Reactions of Oxygenated Radicals in the Gas Phase. Part 14.[1] Reactions of t-Butylperoxyl Radicals

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The photo-oxidation of *trans*-2,2′-azoisobutane has been studied between 313 and 393 K. The principal products are acetone, t-butyl alcohol, t-butyl hydroperoxide, and formaldehyde. The yields of hydroperoxide and formaldehyde come to a limiting value during photolysis. Detailed analyses of products were carried out at different temperatures and total pressures. Further experiments were performed in which t-butyl hydroperoxide was added. The reaction was simulated over this wide range of conditions. The importance of reactions between the various alkylperoxyl radicals is emphasised.

We have been examining in detail the reactions of alkylperoxyl radicals in the gas phase, as they play an important role in the combustion of hydrocarbons and in reactions occurring in the atmosphere. In particular, the self-reactions involving primary (ethylperoxyl[2]) and secondary (isopropylperoxyl[3–5]) peroxyl radicals have been studied. Although the rates of self-reaction of the secondary alkylperoxyl radicals is several orders of magnitude less than that of the primary, the chemistry of the reactions is similar. The self-reaction goes *via* two main routes, one being a termination and the other a propagation reaction. Their relative magnitudes are temperature dependent.

$$2\,RO_2\cdot \longrightarrow \text{alcohol} + \text{carbonyl} + O_2 \qquad \text{(a)}$$

$$2\,RO_2\cdot \longrightarrow 2\,RO\cdot + O_2 \qquad \text{(b)}$$

In contrast, only route (b) is available for the self-reaction of t-butylperoxyl radicals. Arrhenius parameters for this reaction have been obtained by flash photolysis[6] and molecular modulation spectroscopy[7] studies. More recently, Kirsch and Parks have reported product studies (between 298 and 373 K).[8] We were carrying out a similar product study and found some significant differences, which we report in this paper.

Further, we have tested the mechanism with a range of experiments in which the reactant concentrations have been altered and additives introduced into the reaction system.

Experimental

A cylindrical Pyrex reaction vessel (length 15 cm, diameter 4.4 cm, surface area: volume ratio $1.1:1\ \mathrm{cm}^{-1}$) was immersed in an aluminium block, which was electrically heated. The temperature, measured by a thermocouple which could be moved down the length of the metal block, was kept to within ± 0.5 °C, using a Sirect temperature controller. Photolysis was carried out with a 200 W high-pressure u.v. mercury lamp (Wotan HBO 200W/4). Teflon taps were used on all gas lines leading to the reaction vessel and to the sampling and analytical systems.

trans-2,2′-Azoisobutane was prepared from t-butylamine *via NN′*-di-t-butylsulphamide by the method described by Stowell.[9] The final purification involved distillation at atmospheric pressure (b.p. 381—383 K) and under reduced pressure (b.p. 313—315 K at 55 mmHg).

t-Butyl hydroperoxide, obtained commercially (Koch–Light Laboratories), was purified by preparative g.c., using a column of Gas Chrom Q with a liquid phase of 20% (w/w) Apiezon L and 12% (w/w) dinonyl phthalate. The purity of the material determined by g.c. using f.i.d. and katharometer detectors was >99%.

Di-t-butyl peroxide, obtained commercially (Koch–Light Laboratories), was purified by passage through activated alumina and by preparative g.c. using a column of Gas Chrom Q with a liquid phase of 10% (w/w) bis-(2-ethylhexyl) sebacate.

Formaldehyde was determined colorimetrically using chromotropic acid;[10] other products and 2,2′-azoisobutane were determined by g.c. and analysed on a column of Gas Chrom Q with a liquid phase of 10% (w/w) dinonyl phthalate (for 2,2′-azoisobutane and oxygenated products) and a column of silica gel (for hydrocarbons). The identities of the products were confirmed by mass spectrometry (Kratos MS 3074).

The concentrations of reactants and products were determined *via* prior calibration in which known amounts were allowed into the reaction vessel under identical conditions of the experiments. Formaldehyde was prepared by gently heating paraformaldehyde. Minute traces of a dimer and trimer of formaldehyde were found but do not interfere with the analysis.

Results

(a) *Thermolysis and Photolysis of* trans-*2,2′-Azoisobutane between* 343 *and* 453 K.—In the absence of oxygen *trans*-2,2′-azoisobutane on thermolysis at 453 K yielded 2-methylpropane, 2-methylpropene, and 2,2,3,3-tetramethylbutane. The yields of 2-methylpropane and 2-methylpropene were equal and exceeded that of 2,2,3,3-tetramethylbutane (Table 1). Using product yields the thermal decomposition was found to obey first-order kinetics with a rate constant of $4.66 \pm 0.23 \times 10^{-5}\ \mathrm{s}^{-1}$. This compares favourably with the value of $5.4 \times 10^{-5}\ \mathrm{s}^{-1}$ calculated from Arrhenius parameters reported earlier by McKay *et al.*[11]

Table 1. Photolysis and thermolysis of *trans*-2,2′-azoisobutane (t-AIB)

p(t-AIB)/Torr	*p*(Nitrogen)/Torr	Technique	*T*/K	[2-MPane]/[TMB]	[2-MPene]/[TMB]
5	195	Photolysis	343	2.73 ± 0.14 (6)	2.70 ± 0.16 (6)
5	195	Photolysis	393	2.67 ± 0.15 (9)	2.58 ± 0.14 (9)
5	195	Thermolysis	453	2.64 ± 0.15 (11)	2.56 ± 0.15 (11)

( ) = number of observations, 2-MPane = 2-methylpropane, 2-MPene = 2-methylpropene, TMB = 2,2,3,3-tetramethylbutane.

Table 2. Photolysis of 2,2′-azoisobutane at 393 K: p(t-AIB) 5 Torr, photolysis for 30 min

p(Nitrogen)/Torr	p(2-Methylpropane)/Torr	p(2,2,3,3-Tetramethylbutane)/Torr	[2-MPane]/[TMB]
25	0.50	0.19	2.63
50	0.46	0.17	2.71
75	0.45	0.17	2.65
100	0.43	0.17	2.53
150	0.42	0.16	2.63
200	0.42	0.16	2.63
300	0.39	0.16	2.44
400	0.40	0.16	2.50
500	0.39	0.15	2.60

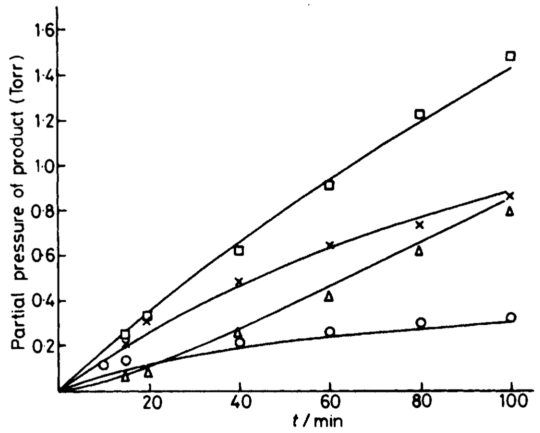

Figure 1. Photo-oxidation of *trans*-2,2′-azoisobutane at 343 K. *trans*-2,2′-Azoisobutane, 5 Torr; oxygen, 20 Torr; nitrogen, 175 Torr. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde. The lines are computed results

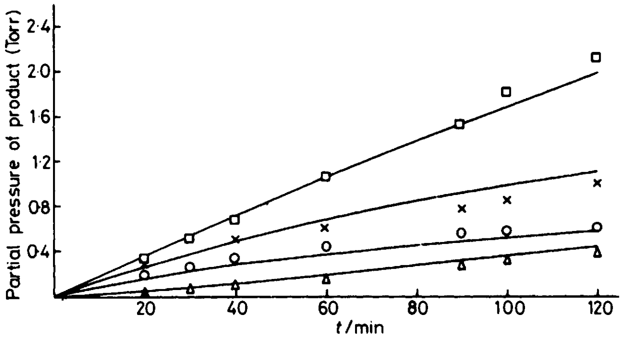

Figure 2. Photo-oxidation of *trans*-2,2′-azoisobutane at 393 K. *trans*-2,2′-Azoisobutane, 5 Torr; oxygen, 20 Torr; nitrogen, 175 Torr. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde. The lines are computed results

Mixtures of *trans*-2,2′-azoisobutane and nitrogen were photolysed at 343 and 393 K (Table 1). Variation of the nitrogen pressure had little effect on the relative yields of products although their rate of formation was lowered as the nitrogen pressure was increased (Table 2).

(b) *Photolysis of* trans-2,2′-*Azoisobutane in the Presence of Oxygen between* 313 *and* 393 K.—The principal products of the photolysis of *trans*-2,2′-azoisobutane were acetone, t-butyl alcohol, t-butyl hydroperoxide, and formaldehyde. At very long photolysis times (>4 h) at 393 K, small amounts of carbon monoxide and methanol were detectable, but carbon dioxide and hydrocarbons were never detected. Nor was di-t-butyl peroxide observed amongst the products (Figures 1—3).

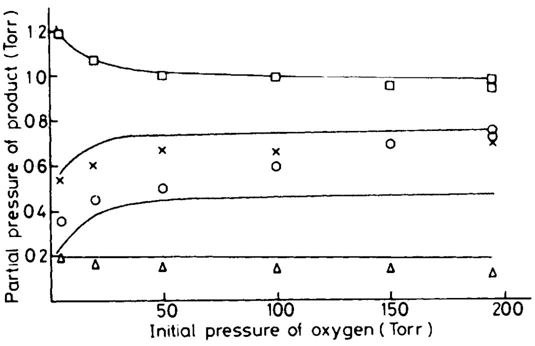

Figure 3. Photo-oxidation of *trans*-2,2′-azoisobutane at 393 K: effect of oxygen on the yields of products. *trans*-2,2′-Azoisobutane, 5 Torr; nitrogen and oxygen added to a total pressure of 200 Torr. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde. The lines are computed results

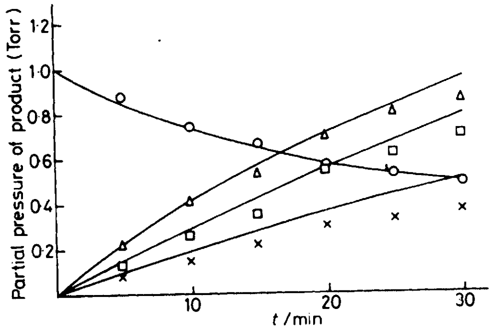

Figure 4. Photo-oxidation of *trans*-2,2′-azoisobutane at 343 K: effect of t-butyl hydroperoxide on the yields of products. *trans*-2,2′-Azoisobutane, 5 Torr; t-butyl hydroperoxide, 1 Torr; oxygen, 20 Torr; nitrogen, 174 Torr. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde. The lines are computed results

The yields of acetone and t-butyl alcohol increased linearly with photolysis times, the yields of acetone always exceeding those of the alcohol. The ratio of the yields of ketone to alcohol increased with increasing temperature.

Initially the concentration of formaldehyde increased with photolysis time; however, at longer times, a 'tailing-off' was observed.

The yields of t-butyl hydroperoxide increased with photolysis time until a limiting value was reached. The magnitude of this value was temperature dependent.

A series of experiments was performed in which t-butyl hydroperoxide was added to the reactant mixtures. Its presence affected the product distribution but not the nature of the products (examples are given in Figures 4 and 5). The yield of acetone was decreased at 313 K but increased at 393 K; the yield of alcohol was increased significantly at all temperatures while that of formaldehyde decreased slightly. In separate control experiments, it was shown that the hydroperoxide is not subject to photochemical decomposition under these conditions.

A further series of experiments was carried out in which the initial nitrogen pressure was varied. The product yields

Table 3. Photo-oxidation of *trans*-2,2'-azoisobutane: *p*(t-AIB) 5 Torr; total pressure (with nitrogen) 200 Torr

				Product yields (Torr)		
T/K	Photolysis time (min)	Initial oxygen pressure (Torr)	Acetone	t-Butyl alcohol	t-Butyl hydroperoxide	Formaldehyde
313	80	5	0.87	0.89	0.09	0.52
			(1.02)	(1.00)	(0.10)	(0.58)
		20	0.88	0.97	0.09	0.52
			(1.01)	(1.00)	(0.11)	(0.58)
		195	0.86	0.91	0.10	0.53
			(1.00)	(1.01)	(0.11)	(0.59)
393	60	5	1.19	0.19	0.36	0.54
		20	1.07	0.16	0.45	0.61
		50	1.00	0.15	0.50	0.67
		100	0.99	0.14	0.60	0.66
		150	0.95	0.14	0.69	....
		195	0.98	0.12	0.76	0.70
		195	0.94	0.13	0.73	....

.... Experiment not performed. ( ) Simulated values.

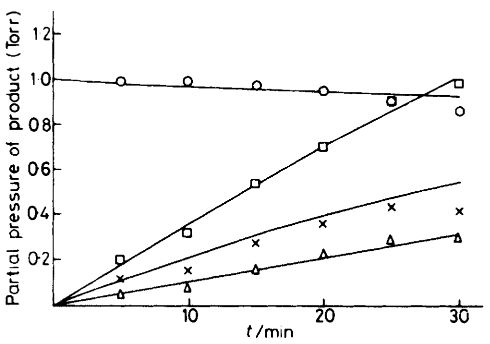

Figure 5. Photo-oxidation of *trans*-2,2'-azoisobutane at 393 K: effect of t-butyl hydroperoxide on the yields of products. *trans*-2,2'-Azoisobutane, 5 Torr; t-butyl hydroperoxide, 1 Torr; oxygen, 20 Torr; nitrogen, 174 Torr. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde. The lines are computed results

decreased on increasing the pressure of nitrogen but all the products showed the same dependency (Figures 6 and 7).

Finally, the effect of oxygen on yield of products was studied at 313 and 393 K, the extremes of the temperature range (Table 3). At 313 K, changing the oxygen pressure is of negligible importance. At 393 K, however, there was a decrease in the yield of acetone and t-butyl alcohol as the oxygen pressure was increased, while the yields of t-butyl hydroperoxide and formaldehyde increased.

Discussion

(a) *Photolysis and Thermolysis of 2,2'-Azoisobutane.*—A simple model can be used to explain the reactions occurring on photolysis or thermolysis of *trans*-2,2'-azoisobutane:

$$\text{t-}C_4H_9\text{-N=N-t-}C_4H_9 \longrightarrow 2\text{t-}C_4H_9\cdot + N_2 \qquad (1)$$

$$2\text{t-}C_4H_9\cdot \longrightarrow C_4H_{10} + C_4H_8 \qquad (d)$$

$$2\text{t-}C_4H_9\cdot \longrightarrow C_8H_{18} \qquad (c)$$

The ratio of k_d/k_c (Tables 1 and 2) agrees closely with that reported by Parkes and Quinn,[12] of 2.8 ± 0.2 obtained at room temperature, and by McKay *et al.*[11] of 2.60 ± 0.04 between 483 and 515 K. These recent studies report higher values than those

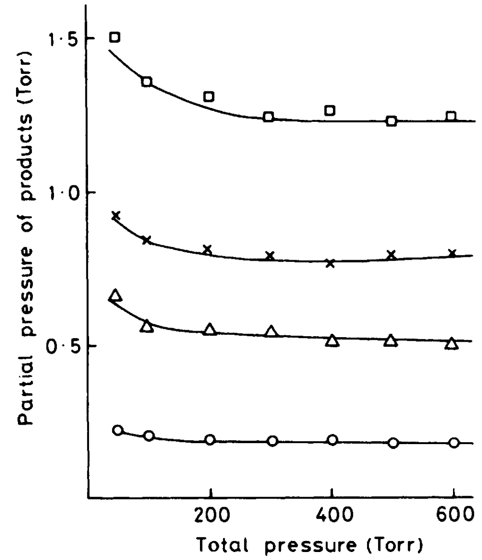

Figure 6. Photo-oxidation of *trans*-2,2'-azoisobutane at 343 K: effect of total pressure on the yields of products. *trans*-2,2'-Azoisobutane, 5 Torr; oxygen, 20 Torr; nitrogen added. Time, 60 min. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde

obtained by James and Suart[13] (2.3 ± 0.3; 297—400 K) and Terry and Futrell[14] (2.32 ± 0.05; room temperature).

The ratios obtained from k_d/k_c are independent of the nature of the decomposition of *trans*-2,2'-azoisobutane, be it thermal or photochemical, suggesting that formation of products in either system involves t-butyl radicals of comparable energy.

Although the product yields on photolysis are dependent on the total pressure, their relative yields are unchanged. This suggests that as the pressure increases the excited azo molecules, A*, are quenched:

$$A \longrightarrow A^*$$

$$A^* + M \longrightarrow A + M$$

$$A^* \longrightarrow \text{Products}$$

Data from Table 3 do not give linear Stern–Volmer plots, but similar behaviour has been observed for the decomposition of

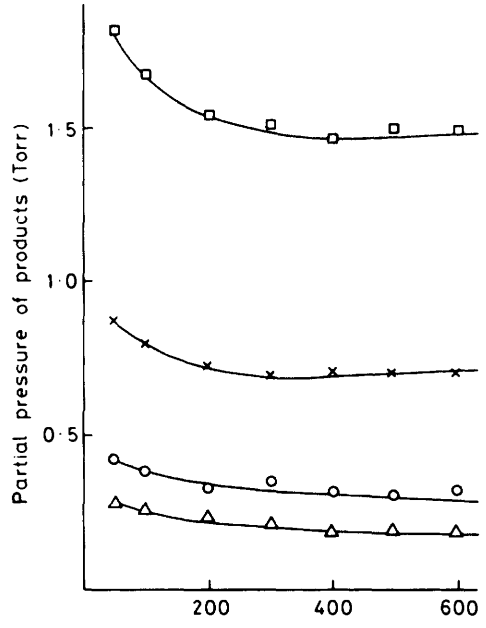

Figure 7. Photo-oxidation of *trans*-2,2′-azoisobutane at 343 K: effect of total pressure on the yields of products. *trans*-2,2′-Azoisobutane, 5 Torr; oxygen, 20 Torr; nitrogen added. Time, 60 min. □, Acetone; ○, t-butyl hydroperoxide; △, t-butyl alcohol; ×, formaldehyde

azoethane,[15] 1,1′-azopropane,[16] 2,2′-azopropane,[16] and hexafluoroazomethane.[17] In the case of the last named, two excited species have been suggested to account for the non-linearity, $^1A^*$ and $^3A^*$, the triplet being longer lived. At high pressures of M, the collisional deactivation of $^1A^*$ will compete more favourably than with decomposition at lower pressures but the effect of M will be less significant for $^3A^*$.

Unlike the gas-phase u.v. irradiation of *trans*-2,2′-azopropane,[4] *trans*-2,2′-azoisobutane failed to produce detectable quantities of the *cis*-isomer. However, this result does not preclude its formation; it simply tells us that, if formed, the decomposition of the *cis*-isomer must be very rapid.

It is important to note, for studies with oxygen, that the photolysis rate is independent of temperature.

(b) *Photolysis of* trans-*2,2′-Azoisobutane in the Presence of Oxygen*.—This paper is the third to report detailed product studies of the self-reaction of t-butylperoxyl radicals. The first, by Thomas and Calvert,[18] involved the photolysis of small amounts (<0.1 Torr) of *trans*-2,2′-azoisobutane in a large excess of oxygen. They reported acetone, formaldehyde, t-butyl hydroperoxide, and t-butyl alcohol as major products at 298 K (these yields being in descending order of magnitude) with smaller amounts of methanol and carbon dioxide being also formed. Kirsch and Parkes,[8] on the other hand, using larger quantities of the azo compound (4—5 Torr) found that yields of the alcohol were larger than the hydroperoxide at 298 K but the ratio decreased rapidly as the temperature was increased. They also observed the peroxide at 298 K. They did not determine formaldehyde.

Our results agree broadly with those of Kirsch and Parkes but, as the discussion develops, we will point out the significant differences.

A mechanism for the photo-oxidation of 2,2′-azoisobutane similar to that for 2,2′-azopropane[3-5] is proposed (Table 4) and has been used as the basis of a computer simulation based on the CHEKIN program.[19] The values chosen for the simulation are based, where possible, on well established literature values. In the absence of such data, values were adopted, based either on similar reactions involving related species or on comparisons with related reactions. In no case were these out of line with acceptable values.

The initiation reaction is the decomposition of the azo compound which can be described in the simple equation (1).

$$Bu^t{-}N{=}N{-}Bu^t \longrightarrow 2Bu^t\cdot + N_2 \qquad (1)$$

The values for k_1 were obtained experimentally and based on the overall rate of formation of hydrocarbons produced as a result of the photodecomposition of 2,2′-azoisobutane in absence of oxygen.

Under the conditions of the experiments, there is little doubt that all the t-butyl radicals are scavenged by oxygen; no hydrocarbons are formed.

$$Bu^t\cdot + O_2 \longrightarrow Bu^tO_2\cdot \qquad (2)$$

Experimental data are not available for k_2, the addition reaction between t-butyl radicals and oxygen. The reaction is very likely to be second order in the pressure region used[20] and a rate constant similar to that of the corresponding reaction with methyl and oxygen, k_{12}, was adopted.[21] It was found that variation of k_2 or k_{12} within sensible limits had no effect on the simulations.

$$CH_3\cdot + O_2(+M) \longrightarrow CH_3O_2\cdot(+M) \qquad (12)$$

t-Butylperoxyl radicals undergo self-reaction (3)

$$2Bu^tO_2\cdot \longrightarrow 2Bu^tO\cdot + O_2 \qquad (3)$$

Parkes[7] has reported values of (log A_3/dm^3 mol^{-1} s^{-1}) = 11.0 and E_3 = 39.7 kJ mol^{-1} for this reaction. These values were used successfully to find rate constants for the reaction at the three temperatures studied.

The decomposition (11) of t-butoxyl radicals is pressure dependent. The reaction has been discussed in considerable detail. The Arrhenius parameters determined by Batt,[22-25] log(A_4/s^{-1}) = 14.5 and E_4 = 71.6 kJ mol^{-1}, were used and allowance was made for the pressure dependency using RRK theory[26,27] developed by Golden *et al.*[28] and used successfully by Selby[29] and Al-Akeel[30] for the decomposition of t-butoxyl and isopropoxyl radicals, respectively.

$$Bu^tO\cdot(+M) \longrightarrow Me_2CO + Me\cdot(+M) \qquad (11)$$

Methylperoxyl radicals formed *via* reaction (12) can undergo self-reaction and cross-reaction with t-butylperoxyl radicals. Rate constants for the overall self-reaction (13) have been obtained recently in several laboratories and with remarkable agreement. Values of 3.3 ± 0.7,[31] 2.3 ± 0.3,[32] 2.7 ± 0.3,[6] 2.5 ± 0.3,[33] and 3.5 ± 0.3 × 10^8 dm^3 mol^{-1} s^{-1}[34] have been reported.

$$2MeO_2\cdot \longrightarrow \text{Products} \qquad (13)$$

These observed rate constants are made up of contributions of two, and possibly three, reactions (13). The observed rate constants also include a contribution from side-reactions of methylperoxyl radicals with methoxyl and hydroperoxyl radicals. Parkes[31] has proposed that the observed values are approximately 1.2 ± 0.1 times greater than the true value. Thus an overall rate constant of 2.8 ± 0.7 × 10^8 dm^3 mol^{-1} at 298 K was used in the present work. This value is composed of two components, (k_{13b} + k_{13c}) = 1.8 × 10^8 dm^3 mol^{-1} s^{-1} and k_{13a} = 1.0 × 10^8 dm^3 mol^{-1} s^{-1} at 298 K. However, there was

Table 4. Rate constants* used in the simulation of the photo-oxidation of *trans*-2,2′-azoisobutane

Reaction†		313 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)	$2Bu^tO_2\cdot \rightarrow 2Bu^tO\cdot + O_2$	2.4×10^4	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
(8)	$Bu^tO\cdot + Bu^tO_2H \rightarrow Bu^tOH + Bu^tO_2\cdot$	7.5×10^6	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
(10)	$2HO_2\cdot \rightarrow H_2O_2 + O_2$	2.2×10^9	2.2×10^9	2.2×10^9
(11)	$Bu^tO\cdot (+M) \rightarrow Me_2CO + Me\cdot (+M)$	6.5×10^1	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
(13a)	$2MeO_2\cdot \rightarrow 2MeO\cdot + O_2$	1.3×10^8	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
(13c)	$2MeO_2\cdot \rightarrow MeO_2Me + O_2$		See below	
(14a)	$MeO_2\cdot + Bu^tO_2\cdot \rightarrow MeO\cdot + Bu^tO\cdot + O_2$	3.8×10^5	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	2.7×10^6	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
(16)	$MeO\cdot + O_2 \rightarrow HCHO + HO_2\cdot$	9.6×10^5	1.4×10^6	2.2×10^6
(18)	$MeO\cdot + Bu^tO_2H \rightarrow MeOH + Bu^tO_2\cdot$	1.5×10^7	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
(23)	$2Bu^tO_2\cdot \rightarrow Bu^tO_2Bu^t + O_2$		See p. 1866	
(24)	$MeO\cdot + MeO_2\cdot \rightarrow MeO_2H + HCHO$	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	2.5×10^6	1.0×10^7
(26)	$MeO\cdot + HCHO \rightarrow MeOH + \dot{C}HO$	9.0×10^5	2.5×10^6	1.0×10^7
(27)	$\dot{C}HO + O_2 \rightarrow CO + HO_2\cdot$	3.8×10^5	7.1×10^5	1.6×10^6

† Numbering corresponds to corresponding reactions in the azoethane[2] and 2,2′-azopropane[3-5] systems. * Units $dm^3 mol^{-1} s^{-1}$ except for reaction (**11**) which are s^{-1}.

no evidence of dimethyl peroxide being formed in these studies and reaction (13c) was not included in the simulation. A value of $(E_{13a} - E_{13b}) = 9 \pm 1$ kJ mol^{-1}, with $E_{13b} = 0$, has been suggested[35] and rate constants for reactions (13a and b) were calculated for each temperature. Values of k_{13b}/k_{13a} of 1.39, 1.16, and 0.72 at 313, 343, and 393 K were calculated, lying within the figures found earlier of 1.8 at 298 K[31] and 0.69 at 410 K.[35]

$$2MeO_2\cdot \longrightarrow 2MeO\cdot + O_2 \qquad (13a)$$

$$2MeO_2\cdot \longrightarrow MeOH + HCHO + O_2 \qquad (13b)$$

$$2MeO_2\cdot \longrightarrow MeO_2Me + O_2 \qquad (13c)$$

Variations in values for k_{13a} and k_{13b} produce significant differences in the product distributions. Increase in the value of k_{13b} results in increased yields of acetone at the expense of t-butyl alcohol, t-butyl hydroperoxide, and formaldehyde at 313 and 343 K. At 393 K, the yield of formaldehyde also increases. Variation in the value of k_{13a} affects the product distribution in an equal and opposite way. It is the ratio of the two rate constants that is the key.

Directly determined data for the cross-reactions involving t-butylperoxyl and methylperoxyl radicals, (14a and b), are not available. Parkes[31] has suggested that the overall rate constants are closer in value to those of the self-reactions of methylperoxyl radicals. If we used these values, we found that the simulated yields of products bore little resemblance to the experimental results. To correct this we had to use rate constants for other kinetically important reactions which were clearly unacceptable. We found that we had to assume that the cross-reactions were significantly slower and indeed we had to choose values similar to those obtained for the self-reactions of isopropylperoxyl radicals.[5] If the ratio of k_{14a}/k_{14b} is increased, there is a simulated increase in the yields of t-butyl alcohol, t-butyl hydroperoxide, and formaldehyde at the expense of acetone. This becomes less significant as the temperature is increased. If the value of k_{14b} is increased, the simulated yields of t-butyl alcohol and formaldehyde increase at the expense of t-butyl hydroperoxide and acetone.

$$MeO_2\cdot + Bu^tO_2\cdot \longrightarrow MeO\cdot + Bu^tO\cdot + O_2 \qquad (14a)$$

$$MeO_2\cdot + Bu^tO_2\cdot \longrightarrow Bu^tOH + HCHO + O_2 \qquad (14b)$$

Values for rate constants for reactions (6) and (21) were set at 9.2×10^8 dm^3 mol^{-1} s^{-1}, a value chosen in earlier studies because of the similarity of the reactions to the self-reaction of hydroperoxyl radicals[36,37] [reaction (10)] (Table 4).

$$Bu^tO_2\cdot + HO_2\cdot \longrightarrow Bu^tO_2H + O_2 \qquad (6)$$

$$MeO_2\cdot + HO_2\cdot \longrightarrow MeO_2H + O_2 \qquad (21)$$

Similar values for the rate constant for reactions (9), (15), and (24) were also given. This is a reasonable value for exothermic radical–radical reactions.

$$Bu^tO\cdot + HO_2\cdot \longrightarrow Bu^tOH + O_2 \qquad (9)$$

$$MeO\cdot + Bu^tO_2\cdot \longrightarrow Bu^tO_2H + HCHO \qquad (15)$$

$$MeO\cdot + MeO_2\cdot \longrightarrow MeO_2H + HCHO \qquad (24)$$

The value of k_{24} is kinetically unimportant but increase in the value of k_{15} alters the simulated yields of t-butyl hydroperoxide and formaldehyde at the expense of acetone and t-butyl alcohol. This variation is enhanced as the temperature is increased.

Other radical–radical reactions, involving alkoxyl, alkylperoxyl, and hydroperoxyl radicals, were also considered for the reaction scheme but were found to be unimportant in the simulation procedures.

t-Butyl hydroperoxide is a major product under all the conditions studied, formed as we have seen *via* reactions (6) and (15). However, it comes to a limiting value. Kirsch and Parkes[8] did not observe this at higher temperatures but examination of their data at 333 K suggests that as they only followed the reaction to *ca.* 15% consumption of the reactant, they may well have obtained a similar result to ours, where the reaction was taken to *ca.* 20% consumption. The way in which the rate of formation of t-butyl hydroperoxide decreases with time (Figures 1 and 2), coupled with the experiments in which t-butyl hydroperoxide was added to the mixture and was rapidly consumed yielding t-butyl alcohol, suggests that reactions (8) and (18) play an important role. The relative importance of reactions (8) and (18) varies with temperature. We found in our simulation procedures that reaction (18) was not important at the lower temperatures. At higher temperatures, reaction (18) although becoming more important still only plays a significant role at low oxygen pressures {presumably there is competition between t-butyl hydroperoxide and oxygen [reaction (16), Table 4] for the methoxyl radicals}.

$$Bu^tO\cdot + Bu^tO_2H \longrightarrow Bu^tOH + Bu^tO_2\cdot \quad (8)$$

$$MeO\cdot + Bu^tO_2H \longrightarrow MeOH + Bu^tO_2\cdot \quad (18)$$

There are, however, no direct data for hydrogen atom abstraction from hydroperoxides by alkoxyl radicals in the gas phase. A liquid-phase study[38] of radical-induced decompositions suggested a value of *ca.* 4×10^6 dm^3 mol^{-1} s^{-1} at 303 K. Recent studies using mixtures of 2,2′-azopropane, oxygen, nitrogen, and either 2-methylpropane or t-butyl hydroperoxide have shown that the hydroperoxide is consumed much more rapidly than the hydrocarbon.[5,39] Consequently, one would expect the activation energies for reactions (8) and (18) to be considerably smaller than those for the reactions between alkoxyl radicals and alkanes. Values for the latter reactions have been obtained in two studies[1,40] and values, based on this evidence of $\log(A/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 8.7$ and a value for the activation energies of 12.4 kJ mol^{-1}, were chosen for both reactions (8) and (18).

We did not observe di-t-butyl peroxide (and in this case, we agree with the results of Thomas and Calvert[18]). We therefore did not include reaction (23) (Table 4) in our scheme.

Yields of methanol were not routinely determined in this study; it is a relatively minor product. The more important product, formaldehyde, was determined. Unfortunately we are unable to make a direct comparison with the work of Kirsch and Parkes.[8] Nevertheless, we observed, as did Thomas and Calvert, that the rate of formation of formaldehyde decreased with increasing photolysis time. It is a matter of crucial importance to interpreting the mechanism to account for the formation and subsequent reactions of formaldehyde.

The principal source of formaldehyde is most likely to be from methoxyl radicals, which are formed *via* reactions of methylperoxyl radicals. Values of k_{16} chosen for the simulations correspond to Arrhenius parameters of $\log(A_{16}/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 8.7$ and $E_{16} = 22.6$ kJ mol^{-1}, well within the error limits set by Batt *et al.*[41] of 9.0 ± 0.6 and 20.2 ± 4.6 and by Barker *et al.*[42] of 8.5 ± 1.5 and 16.8 ± 11.8, respectively.

$$MeO\cdot + O_2 \longrightarrow HCHO + HO_2\cdot \quad (16)$$

Reactions (25)—(27) account for the fall in rate of formation of formaldehyde.

$$Bu^tO\cdot + HCHO \longrightarrow Bu^tOH + \dot{C}HO \quad (25)$$

$$MeO\cdot + HCHO \longrightarrow MeOH + \dot{C}HO \quad (26)$$

$$\dot{C}HO + O_2 \longrightarrow CO + HO_2\cdot \quad (27)$$

Arrhenius parameters for reaction (25) have been obtained in a parallel study[30] and these were also used successfully in the simulation procedure for reaction (26). Several reports exist which give a rate constant for reaction (27).[43–45] Although a value similar to that used in reaction (16) was assigned for the rate constant, it was found, within sensible limits, that the reaction was kinetically unimportant in the system.

Figures 1—3 illustrate data obtained by experiment and by simulation at three different temperatures using the reaction mechanism described above. There is good agreement, with results at the higher reaction temperatures being more consistent.

Figure 4 illustrates results obtained when the oxygen pressure was varied over a wide range at 393 K and Table 4 gives equally convincing results at 313 K.

In separate experiments to test the mechanism further, we added t-butyl hydroperoxide to the system. The results are less impressive but sampling and data processing errors of at least 5% must be anticipated and agreement can be regarded as reasonable (Figures 4 and 5).

We have thus tested the mechanism and the rate data used under a wide range of conditions, varying temperature (examples are shown in Figures 1 and 2), oxygen pressure (Figure 3), and added t-butyl hydroperoxide (examples are shown in Figures 4 and 5). This enables us now to examine in more detail the reactions of t-butylperoxyl radicals under conditions in which peroxyl radicals play an important role in hydrocarbon oxidation. In a subsequent paper, we exploit this technique by examining their reactions with hydrocarbons.

Acknowledgements,

One of us (D. A. O.) is grateful to the S.E.R.C for a Research Studentship. We are pleased to acknowledge the considerable help give to us by Dr. A. Prothero, Shell Research Limited, with the CHEKIN program and to Mrs. M. E. Morgan, University of York, for much assistance with the simulations.

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Received 25*th October* 1983; *Paper* 3/1897