

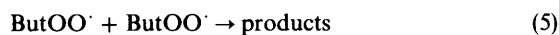
Kinetic Electron Paramagnetic Resonance Study of the Reactions of t-Butylperoxyl Radicals in Aqueous Solution

John E. Bennett

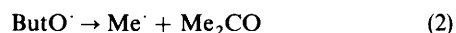
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The kinetics of reactions of t-butylperoxyl radicals in aqueous solution have been measured using electron paramagnetic resonance, ultraviolet absorption spectroscopy and gas chromatography. The rate constants for the overall self-reaction, the separate terminating and non-terminating reactions are very similar to those observed in non-polar solvents and the gas phase. The t-butoxyl radicals, formed by the non-terminating reaction, can either undergo scission, which leads to methylperoxyl radicals, or react with further t-butyl hydroperoxide to regenerate t-butylperoxyl radicals. The cross-termination reaction between methylperoxyl and t-butylperoxyl radicals is an important route in the overall termination sequence. The propagation reaction occurs significantly only at high concentrations of t-butyl hydroperoxide, ($[ButOOH] > 0.3 \text{ mol dm}^{-3}$) and its rate constant is much lower than that in non-polar solutions.

The self-reactions of t-butylperoxyl radicals in organic solvents have been studied extensively by electron paramagnetic resonance spectroscopy. The values obtained for the rate constants of the overall termination reaction (5) and for the separate terminating (5a) and non-terminating (5b) reactions have varied widely.†



In a review of the results, Howard¹ has concluded that the 'best' values are $2k_5 \approx 1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2k_{5a} = (1 - 2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. More recent measurements in the gas phase by molecular modulation spectroscopy² have given $2k_5 = 1.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Similar values have been obtained in the liquid phase³ in non-polar hydrocarbons by EPR ($2k_5 = 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and by UV absorption spectroscopy ($2k_5 = 1.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). In contrast, the few measurements, which have been reported in aqueous solution,⁴⁻⁶ give a higher value for $2k_5 \approx (2.5 - 3.0) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The similarity of this value with the latest measurements in non-polar solvents and the gas phase suggests that the kinetics of the overall reaction is comparable in the three systems. This conclusion contrasts with the findings of Lebedev⁶ and coworkers that the polarity of the solvent has a marked effect on the rate of the overall reaction. Thus it seemed appropriate to study the kinetics of the reaction in aqueous solution in more detail, particularly in the light of the extensive interest in the role of peroxyl radicals in biological systems. Furthermore, as the rate of scission of the t-butoxyl radical [reaction (2)] is much faster in aqueous solution⁷ than in non-polar hydrocarbons and the gas phase,⁸ the subsequent effects of reaction (5b) on the overall reaction in the various media may be markedly different.



In this work, t-butylperoxyl radicals have been generated by two methods, the photolysis of aqueous solutions of t-butyl hydroperoxide or the reaction between solutions of t-butyl hydroperoxide and cerium(IV) in a flow system. The rates of growth and decay of the t-butylperoxyl radical have been measured in both systems using kinetic EPR spectroscopy. In addition, the rate of reaction between cerium(IV) and t-butyl

hydroperoxide has been measured directly by UV spectroscopy and the major products from this reaction have been analysed by gas chromatography (GC). All the experiments were carried out at room temperature.

Experimental

EPR Experiments

The EPR measurements were made using a standard Varian E-4 spectrometer. Because the rates of decay of the t-butylperoxyl radicals were relatively slow, the normal unfiltered response time of the spectrometer was sufficiently fast to follow the decays. In some experiments, it was possible to improve the signal-to-noise ratio by introducing spectrometer time constants of up to 8 ms. The flow experiments were made using a standard aqueous-sample cell and two-stream mixer.

Continuous-flow measurements were made using a syringe pump, with the solutions contained in 100 cm³ syringes. Mixing times could be varied in the range from 40 ms to several seconds, though above 1 s the solutions were not mixed homogeneously. The kinetics of the reaction were measured by recording the EPR signal at different mixing times from 40 ms to ca. 0.5 s.

Stopped-flow measurements were made with a simple two-syringe system. The solutions were contained in 1 cm³ syringes, which were driven by a piston actuated by compressed air. Mixing times were ca. 20 ms and the stop time for the solution in the aqueous sample cell was also ca. 20 ms. These times were sufficiently fast for accurate measurement of the reactions of t-butylperoxyl radicals. The growth and decay curves of the concentration of t-butylperoxyl radicals were recorded by feeding the output of the EPR spectrometer into a Datalab DL 4000 Signal Averager. The signal averager was triggered by a signal from the syringe drive unit. Between 1 and 16 separate curves were accumulated depending on the signal-to-noise ratio and the averaged curve was plotted on an x-y recorder.

The photolysis experiments were carried out using a 100 W mercury compact arc lamp, which was focussed into the sample cavity of the EPR spectrometer by a fused silica lens (focal length 50 mm). Exposure times were controlled by a magnetic shutter placed in front of the cavity. The growth and decay curves of the concentration of t-butylperoxyl radicals were recorded in the same manner as that used for the stopped-flow experiments. Up to 128 separate curves were

† Numbering follows the sequence in the full reaction scheme.

accumulated and averaged depending on the signal-to-noise ratio.

The concentration of t-butylperoxyl radicals was measured by comparing the intensity of its EPR signal with that from a standard solution of vanadyl sulphate, which was recorded at the beginning and end of each series of experiments.

When necessary the values of the rate constants were determined from the experimental curves by mathematical modelling of the reaction. The kinetic simulation program, SIMULA, is based on CHEKIN, developed for handling linked-reaction schemes by computer.⁹

UV Absorption Experiments

The rate of reaction between Ce^{IV} and t-butyl hydroperoxide was measured independently using UV absorption spectroscopy to follow the concentration of Ce^{IV} . The optical system was basically the same as that described in a previous paper.³ To permit direct comparison with the EPR results, the aqueous-sample cell was used as the optical sample cell. Measurements were made using both stopped-flow and continuous-flow techniques. The concentration of Ce^{IV} was followed by monitoring the strong absorption at 340 nm ($\epsilon = 3700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), whereas the absorptions of t-butyl hydroperoxide and Ce^{III} are negligible at this wavelength.

Product Analysis

Product analysis was carried out by GC to measure the main products from the reaction between solutions of t-butyl hydroperoxide and Ce^{IV} . Analysis was carried out at constant temperature (60–90 °C) on a 1 m column packed with 20% SE30/0.1% Carbowax 1500 on 100/120 mesh support. The eluted material was detected by a flame-ionisation detector. The solutions of t-butyl hydroperoxide and Ce^{IV} were mixed in the stopped flow apparatus to ensure mixing conditions similar to those for the kinetic experiments. A slight excess of Ce^{IV} was used to ensure that the t-butyl hydroperoxide reacted completely and so could not decompose on the GC column. It was found that di-t-butyl peroxide did not remain in solution in water even at $10^{-5} \text{ mol dm}^{-3}$. Thus in the experiments to measure the yield of di-t-butyl peroxide, the aqueous solution containing the products was shaken with 2-methylbutane and this solution was used for the analysis. Tests showed that all the products could be removed from the aqueous phase.

Identification of the products was made by comparing retention times with those of standard materials. Concentration measurements were made by preparing standard solutions of similar composition and comparing peak areas. Methyl-t-butyl peroxide was identified from GC data provided by Mr R. S. Lower in the department.

Analysis for methanal was made using the method described by Nash.¹⁰ Blank tests showed that the small amount of excess Ce^{IV} did not interfere with the colorimetric determination made at 412 nm.

Materials

Standard commercially available reagents were used without further purification. Ammonium ceric nitrate was 'AnalaR' grade and the t-butyl hydroperoxide was a standardised aqueous solution (70%). Analysis of the hydroperoxide showed that none of the major reaction products were present in significant amounts. Methyl-t-butyl peroxide and di-t-butyl peroxide were not detected and the amounts of t-butanol and acetone were not greater than 2%.

Results

EPR Continuous-flow Experiments

As the rate of reaction between t-butyl hydroperoxide and Ce^{IV} is very slow in neutral solution, the flow experiments were carried out in solutions acidified with sulphuric acid ($\text{pH} \approx 1.0$). Measurements were made for solutions of both reactants over a wide range of concentrations $\{[\text{ButOOH}] = (5 \times 10^{-4})-(2 \times 10^{-1}) \text{ mol dm}^{-3} \text{ and } [\text{Ce}^{\text{IV}}] = (5 \times 10^{-4})-(1 \times 10^{-2}) \text{ mol dm}^{-3}\}$. The concentrations of reactants are given for the solutions after mixing. For each set of reactant concentrations, the EPR signal of the t-butylperoxyl radicals was recorded at increasing mixing times and the results were plotted as concentration *vs.* time curves. The overall reaction sequence is given by reactions (1) and (5). It is not possible to solve these equations easily for the time dependence of $[\text{ButOO}^\cdot]$, so the experimental curves were fitted using the computer simulation program.



A typical experimental result is shown in fig. 1, together with the computer fit. Good fits were obtained for all the experiments in which the t-butyl hydroperoxide was in excess. The fit was not quite so good when the Ce^{IV} was in excess, which may indicate that there is some reaction between t-butylperoxyl radicals and the metal ion. From all the experiments, the average value for the rate constants was $k_1 = (1.3 \pm 0.3) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2k_5 = (2.0 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (table 1). No decrease in $2k_5$ was observed at the highest concentration of t-butyl hydroperoxide (0.2 mol dm^{-3}) used. This indicates that the propagation reaction (4)

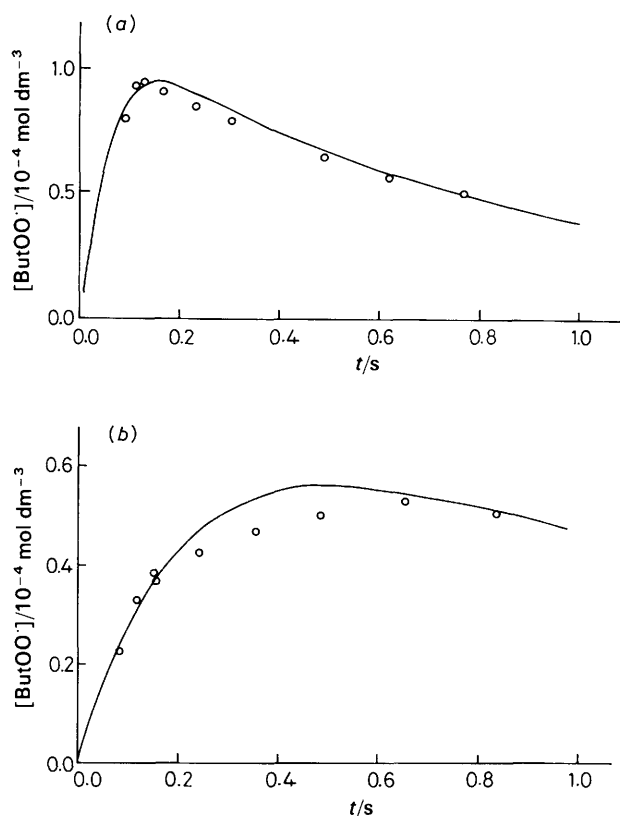


Fig. 1. Growth and decay of $[\text{ButOO}^\cdot]$, formed by reaction between Ce^{IV} and ButOOH in a continuous-flow EPR system. (a) $[\text{Ce}^{\text{IV}}] = 1.26 \times 10^{-4}$, $[\text{ButOOH}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; (b) $[\text{Ce}^{\text{IV}}] = 1.04 \times 10^{-4}$, $[\text{ButOOH}] = 2.51 \times 10^{-4} \text{ mol dm}^{-3}$. (○) Experimental results; (—) calculated time dependence.

Table 1. Measured rate constants at 293 K

rate constant	value/dm ³ mol ⁻¹ s ⁻¹	method
k_1	$(1.3 \pm 0.2) \times 10^4$	a, c
k_4	$(1.2 \pm 0.2) \times 10^6$	b
$2k_5$	$(2.0 \pm 0.4) \times 10^4$	a, b
$2k_{5a}$	$(1.5 \pm 0.3) \times 10^3$	a, e
$2k_{5b}$	$(9.0 \pm 0.5) \times 10^3$	a, e
k_{6a}	$(1.5 \pm 0.5) \times 10^7$	b, d
k_{6b}	$(1.8 \pm 0.5) \times 10^6$	b, d
k_{10}/k_{11}	0.8 ± 0.2	d

(a) Continuous-flow EPR; (b) stopped-flow EPR; (c) continuous- and stopped-flow UV spectroscopy; (d) UV photolysis EPR; (e) Ratio $2k_{5b}/2k_{5a} = 6.0 \pm 1.0$, by GC.

does not occur appreciably in this concentration range



EPR Stopped-flow Experiments

Measurements were carried out over a similar concentration range to that used for the continuous-flow experiments, but in particular measurements were made at higher concentrations of t-butyl hydroperoxide ($0.3\text{--}1.0 \text{ mol dm}^{-3}$). At concentrations of $[\text{ButOOH}] \leq 0.2 \text{ mol dm}^{-3}$ the decays were second order with an overall rate constant, $2k_5 = (2.0 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Above $[\text{ButOOH}] = 0.3 \text{ mol dm}^{-3}$ the decays were still close to second order, but the rate decreased with increasing concentration of t-butyl hydroperoxide. This decrease in rate is attributed to the occurrence of the propagation reaction (4), which regenerates t-butylperoxy radicals. From an analysis of the decays it is possible to obtain the rate constant for this reaction, $k_4 = (1.2 \pm 0.4) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (table 1). A typical decay, together with the computer simulated fit, is shown in fig. 2. The full reaction scheme is presented in the Discussion section.

UV Absorption Experiments

Both continuous- and stopped-flow experiments were carried out to obtain a direct measurement of the rate of reaction between Ce^{IV} ions and t-butyl hydroperoxide in the concen-

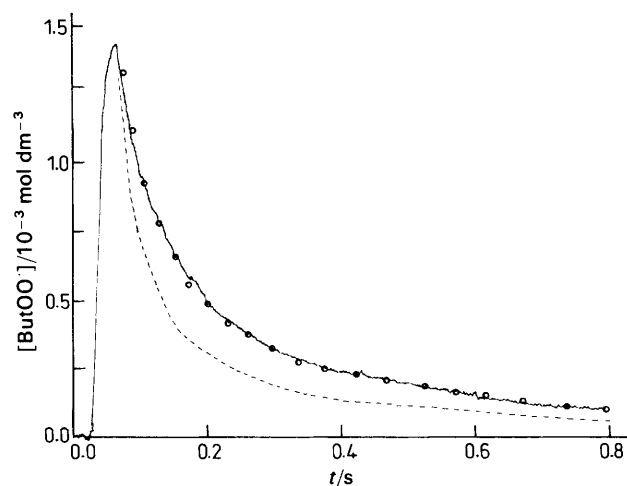


Fig. 2. Growth and decay of $[\text{ButOO}^\cdot]$, formed by reaction between Ce^{IV} and ButOOH in a stopped-flow EPR system. $[\text{Ce}^{\text{IV}}] = 2.02 \times 10^{-3}$, $[\text{ButOOH}] = 1.01 \text{ mol dm}^{-3}$. (—) Experimental results; (○) calculated decay curve; (---) simple bimolecular decay with $2k_5 = 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

tration range (5×10^{-4})–(2×10^{-3}) mol dm^{-3} . The rate of reaction was such that accurate measurements could not be made in the presence of a large excess of t-butyl hydroperoxide and so the decays of Ce^{IV} could not be analysed by a simple pseudo-first-order treatment. A second-order analysis was used, assuming that the reaction was stoichiometric in both Ce^{IV} and ButOOH . Plots of the continuous-flow results are shown in fig. 3. The stopped-flow measurements were analysed by fitting a computed curve to the experimental decay of Ce^{IV} (fig. 4). The average of all the experiments gave $k_1 = (1.4 \pm 0.3) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is in good agreement with that determined from the continuous-flow EPR experiments (table 1). There was no

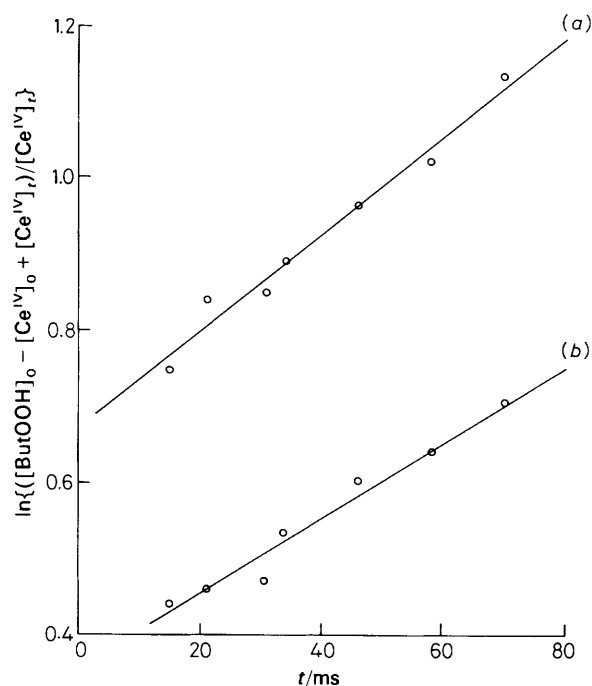


Fig. 3. Reaction of Ce^{IV} with ButOOH in a steady-flow system. $[\text{Ce}^{\text{IV}}]$ followed by UV absorption spectroscopy. (a) $[\text{Ce}^{\text{IV}}] = 5.10 \times 10^{-4}$, $[\text{ButOOH}] = 9.96 \times 10^{-4} \text{ mol dm}^{-3}$; (b) $[\text{Ce}^{\text{IV}}] = 1.03 \times 10^{-3}$, $[\text{ButOOH}] = 1.46 \times 10^{-3} \text{ mol dm}^{-3}$.

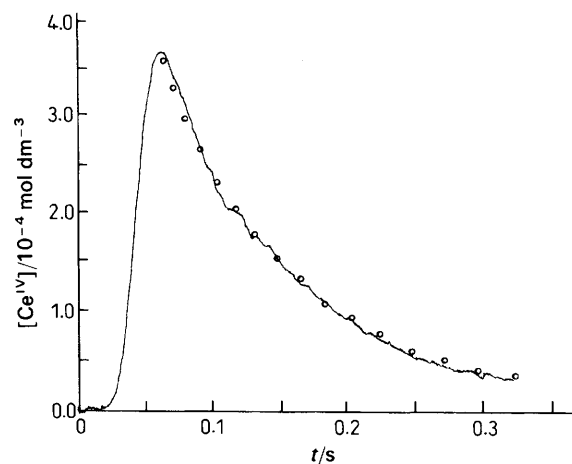


Fig. 4. Reaction of Ce^{IV} with ButOOH in a stopped-flow system, $[\text{Ce}^{\text{IV}}]$ followed by UV absorption spectroscopy. $[\text{Ce}^{\text{IV}}] = 4.66 \times 10^{-4}$, $[\text{ButOOH}] = 1.01 \times 10^{-3} \text{ mol dm}^{-3}$. (—) Experimental results; (○) calculated decay.

evidence for a reaction between the t-butylperoxyl radicals and either valence state of the metal ion.

Product Analysis

A series of separate experiments was carried out for solutions of t-butyl hydroperoxide ($1.8 \times 10^{-3} \text{ mol dm}^{-3}$) and Ce^{IV} ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$). Analysis by GC showed that the major products were methanol, acetone, t-butanol, di-t-butylperoxide and methyl-t-butylperoxide. Colorimetric analysis showed that appreciable amounts of methanal were also formed. The yields of these products are given in table 2.

The yields of acetone, formaldehyde and methyl-t-butylperoxide show that a large fraction of t-butoxyl radicals undergo scission. The total amount of product in terms of t-butoxyl groups is given by $[\text{Me}_2\text{CO}] + [\text{ButOH}] + (2 \times [\text{ButOOBut}]) + [\text{MeOOBut}] = 17.8 \times 10^{-4} \text{ mol dm}^{-3}$, which is close to $[\text{ButOOH}] = 18.3 \times 10^{-4} \text{ mol dm}^{-3}$. The total amount of product formed by scission of t-butoxyl radicals is given by $[\text{MeOH}] + [\text{MeOOBut}] + [\text{HCHO}] = 5.1 \times 10^{-4} \text{ mol dm}^{-3}$, which is only 52% of $[\text{Me}_2\text{CO}] = 9.8 \times 10^{-4} \text{ mol dm}^{-3}$. As discussed later the predictions from the modelling of the full reaction scheme indicate that the experimental yield of methanal is low.

Table 2. Experimental and predicted product yields

product	yield/ $10^{-4} \text{ mol dm}^{-3}$	
	experimental	predicted
HCHO	3.7	6.1
MeOH	0.1	0.06
Me_2CO	9.8	9.7
ButOH	5.6	6.1
MeOOBut	0.8	0.8
ButOOBut	0.8	0.7

EPR Photolysis Experiments

These experiments were originally carried out to ascertain whether the metal ions or the presence of acid affect the kinetics of t-butylperoxyl radicals. t-Butylperoxyl radicals were observed only when the concentration of t-butyl hydroperoxide was above 0.3 mol dm^{-3} , i.e. the region where the overall rate of termination decreased in the stopped-flow experiments. The decays after a short period (2–4 s) of photolysis were second order, with rate constants similar to those observed from the flow experiments at the same concentrations of t-butyl hydroperoxide. Thus, it appears that neither the metal ion nor the acid affects the termination rate constant. However, the behaviour of the growth and decay curves (fig. 5) was not typical of that expected for a first-order generation of radicals, followed by simple bimolecular termination. In particular, the steady-state concentration of t-butylperoxyl radicals was much lower than that calculated from the rates of initiation and decay.

As discussed fully in the next section, this anomalous behaviour is attributed to the presence of substantial amounts of methylperoxyl radicals, which are formed by reactions following the non-terminating reaction (5b).

Discussion

Basic Kinetic Results

Several conclusions can be drawn directly from the present results. The rate constant, k_1 , for the reaction of Ce^{IV} with t-butyl hydroperoxide, is determined directly by the UV spectroscopic results and also from the continuous-flow EPR experiments at low concentrations of reactants (table 1). The values are in good agreement with that ($k_1 = 1.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) measured by Lebedev and coworkers.¹¹

The overall rate constant, $2k_5$, for the mutual termination reaction of t-butylperoxyl radicals can be determined from

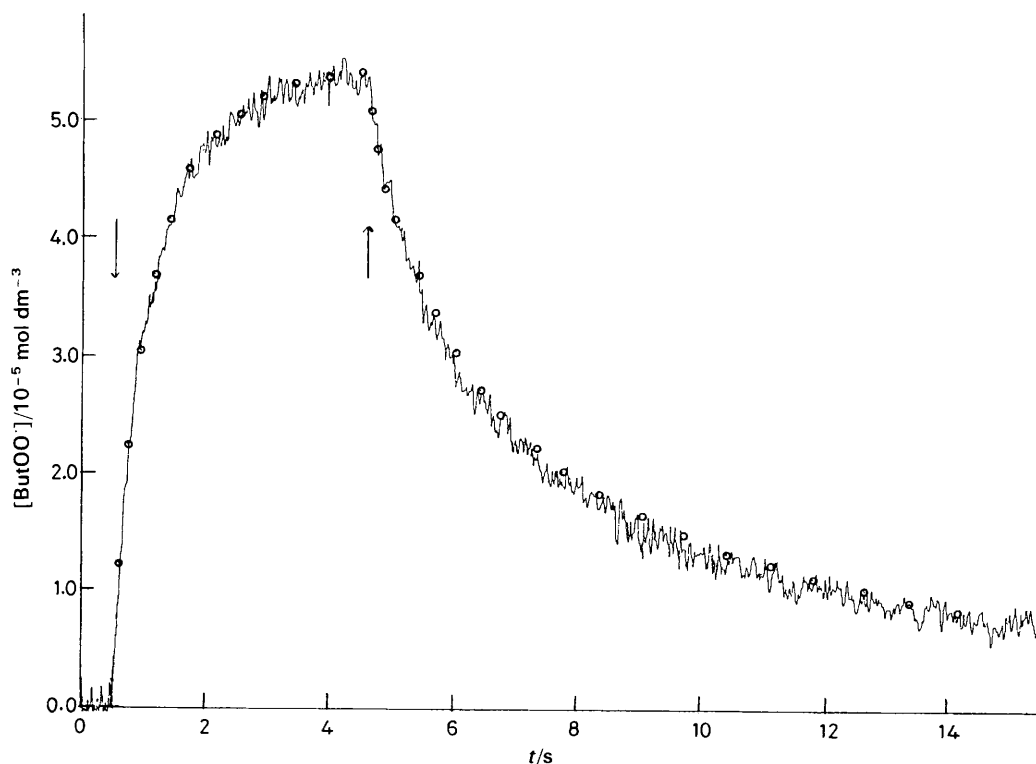


Fig. 5. Growth and decay of $[\text{ButOO}\cdot]$, formed by photolysis of ButOOH . $[\text{ButOOH}] = 1.25 \text{ mol dm}^{-3}$. (—) Experimental results; (○) calculated curve. Vertical arrows mark start and end of photolysis.

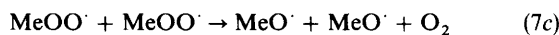
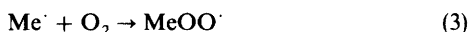
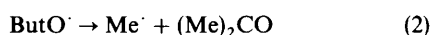
the continuous- and stopped-flow EPR experiments at low concentrations of reactants (table 1). It is slightly lower than those⁴⁻⁶ found earlier [$2k_5 = (2.5-3.0) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$], but is very similar to those measured in hydrocarbon solution³ and the gas phase² ($2k_5 = 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2k_5 = 1.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively). Thus it appears that the overall termination reaction is very similar in the gas phase and in polar and non-polar solvents. This finding differs from that of Lebedev and coworkers,⁶ who conclude that the polarity of the solvent has a marked effect on the rate of reaction.

From the product studies it is possible to obtain an estimate of the ratio of the non-terminating, $2k_{5b}$, and terminating, $2k_{5a}$, rate constants. On the assumption (substantiated by the full reaction scheme discussed below) that virtually all the t-butoxyl radicals formed in the non-terminating reaction undergo scission to give acetone and methyl radicals, then $2k_{5b}/2k_{5a} \approx [\text{Me}_2\text{CO}]/(2 \times [\text{ButOOBut}]) = 6 \pm 1$ (table 1). This value is very similar to those determined in hydrocarbon solution¹² and the gas phase.¹³

It is not possible to obtain further kinetic information from a simple analysis of the experimental results, as the reaction sequence is complicated by the involvement of methylperoxyl radicals formed *via* the scission of t-butoxyl radicals.

Detailed Reaction Scheme

As the non-terminating reaction (5b), which is a major pathway in the mutual reaction of t-butylperoxyl radicals, is followed rapidly by reactions (2) and (3), it is necessary to include methylperoxyl radicals in the overall reaction scheme. On the basis of the studies in the gas phase,^{2,13} the following scheme contains the major reactions needed to allow for the inclusion of methylperoxyl radicals.



To analyse the present results using this scheme, it is necessary to have reliable values of the rate constants for the additional reactions [(6)–(9)] and most are only available from the gas phase. However, the rate constant for reaction (2) has been measured⁷ in aqueous solution, $k_2 = 1.4 \times 10^6 \text{ s}^{-1}$.

The rate constant for the addition of oxygen to methyl radicals¹⁴ is $k_3 \approx 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Reliable values¹⁵ of the rate constants for reactions (7a)–(7c) have been measured in the gas phase, $k_{7a} = 2.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{7b} = 2.2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{7c} = 5.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Estimates for the rates of reactions (6) and (9) have also been

made in the gas phase,¹⁶ $k_{6a} \approx 3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{6c} \approx 1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_9 = 3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. More recently it has been suggested⁹ that the rates of reactions (6a) and (6c) are considerably lower ($k_{6a} = 2.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{6c} = 3.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). As the rate constants for the reactions of methoxyl¹⁷ and t-butoxyl^{18,19} radicals with methanol in solution are very similar, it is reasonable to assume that their reactions with t-butyl hydroperoxide will be comparable, thus $k_8 \approx 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

EPR Flow Experiments

Initially, the reaction scheme can be simplified by neglecting the non-terminating reactions (6c) and (7c), as each is less than 30% of the corresponding total reaction. Consequently, methoxyl radicals are not involved and reactions (8) and (9) are not required in the scheme.

Using this simplified model, the rate constant for the propagation reaction (4) was obtained from the stopped-flow EPR experiments at high concentrations of t-butyl hydroperoxide. The calculated fit to the decay curve (fig. 2) is very sensitive to the value of k_4 , but much less so to either k_{6a} or k_{7a} . The best fit was obtained for $k_4 = (1.2 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{6a} \geq 1.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The full reaction scheme, including the non-terminating reactions (6c) and (7c), together with reactions (8) and (9), leads to a slightly better fit to the experimental curves without altering the values of the other rate constants.

The value of k_4 is much smaller than that¹⁸ determined in hydrocarbon solution ($k_4 = 2.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The decrease is attributed mainly to hydrogen bonding between the hydroperoxyl group and water molecules. A similar decrease has been noted for the reaction of t-butylperoxyl radicals with the hydroxyl group of phenols in increasingly polar solvents. On the other hand, the rate constant for scission of the t-butoxyl radical is much higher in aqueous solutions⁷ ($k_2 = 1.4 \times 10^6 \text{ s}^{-1}$) than in hydrocarbon solutions⁸ ($k_2 < 1.0 \times 10^3 \text{ s}^{-1}$). Thus, whereas in hydrocarbons the main reaction of the t-butoxyl radical will be hydrogen abstraction from the solvent or t-butyl hydroperoxide, in aqueous solution the scission reaction will predominate.

With these values for the rate constants, the model shows that most of the methylperoxyl radicals undergo cross-termination with t-butylperoxyl radicals. Thus, at low concentration of t-butyl hydroperoxide, the overall rate of termination, $2k_5 \approx 2k_{5a} + (2 \times 2k_{5b}) = 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Then using the ratio, $2k_{5b}/2k_{5a} = 6$, the values of the terminating and non-terminating rate constants are calculated to be $2k_{5a} = 1.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2k_{5b} = 9.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively (table 1).

EPR Photolysis Experiments

The reaction scheme for the photolysis experiments is more complex, because the initiation reaction leads to the formation of both t-butoxyl and hydroxyl radicals. Reaction (1) is replaced by reaction (1') and two additional reactions involving hydroxyl radicals must be added to the scheme:



The rate of initiation is taken to be proportional to $[\text{ButOOH}]$ for constant conditions of photolysis and is determined from the initial rate of growth of t-butylperoxyl radicals. In reaction (11) it is assumed that the alkyl radical adds to oxygen rapidly to give a peroxy radical, whose reactivity is the same as that of methylperoxy. It is also assumed

that k_{11} is comparable to the rate constant for the corresponding abstraction²⁰ by OH from t-butanol, which is $6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Gas-phase measurements²¹ for the reactions of OH with methyl hydroperoxide show that abstraction from the hydroperoxyl group is twice as fast as from the methyl group. Thus, allowing for the three methyl groups in t-butyl hydroperoxide, $k_{10} \approx k_{11} = 6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

As a simplification, reactions (6c) and (7c) were again neglected, together with reactions (8) and (9). Then this scheme requires only the ratio of k_{10}/k_{11} , together with the values of the rate constants from the previous model. The best fits to the experimental results were obtained for $k_{10}/k_{11} \approx 1.2$. The fit was more sensitive to k_{6a} than for the flow experiments and leads to a value of $k_{6a} = 1.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The complete scheme, including reactions (6c), (7c), (8) and (9) can be used to fit the experiments reasonably well simply by changing the ratio, $k_{10}/k_{11} \approx 0.8$, and keeping the values of the other rate constants unchanged. This set is not unique as other combinations of the rate constants also give reasonable fits. However, this set gives the best fit between the calculated and observed curves for all the kinetic experiments, including flow and photolysis.

The value of the rate constant for the cross-termination reaction (6a) (table 1) is similar to the gas-phase value ($k_{6a} \approx 3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) estimated by Parkes,¹⁶ but is higher than that ($k_{6a} \approx 2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) obtained more recently by Osborne and Waddington.⁹ In accord with previous measurements of the cross-termination reactions of peroxy radicals, our value is considerably higher than the geometric mean of the rate constants for the separate mutual termination reactions, $\phi = 2k_6/(2k_5 \times 2k_7)^{1/2} = 6$. This value is similar to those reported¹ for other cross-termination reactions of peroxy radicals in the liquid phase, for which $\phi = 5\text{--}20$.

GC Experiments

Using the rate constants determined in the kinetic experiments, the yields of the major products were predicted using the full reaction scheme. The rate constant for reaction (6b) was obtained by fitting the calculated and experimental yields of methyl-t-butyl peroxide (table 1). The agreement with experiment is reasonable (table 2) for acetone, di-t-butyl peroxide, and methyl-t-butyl peroxide. The experimental yield of

t-butanol is slightly less than predicted, while that of methanal is only ca. 50% of the predicted value. This low yield may indicate that methanal undergoes further attack, probably by alkoxy radicals.

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