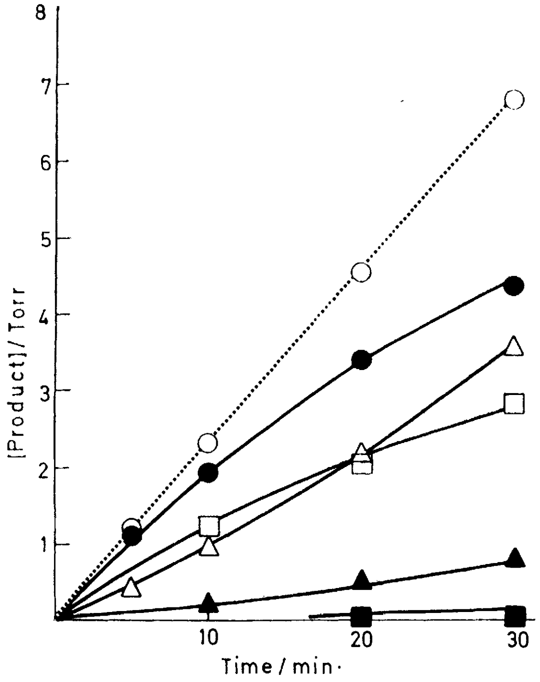

FIGURE 2 Oxidation of DTBP at 410 K. Initial pressures: DTBP, 70 Torr; oxygen, 200 Torr; argon, 230 Torr. For key, see legend to Figure 1

Methyl hydroperoxide is the only product where the methylperoxyl radical retains its identity. The problems encountered in the past in the handling and analysis of the compound, since it undergoes rapid heterogeneous decomposition in contact with metal surfaces,[25,26] were overcome by using an all-glass sampling system. Homogeneous decomposition of the product is unimportant at 410 K.[27] It has been proposed that it is formed from methylperoxyl radicals by abstraction reactions at higher temperatures with acetone,[28] and, under conditions used in our study, with formaldehyde.[7] Such reactions are slow at 410 K and, indeed, addition of acetone to the DTBP–oxygen system had no effect, while addition of formaldehyde had but a marginal effect, on the rate of formation of methyl hydroperoxide. These results, coupled with the strong effect of increasing the pressure of oxygen on the rate of formation of the hydroperoxide, suggest that it is formed by reactions (5) and (7). Reactions (8) and (9) will no doubt play a part at very low oxygen concentrations. In oxygen-rich mixtures, the yield of methyl hydroperoxide accounts for 37% of methylperoxyl radicals. In a study of the photo-oxidation of azomethane at 298 K, it was found that the yield of the hydroperoxide also increased on increasing the oxygen pressure and that 30% of methylperoxyl radicals formed methyl hydroperoxide.[29] In this study, the ratio of yields of the hydroperoxide to those of methanol also increases with oxygen pressure, at variance with an earlier report.[30] One can therefore envisage two distinct routes for the reactions of methylperoxyl radicals. They may react either *via* reactions (4a) or *via* (4b) and (6) to yield equimolar quantities of methanol and formaldehyde. Alternatively, the radicals react *via* reactions (4b), (5), and (7) to yield equimolar quantities of methyl hydroperoxide and formaldehyde. This agrees with the results in Table 1.

$$CH_3O_2^{\bullet} + HO_2^{\bullet} \longrightarrow CH_3O_2H + O_2 \qquad (7)$$

$$CH_3O_2^{\bullet} + CH_3O^{\bullet} \longrightarrow CH_3O_2H + HCHO \qquad (8)$$

$$HO_2^{\bullet} + CH_3O^{\bullet} \longrightarrow CH_3OH + O_2 \qquad (9)$$

It is significant that the concentration of methyl hydroperoxide levels off with time, while the concentrations of acetone and methanol are still increasing. This suggests that the hydroperoxide is itself being attacked by radicals, *e.g.* reaction (10). Analogous reactions have been proposed for the t-butyl–oxygen[31] and isopropyl–oxygen[32] systems.

$$CH_3O_2H + CH_3O^{\bullet} \longrightarrow CH_3O_2^{\bullet} + CH_3OH \qquad (10)$$

The concentration of carbon monoxide increases with time whereas the rate of formation of formaldehyde decreases (Figures 1 and 2), consistent with radical attack on the aldehyde,[33,34] *e.g.* reactions (11) and (12).

$$CH_3O^{\bullet} + CH_2O \longrightarrow CH_3OH + {}^{\bullet}CHO \qquad (11)$$

$${}^{\bullet}CHO + O_2 \longrightarrow CO + HO_2^{\bullet} \qquad (12)$$

Carbon dioxide, produced in smaller amounts than carbon monoxide, may be formed by reactions (13)—(15).

$${}^{\bullet}CHO + O_2 \longrightarrow HCO_3^{\bullet} \qquad (13)$$

$$CH_3O_2^{\bullet} + HCO_3^{\bullet} \longrightarrow CH_3OH + CO_2 + O_2 \qquad (14)$$

$$HO_2^{\bullet} + HCO_3^{\bullet} \longrightarrow H_2O + CO_2 + O_2 \qquad (15)$$

Assuming $k_{11} : k_5 = 10—20 : 1$ by analogy with similar reactions involving acetaldehyde,[35] reactions (1)—(10) can be considered to constitute the reaction scheme, when the DTBP to oxygen ratio is below 1.3 : 1. Indeed, this is supported by analysis, since below this ratio the formation of carbon oxides is unimportant.

Under these conditions, the rates of formation of the main products are given by equations (i)—(v). The experimental results are found to satisfy relation (v) except at low concentrations of oxygen, where methoxyl radicals react with formaldehyde [reaction (11)].

$$\mathrm{d}[(\mathrm{CH_3})_2\mathrm{CO}]/\mathrm{d}t = 2k_1[\mathrm{DTBP}] \qquad \text{(i)}$$

$$\mathrm{d}[\mathrm{HCHO}]/\mathrm{d}t = k_{4a}[\mathrm{CH_3O_2^{\bullet}}]^2 + k_6[\mathrm{CH_3O^{\bullet}}]^2 + k_5[\mathrm{CH_3O^{\bullet}}][\mathrm{O_2}] + k_8[\mathrm{CH_3O_2^{\bullet}}][\mathrm{CH_3O^{\bullet}}] \qquad \text{(ii)}$$

$$\mathrm{d}[\mathrm{CH_3OH}]/\mathrm{d}t = k_{4a}[\mathrm{CH_3O_2^{\bullet}}]^2 + k_6[\mathrm{CH_3O^{\bullet}}]^2 + k_9[\mathrm{CH_3O^{\bullet}}][\mathrm{HO_2^{\bullet}}] + k_{10}[\mathrm{CH_3O^{\bullet}}][\mathrm{CH_3O_2H}] \qquad \text{(iii)}$$

$$\mathrm{d}[\mathrm{CH_3O_2H}]/\mathrm{d}t = k_7[\mathrm{CH_3O_2^{\bullet}}][\mathrm{HO_2^{\bullet}}] + k_8[\mathrm{CH_3O_2^{\bullet}}][\mathrm{CH_3O^{\bullet}}] - k_{10}[\mathrm{CH_3O^{\bullet}}][\mathrm{CH_3O_2H}] \qquad \text{(iv)}$$

$$\mathrm{d}[\mathrm{HCHO}]/\mathrm{d}t = \tfrac{1}{2}\mathrm{d}[(\mathrm{CH_3})_2\mathrm{CO}]/\mathrm{d}t = \mathrm{d}[\mathrm{CH_3OH}]/\mathrm{d}t + \mathrm{d}[\mathrm{CH_3O_2H}]/\mathrm{d}t \qquad \text{(v)}$$

The results show clearly that reaction (4a) is important, for otherwise the yield of methanol would approach zero, and that the rate of formation of the hydroperoxide would tend to equal that of formaldehyde at high initial pressures of oxygen. It is possible to place an upper limit on the ratio of k_{4a} to k_{4b}, for at high oxygen concentrations relation (iii) becomes relation (vi). It

$$\mathrm{d}[\mathrm{CH_3OH}]/\mathrm{d}t = k_{4a}[\mathrm{CH_3O_2^{\bullet}}]^2 \qquad \text{(vi)}$$

can be calculated that the other reactions leading to methanol account for *ca.* 1% of its concentration. This leads to

$$k_3[^{\bullet}\mathrm{CH_3}][\mathrm{O_2}][\mathrm{M}] = 2(k_{4a} + k_{4b})[\mathrm{CH_3O_2^{\bullet}}]^2 + k_7[\mathrm{CH_3O_2^{\bullet}}][\mathrm{HO_2^{\bullet}}] \qquad \text{(vii)}$$

$$\mathrm{d}[(\mathrm{CH_3})_2\mathrm{CO}]/\mathrm{d}t = 3(k_{4a} + k_{4b})[\mathrm{CH_3O_2^{\bullet}}]^2 + \mathrm{d}[\mathrm{CH_3O_2H}]/\mathrm{d}t \qquad \text{(viii)}$$

$$\frac{k_{4a}}{k_{4a} + k_{4b}} = \frac{2\mathrm{d}[\mathrm{CH_3OH}]/\mathrm{d}t}{\mathrm{d}[(\mathrm{CH_3})_2\mathrm{CO}]/\mathrm{d}t - \mathrm{d}[\mathrm{CH_3O_2H}]/\mathrm{d}t} \qquad \text{(ix)}$$

relation (ix). At high oxygen pressures, the value of $k_{4a}/(k_{4a} + k_{4b})$ tends to 0.41 ± 0.04 and thus $k_{4a}/k_{4b} = 0.69 \pm 0.08$.

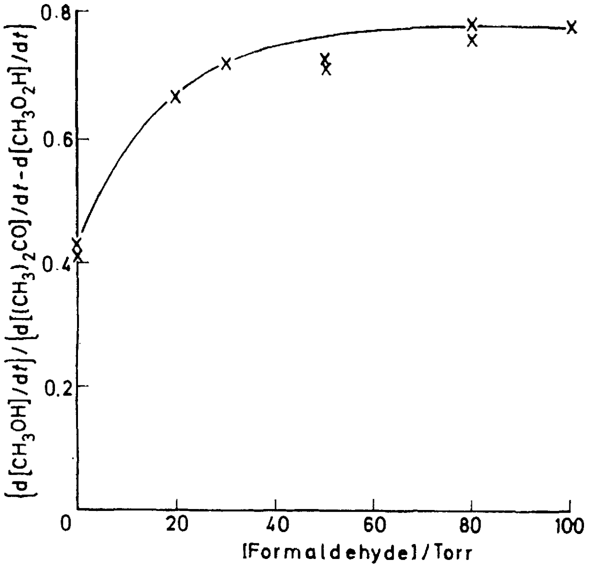

FIGURE 3 Oxidation of DTBP at 410 K. Influence of addition of formaldehyde. Initial pressures: DTBP, 50 Torr; oxygen, 20 Torr. Total pressure (with argon), 500 Torr

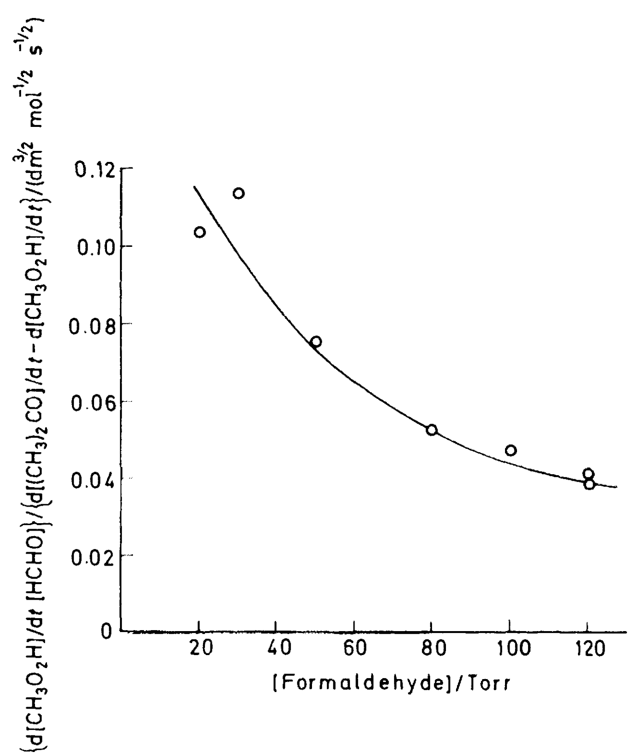

FIGURE 4 Oxidation of DTBP at 410 K. Influence of addition of formaldehyde. Initial pressures: DTBP, 50 Torr; oxygen, 20 Torr. Total pressure (with argon), 500 Torr

A way of checking the value of k_{4a}/k_{4b}) is by considering the effect of formaldehyde on the rates of formation of products (Table 3). Accepting that $k_{11} : k_5 = ca.\ 10\text{—}20 : 1$, then, under the conditions of the experiments, reaction (16) will become the dominant source of methyl hydroperoxide. Relations (x) and (xi)

$$\mathrm{CH_3O_2^{\bullet}} + \mathrm{HCHO} \longrightarrow \mathrm{CH_3O_2H} + {}^{\bullet}\mathrm{CHO} \qquad (16)$$

$$\mathrm{d}[(\mathrm{CH_3})_2\mathrm{CO}]/\mathrm{d}t - \mathrm{d}[\mathrm{CH_3O_2H}]/\mathrm{d}t = 2(k_{4a} + k_{4b})[\mathrm{CH_3O_2^{\bullet}}]^2 \qquad \text{(x)}$$

$$\mathrm{d}[\mathrm{CH_3OH}]/\mathrm{d}t = (k_{4a} + 2k_{4b})[\mathrm{CH_3O_2^{\bullet}}]^2 \qquad \text{(xi)}$$

$$\frac{\mathrm{d}[\mathrm{CH_3OH}]/\mathrm{d}t}{\mathrm{d}[(\mathrm{CH_3})_2\mathrm{CO}]/\mathrm{d}t - \mathrm{d}[\mathrm{CH_3O_2H}]/\mathrm{d}t} = c = \frac{k_{4a} + 2k_{4b}}{2(k_{4a} + k_{4b})} \qquad \text{(xii)}$$

lead to relation (xii). A plot of c against the initial pressure of formaldehyde (Figure 3) approaches a maximum as reaction (5) becomes less important, and tends to a value of 0.77 ± 0.03. $k_{4a}/k_{4b} = 2(c - 1)/(1 - 2c)$, and thus $k_{4a}/k_{4b} = 0.85 \pm 0.14$, which may be compared with the value estimated above. These values compare with 2.0 at 295 K from a direct kinetic spectroscopic determination,[31] and a value of 1.0 at 373 K which was used in a simulation procedure to explain results of a study of reactions between methylperoxyl radicals and 2,3-dimethylbutane.[18] The difference in activation energy ($E_{4b} - E_{4a}$) is thus estimated to be 8—10 kJ mol^{-1}.

The rate of formation of acetone from DTBP is reduced on addition of formaldehyde (Table 3), presumably because the resulting t-butoxyl radical reacts with formaldehyde as in reaction (17), as well as *via* reaction (2).

$$(CH_3)_3CO^\bullet + HCHO \longrightarrow (CH_3)_3COH + {}^\bullet CHO \quad (17)$$

The rate of formation of methyl hydroperoxide also increases. If, at high concentrations of formaldehyde, reaction (16) is the dominant reaction in the formation of the hydroperoxide, relations (xiii) and (viii) may be written. Thus, from Figure 4, $k_{16}/[2(k_{4a} + k_{4b})]^{1/2}$ is

$$CH_3O_2^\bullet + HCHO \longrightarrow CH_3O_2H + {}^\bullet CHO \quad (16)$$

$$d[CH_3O_2H]/dt = k_{30}[CH_3O_2^\bullet][HCHO] \quad (xiii)$$

$$d[(CH_3)_2CO]/dt - d[CH_3O_2H]/dt = 2(k_{4a} + k_{4b})[CH_3O_2^\bullet]^2 \quad (viii)$$

3.8×10^{-2} dm$^{3/2}$ mol$^{-1/2}$ s$^{-1/2}$ when the function is a minimum, *i.e.* when the formaldehyde pressure is greatest. With $k_{4b} = 2 \times 10^8$ dm^3 mol^{-1} s^{-1} (ref. 31) and thus $k_{4b} = 3 \times 10^8$ dm^3 mol^{-1} s^{-1}, $k_{16} = ca.\ 1.2 \times 10^3$ dm^3 mol^{-1} s^{-1} at 410 K. Interestingly, given $\log_{10}(A_{16}/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 9.3$,[36] $E_{16} = 49$ kJ mol^{-1}, which may be compared with values of 43.5 (ref. 37) and 48.8 (ref. 36) kJ mol^{-1} obtained for the corresponding reaction for hydroperoxyl radicals.

In a subsequent paper, we shall use this reaction scheme and the suggested rate constants to model the reaction under a wide range of conditions and then to superimpose upon it additional reactions in which hydrocarbons are added to investigate reactions between them and methylperoxyl radicals.[19]

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