Recombination of Tertiary Butyl Peroxy Radicals

Part 1.—Product Yields between 298 and 373 K

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Overall product distributions resulting from the recombination of t-butyl peroxy radicals have been studied over the temperature range 298-373 K. The results indicate that over this range there is a switch from the terminating channels (forming alcohol and aldehyde/ketone) towards non-terminating channels (forming two alkoxy radicals) for the two further recombination processes that follow the initial combination of t-butyl peroxy radicals:

 CH_3O_2 ·+t-BuO₂· \rightarrow products $2CH_3O_2$ · \rightarrow products.

There is also direct evidence for the presence of a terminating channel to form di-t-butyl peroxide. This reaction proceeds at a rate of ca. 0.14 of the non-terminating recombination rate at 298 K, but this fraction falls to 0.025 at 333 K and the reaction is not evident at 373 K.

Our results demonstrate the importance of abstraction reactions involving alkoxy radicals (t-butoxy and methoxy) and one of the principal recombination products, t-butyl hydroperoxide. Rate constant ratios involving these processes have been derived from the product distributions and from additional studies in which t-butyl hydroperoxide was added. Rate constants of *ca.* 10^{-13} cm³ molecule⁻¹ s⁻¹ for these abstraction processes are consistent with our results.

The question of the kinetic behaviour of alkylperoxy radicals (RO_2 ·) is central to an understanding of hydrocarbon oxidation mechanisms.^{1, 2} We have recently studied the kinetics of primary, secondary and tertiary radical recombination using both molecular modulation spectroscopy and single pulse photolysis. Detailed results have been published for the methyl peroxy radical³ and isopropyl peroxy radical^{4, 5} and this paper, together with the accompanying kinetic paper (Part 2), extends the preliminary results^{6, 7} at room temperature for the t-butyl peroxy radical both in detail and in temperature range.

Because peroxy radical recombination leads to both terminating [reactions (I) and (II)] and non-terminating products [reaction (III)]:

$$2 \operatorname{RO}_2 \to \operatorname{ROOR} + \operatorname{O}_2 \tag{I}$$

$$\rightarrow ROH + RCO + O_2$$
 (II)

$$\rightarrow 2RO + O_2$$
 (III)

it is essential to accompany any kinetic study by product analysis. Further reactions of the products of reaction (III) may lead either to further termination [reaction (IV)] by removing peroxy radicals or to regeneration by reaction with products [reaction (V)]:

$$e.g. \ \mathrm{KO}_2 + \mathrm{KO} \to \mathrm{KO}_2 \mathrm{H} + \mathrm{KCO} \tag{IV}$$

$$RO + ROOH \rightarrow RO_2 + ROH.$$
 (V)

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[Reaction (II) can naturally play no rôle for tertiary peroxy radicals.]

This paper describes the product yields from t-butyl radical oxidation. These are then used in Part 2 to discuss the kinetic measurements.

EXPERIMENTAL

APPARATUS

The photolysis system is shown in fig. 1 and was designed to be similar to that used in the corresponding kinetic absorption studies.⁷ The reaction vessel was cylindrical (length 600 mm, internal diameter 40 mm), and constructed of Spectrosil quartz. It was surrounded by a coaxial



FIG. 1.-Photolysis system.

evacuated Pyrex annular vessel and around this were mounted six 20 W 'dark light' fluorescent tubes. These lamps emit in the wavelength range 300-400 nm. The reaction vessel was heated by circulating hot air through the annular space between the reaction vessel and the evacuated vessel, and its temperature was measured by a movable iron/constantan thermocouple mounted in this space. To minimise sampling corrections, the reaction vessel had a larger volume than that used in the kinetic absorption studies. As a result, the temperature distribution along the vessel was less even (± 5 K at 333 K, ± 10 K at 373 K) and the useful upper limit to the temperature range of the apparatus was *ca*, 383 K.

Gas mixtures were admitted to the reaction vessel via a greaseless Pyrex vacuum line. Samples were withdrawn for gas chromatographic analysis using an all-glass sampling system. Thus, portions of the reaction mixture were shared into a small, previously evacuated, sampling volume, whence they could be introduced into the carrier-gas stream of the gas chromatograph. Initial samples containing unphotolysed mixture from the sampling line were discarded, and small corrections were made for the reduction in the total reaction mixture concentration upon successive samplings. A Pye Unicam GCD chromatograph equipped with a flame ionisation detector and a DP88 computing integrator was used for gas chromatographic analysis. The analysis of peroxides and hydroperoxides presents a problem in oxidation systems, hence the need for an all-glass system. A Gas-Chrom Q column coated with 20% w/w dinonyl phthalate has been shown to be particularly suitable,⁸ and was used for the bulk of the present work. This column gave good separation and reproducible results for all the major products, with the exception of methanol and formaldehyde. Methanol was estimated in separate experiments using a Porapak Q column; formaldehyde was not measured in this work.

Retention times of the various products in the gas chromatograph were measured using commercially available samples directly. The sensitivity of the system was calibrated by sampling made-up mixtures in the same way as in the photolysis experiments. The ratios of concentrations in mixtures were reproducible to within 5% and no deviations were found between the results of photolyses and the proposed mechanism which were significantly larger. (See table 1.) The azo precursor is the natural reference, but has a distorted g.l.c. peak and this gives the practical limitation to the accuracy.

MATERIALS

Azo-t-butane was prepared as described previously.⁹ Tertiary butyl hydroperoxide was obtained commercially (Koch-Light, pure) and outgassed before use. Oxygen (B.O.C.) and nitrogen (B.O.C. 'white spot') were taken directly from cylinders.

RESULTS

1. EXPERIMENTS AT ROOM TEMPERATURE (298 K)

In the photolysis of azo-t-butane + oxygen mixtures at room temperature all the major products expected on the basis of earlier studies⁷ (with the expected exception of formaldehyde) were detected. However, the product distribution (fig. 2) was



FIG. 2.—Product analysis during the photolysis of azo-t-butane + oxygen at 298 K. Initial conditions: [azo-t-butane] = 1.30×10^{17} molecule cm⁻³, [oxygen] = 2.45×10^{19} molecule cm⁻³. \bigcirc , (t-Bu)₂N₂; \bigcirc , (CH₃)₂CO; \triangle , t-BuOH; \bigcirc , (t-Bu)₂O₂ × 10; \Box , t-BuO₂H × 10; \bigtriangledown , CH₃OH.

surprising in view of the data of Thomas and Calvert,¹⁰ who reported equal yields of t-BuOH and t-BuO₂H. They interpreted their results in terms of the following mechanism:*

$$t-Bu-N=N-t-Bu \to N_2 + 2t-Bu$$
 (7)

$$t-Bu'+O_2 \to t-BuO_2' \tag{6}$$

$$2t - BuO_2 \cdot \rightarrow 2t - BuO \cdot + O_2 \tag{13a}$$

$$t-BuO \cdot \to (CH_3)_2CO + CH_3 \cdot$$
(14)

$$CH_3 \cdot + O_2 \to CH_3O_2 \cdot \tag{8}$$

$$CH_{3}O_{2}$$
 + t-Bu O_{2} \rightarrow $CH_{3}O$ + t-Bu O + O_{2} (18*a*)

$$\rightarrow CH_{a}O + t - BuOH + O_{a} \qquad (18b)$$

* The nomenclature of the reaction scheme has been chosen to correspond to that of ref. (7).

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$$CH_3O \cdot + t - BuO_2 \cdot \rightarrow CH_2O + t - BuOOH$$
 (16)

$$CH_3O \cdot + O_2 \rightarrow CH_2O + HO_2 \cdot$$
 (21)

$$HO_2 \cdot + t - BuO_2 \cdot \rightarrow t - BuOOH + O_2$$
 (22)

$$2CH_3O_2 \rightarrow 2CH_3O \rightarrow +O_2 \tag{1a}$$

$$\rightarrow CH_3OH + CH_9O + O_9. \tag{1b}$$

In this study acetone and t-BuOH were each produced at close to the photolysis rate, and methanol was produced in low quantum yield (*ca.* 0.1). However, the yield t-BuO₂H was very small and did not increase with continued photolysis. Furthermore, di-t-butyl peroxide, $(t-Bu)_2O_2$, was produced as a product, again in conflict with the results of Thomas and Calvert. Separate experiments with unreacted calibration mixtures showed that there was no problem in detecting hydroperoxide. The mass balance cannot be measured directly because formaldehyde was not measured, but the suggested mechanism implies the formation of one molecule of formaldehyde for each molecule of t-BuOH, t-BuO₂H and CH₃OH. Making this assumption, the mass balance was found to be satisfactory within experimental error, as it was with all the results presented in this paper.

A possible explanation for these observations lies in the abstraction of the hydrogen atom in the hydroperoxide group by the t-butoxy radical:

$$t-BuO' + t-BuO_2H \rightarrow t-BuOH + t-BuO_2'$$
. (25)

The presence of di-t-butyl peroxide amongst the products suggests that the terminating reaction $2t_B P O \rightarrow (t_B P) O \rightarrow O$ (13b)

$$2t-BuO_2 \cdot \rightarrow (t-Bu)_2O_2 + O_2 \tag{13b}$$

is taking place. This process has previously been thought to occur only under 'cage' conditions in the liquid phase.

We have confirmed these postulates with experiments in the presence of added hydroperoxide. Typical results at room temperature are shown in fig. 3. The



FIG. 3.—Product analysis during the photolysis of azo-t-butane + oxygen at 298 K with added t-butyl hydroperoxide. Initial conditions: [azo-t-butane] = 1.34×10^{17} molecule cm⁻³, [oxygen] = 2.45×10^{-19} molecule cm⁻³, [t-BuO₂H] = 3.73×10^{16} molecule cm⁻³. \bigcirc , (t-Bu)₂N₂; \triangle , t-BuOH; \bigcirc , (t-Bu)₂O₂×10; \bigcirc , (cH₃)₂CO; \Box , t-BuO₂H; \bigtriangledown , CH₃OH.

hydroperoxide is removed at a rate an order of magnitude greater than the photolysis rate and is replaced quantitatively by t-BuOH. The quantum yield for di-t-butyl peroxide formation is near unity, and that of acetone is initially near zero, although this product is eventually formed at a rate close to the photolysis rate when the hydroperoxide has been substantially removed. The di-t-butyl peroxide found initially is that present in the hydroperoxide as impurity. With excess added hydroperoxide, such that reaction (25) is the dominant process for removing t-BuO[•], a long chain is set up with reaction (13*b*) being the sole effective termination reaction.

2. EXPERIMENTS AT 333 K

There was a marked change in the product yield from the photolysis of azot-butane + oxygen mixtures when the temperature was raised to 333 K (fig. 4). Again acetone was formed approximately at the photolysis rate, and the methanol yield was



FIG. 4.—Product analysis during the photolysis of azo-t-butane+oxygen at 333 K. Initial conditions: [azo-t-butane] = 1.30×10^{-17} molecule cm⁻³, [oxygen] = 2.48×10^{-19} molecule cm⁻³. \bigcirc , (t-Bu)₂N₂; \bigcirc , (CH₃)₂CO; \triangle , t-BuOH; \Box , t-BuO₂H; \bigtriangledown , CH₃OH; \bigcirc , (t-Bu)₂O₂.

still small (quantum yield ≈ 0.08). However, t-BuO₂H continued to build up as a product throughout the photolysis period and was formed in comparable yield to t-BuOH. In this experiment the yield of $(t-Bu)_2O_2$ was very small (quantum yield ≈ 0.025). After continued photolysis, a fall-off in the *rate* of t-BuO₂H formation became apparent, accompanied by a corresponding increase in the rate of t-BuOH formation. Thus reaction (25) becomes important under these conditions when the hydroperoxide concentration has built up sufficiently. It was therefore necessary to measure the initial rates of product formation at very low degrees of conversion. Under these circumstances, when reaction (25) may be neglected, the quantum yield for hydroperoxide formation (0.53) was found to be higher than that for production of the alcohol (0.40).

Experiments with added t-BuO₂H (*ca.* 3×10^{-16} molecule cm⁻³) were also carried out at this temperature. The hydroperoxide was now removed at a decreasing rate that was only a few times greater than the photolysis rate, and t-BuOH was produced at

a slightly higher rate. Acetone was produced with a quantum yield unity, whilst the yields of methanol and $(t-Bu_2)O_2$ were very small.

3. EXPERIMENTS AT 373 K

When azo-t-butane + oxygen (ca.1 atm) mixtures were photolysed at 373 K, acetone, t-BuOH and t-BuO₂H were again the major products and were each observed to build up steadily throughout the photolysis period (fig. 5). The hydroperoxide was now



FIG. 5.—Product analysis during the photolysis of azo-t-butane + oxygen at 373 K. Initial conditions: [azo-t-butane] = 1.30×10^{17} molecule cm⁻³, [oxygen] = 2.0×10^{19} molecule cm⁻³. (Broken curves show the effect on CH₃OH and t-BuO₂H yields at reduced oxygen concentration, *viz*. Initial [O₂] = 1.30×10^{-17} molecule cm⁻³, initial [N₂] = 2.0×10^{-19} molecule cm⁻³.) \bigcirc , (t-Bu)₂N₂; \bigcirc , (CH₃)₂CO; \bigtriangledown , CH₃OH × 10; \square , t-BuO₂H; \triangle , t-BuOH.

formed at a significantly greater rate than the alcohol. No significant amounts of $(t-Bu)_2O_2$ were formed in this experiment. Methanol was formed initially with a quantum yield of 0.1, but its rate of formation was observed to increase at long times. We attribute this to the reaction

$$CH_3O \cdot + tBuO_2H \rightarrow CH_3OH + tBuO_2 \cdot$$
 (26)

which will compete with reactions (21) and (16) for removal of methoxy radicals under these conditions. This supposition was confirmed by an otherwise identical experiment at reduced oxygen concentration (*i.e.* by replacing a substantial part of the oxygen by nitrogen). The results are indicated by the broken lines in fig. 5. The non-linearity in the methanol-formation curve became very pronounced and the increased methanol yields were achieved at the expense of a fall off in hydroperoxide yield. Consequently, yields of the recombination products were measured at high oxygen pressures and low degrees of conversion, where the effect of reaction (26) is insignificant.

DISCUSSION

Table 1 summarises the quantum yields for product formation, based on the assumption of a quantum yield of unity for the removal of the azo precursor, from

product	temperature/K		
	298	333	373
acetone	1.15	1.05	1.10
t-BuOH	1.10 ^a	0.40	0.20
t-BuO ₂ H	a	0.50	0.55
(t-Bu),O,	0.07	0.025	
methanol	0.10	0.075	0.08
+t-BuOH $+t-BuO_2H$	2.25	1.95	1.85
acetone } + methanol }	1.05	0.95	1.0

 TABLE 1.—INITIAL PRODUCT QUANTUM YIELDS FROM THE PHOTOLYSIS OF

 AZO-t-BUTANE + OXYGEN MIXTURES

^a t-BuO₂H converted into t-BuOH via reaction (25).

the photolysis of azo-t-butane + oxygen mixtures. This definition of quantum yield, although not strictly correct, does give a clear picture of the photochemically induced reactions. These are essentially initial rates of formation measured at low degrees of conversion in the presence of excess oxygen. Thus, the contribution due to reactions (25) and (26) can be considered to be negligible in most instances. At 298 K, however, the steady-state concentration of t-BuO₂H was very low (*ca*. 0.01 Torr), and essentially all initially formed hydroperoxide was converted into alcohol *via* reaction (25). Also shown in table 1 are the combined yields (acetone + t-BuOH + t-BuO₂H) and (acetone + MeOH), which, as a check on the mechanism used to interpret the results, should be equal to 2 and 1, respectively, within experimental error. Table 2 summarises

ratio	temperature/K			
	298	333	373	_
k14/k25	5 × 10 ¹⁴	1 × 10 ¹⁶		
$k_{14}k_{18a}/k_{18}k_{25}$	3×10^{14}			
k_{18a}/k_{18b}		1.0	1.7	
k_{21}/k_{26}			< 0.4	
k_{13b}^{11}/k_{13a}	0.14	0.05	—	

TABLE 2.—APPROXIMATE RATE-CONSTANT RATIOS

the rate constant ratios that may be derived from these data and from the additional experiments carried out in the presence of added hydroperoxide. The significance and accuracy of these rate ratios is discussed in greater detail in Part 2, which uses these analyses to interpret kinetic measurements. As these ratios are directly related to the measured concentration ratios (q.v.), their accuracy must be similar (5-10%), given of course the mechanistic assumptions.

Examination of the results obtained at 298 K reveals two features that are very difficult to reconcile with the results of Thomas and Calvert.¹⁰ These workers, using

infrared spectroscopy to detect the products from the photolysis of azo-tbutane + oxygen mixtures, report yields of acetone and methanol comparable with our own. However, they obtain equal yields (quantum yield ≈ 0.5) of t-BuOH and t-BuO₂H, and were unable to detect (t-Bu)₂O₂ amongst their products. Our experiments with added hydroperoxide confirm its rapid conversion to alcohol under these experimental conditions and are consistent with the low steady-state value attained when we photolyse azo-t-butane + oxygen mixtures. Moreover, this steady-state value should be determined by the ratio $k_{14}k_{18a}/k_{25}k_{18}$ and should not depend on the experimental conditions other than temperature. In hindsight, there is some evidence of reaction (25) from their experimental results. In fig. 2 of their paper, it is apparent that the

(25) from their experimental results. In fig. 2 of their paper, it is apparent that the rate of formation of t-BuOH did not fall off in common with the other products as the photolysis was continued to very high degrees of conversion. However, the concentration of t-BuO₂H builds up towards a value (*ca.* 0.1 Torr) substantially in excess of the steady-state value that we observe and so a genuine discrepancy exists between the two sets of experimental results.

The experimental estimation of t-BuO₂H in Thomas and Calvert's experiments was clearly very difficult because it was obtained from a small shoulder peak superimposed on a much more intense absorption band due to t-BuOH. This may account, in part, for the discrepancy. An alternative explanation may lie in the importance of close temperature control for this particular measurement. The steady-state solution for t-BuO₂H, $k_{14}k_{18a}/k_{25}k_{18}$, is very temperature-sensitive (see below), increasing by ca. 10% per degree rise in temperature. We have observed the measured concentration of t-BuO₂H to increase slowly at long photolysis times, concomitant with the measured increase in temperature. A relatively small temperature discrepancy (5-10 K) between the two experiments would substantially account for the differences in final products yields, including Thomas and Calvert's failure to detect $(t-Bu)_2O_2$, which we observe to decrease in yield at elevated temperatures.

The existence of a terminating channel for reaction (13) forming $(t-Bu)_2O_2$ is a significant observation for the interpretation of gas-phase experiments at room temperature and below. However, the yield of this product falls rapidly with increasing temperature, indicating an activation energy substantially lower than that for the main channel.



FIG. 6.—Basic mechanism for t-BuO₂ recombination.

The interplay between the various reactions is best appreciated by setting the mechanism out in diagrammatic form, as has been done in fig. 6. The original reaction scheme of Dever and Calvert¹¹ is given in the solid lines. Here the initial recombination [reaction (13a)] is non-terminating, but the product alkoxy radicals lead to further radical removal *via* the sequence of reactions (14), (8), (18), (16), (21) and (22).

Therefore, many t-BuO₂ radicals may be removed per initial recombination, particularly as the sequence (14), (8), (18*a*) represents a chain cycle. The effective rate of termination as seen by the rate of t-BuO₂ removal will be reduced, however, if reaction (18*b*) competes effectively with (18*a*), or if CH₃O₂ recombination, reaction (1), can compete with the cross-termination (18). The alternative terminations do not remove t-butyl peroxyradicals but other active species.

The lifetime of the t-BuO₂ radical is very long under our experimental conditions (up to *ca.* 20 s), and it is a good approximation to assume that the remaining radicals are held in their steady-state concentrations during the overall recombination process. We assume that reactions (14), (8) and (22) are sufficiently fast to constitute the only removal process for t-BuO, CH_3 , and HO_2 , respectively. Describing the overall recombination rate for t-BuO₂ radicals by a second-order coefficient k_t

$$\frac{\mathrm{d}[\mathrm{t}-\mathrm{BuO}_{2}\cdot]}{\mathrm{d}t} = -2k_{t}[\mathrm{t}-\mathrm{BuO}_{2}\cdot]^{2}$$

steady-state analysis (Appendix) yields the following result:

$$k_{t} = k_{13} \left[1 + \frac{k_{1a}}{k_{1}} \right] + \frac{k_{18b}}{8k_{1}} (\phi - 1) \left[k_{18} + k_{18a} - k_{18b} \frac{k_{1a}}{k_{1}} \right]$$

where

$$\phi = 1 + \left[\frac{16k_1k_{13a}}{k_{18b}^2}\right]^{\frac{1}{2}}, \ k_1 = k_{1a} + k_{1b}, \ k_{18} = k_{18a} + k_{18b}.$$

The low yield of methanol reported at room temperature¹⁰ suggests that reaction (1) is relatively unimportant. Provided $16k_1k_{13a} \ll k_{18b}^2$, $(\phi-1) \approx 8k_1k_{13a}/k_{18b}^2$ and $k_t \approx k_{13a}[1 + (k_{18} + k_{18a})/k_{18b}]$, which is the expression used in the earlier analysis.⁷ This illustrates the essential nature of the problem; namely that the relationship between the observed rate constant, k_t , and the initial recombination rate constant, k_{13} , is heavily dependent on the non-terminating/terminating ratio k_{18a}/k_{18b} of the subsequent cross-termination (18). The results of Thomas and Calvert¹⁰ suggest a value of 1 for this ratio at room temperature, and a major aim of the present work was to verify this result and extend the measurements over a range of temperatures. It is likely that reaction (18b) will decrease in importance relative to reaction (18a) with increasing temperature. Also, preliminary results have indicated that reaction (13a) has a high activation energy. Thus, the simplifying assumption $16k_1k_{13a} \ll k_{18b}^2$ will become less valid with increasing temperature, and the complete analysis, including reaction (1), is essential.

During an extended period of photolysis, t-BuO₂ · radicals will approach a steady state, such that 2R - 2k [t BuO 1]²

$$2P = 2k_t [t-BuO_2^{\circ}]^2$$

where P is the rate of photolysis of azo-t-butane. The steady-state rates of product formation as a function of P are also derived in the Appendix. When reaction (1) plays a significant role, these are not simple functions of the various rate constants. However, we note, as a check on the validity of the proposed mechanism, that under all circumstances:

$$\frac{d}{dt} [acetone + t - BuOH + t - BuO_2H] = 2P.$$

and the yield of methanol, which measures the importance of reaction (1b), is such that:

$$\frac{\mathrm{d}}{\mathrm{d}t}[\operatorname{acetone} + \operatorname{methanol}] = P.$$

We note also that production of the alcohols t-BuOH and MeOH signifies the occurrence of the terminating channels (b) of the recombinations (18) and (1), respectively. Both non-terminating channels yield t-BuO₂H via reaction of the methoxy radical.

Also given in fig. 6 in the dotted lines are the extra reactions needed to interpret the present results. From the room temperature data, the following may be concluded. Recombination via reaction (13a) yields two molecules of t-BuOH as overall termination products, whereas (13b) yields one molecule of $(t-Bu)_2O_2$. Hence a value of 0.14 was obtained for the ratio k_{13b}/k_{13a} on the basis of the observed product yields at 298 K. A simplified steady-state analysis, based on reactions (13), (14), (18a), (18b), (16), (21) and (25) predicts the following quantum efficiencies:

$$\frac{\mathrm{d}[\mathrm{t-BuO_2H}]}{\mathrm{d}t} \Big/ P = \frac{k_{25}[\mathrm{t-BuO_2H}]}{k_{14}} - \frac{k_{18\,a}}{k_{18}}$$
$$\frac{\mathrm{d}[\mathrm{t-BuOH}]}{\mathrm{d}t} \Big/ P = \frac{k_{25}[\mathrm{t-BuO_2H}]}{k_{14}} + \frac{k_{18\,b}}{k_{18}}$$
$$\frac{\mathrm{d}[\mathrm{acetone}]}{\mathrm{d}t} \Big/ P = 1.$$

At 298 K t-BuOOH rapidly reaches a steady state which is then given by $k_{14}k_{18\,a}/k_{25}k_{18}$. Our experimental measurement of the hydroperoxide yields a value of 3×10^{14} molecule cm⁻³ for this group of rate constants at room temperature. Finally, the rate of removal of t-BuO₂H in experiments where an excess has been added can be used to obtain a value for k_{14}/k_{25} . Here, removal of t-BuO₂H by t-BuO[•] [reaction (25)] competes with acetone production *via* reaction (14). Hence, this ratio can be obtained from instantaneous measurements of the rates of hydroperoxide removal and acetone formation and our data yield $k_{14}/k_{25} \approx 5 \times 10^{14}$ molecule cm⁻³.

At 333 K the t-BuO₂H builds up initially before the concentration starts to level off and similarly added peroxide is now removed at a slower rate than at 298 K. Our experimental results are consistent with the value $k_{18a}/k_{18b} \approx 1$ that is implied by the experiments in the absence of added hydroperoxide, and then yield a value of ca. 10¹⁶ molecule cm⁻³ for the ratio k_{14}/k_{25} . This value is also consistent with the conversion of hydroperoxide into alcohol observed at long photolysis times in the same experiments.

At 373 K methanol production starts to become significant, indicating that reaction (26) is playing a role, and reaction (16) has faded into insignificance. At low oxygen pressures, the degree of conversion of hydroperoxide into methanol gave an approximate value of ≈ 0.4 for the ratio k_{21}/k_{26} at 373 K. This figure is more properly regarded as providing a lower limit because the above analysis ignores reaction (16) which may also compete for removal of CH₃O radicals at low oxygen pressures (*q.v.*).

With added hydroperoxide, the results are critically dependent on the O_2 :t-Bu O_2H ratio. When oxygen was in excess (6:1), the quantum yield for hydroperoxide removal was only 0.4, and the methanol quantum yield was 0.9. With [t-Bu O_2H] > [O_2] the major products (acetone, t-BuOH and methanol) were each formed at several times the photolysis rate, and t-Bu O_2H was removed, also with high quantum efficiency (*ca.* 3). Traces of (t-Bu)₂ O_2 were also formed in these experiments (quantum yield 0.04).

These observations are consistent with replacement of the terminating route (21)-(22) by reaction (26) which regenerates t-BuO₂•. Hence a chain is set up, the length of which is related to the non-terminating/terminating ratio in reaction (18) and to the proportion of t-BuO• radicals that react *via* (25) or (14), respectively. Accurate measurements are difficult in our experiments owing to the rapid consumption of hydroperoxide. However, taking a value of 1.7 for k_{18a}/k_{18b} derived from the measurements in the absence of added hydroperoxide, and $k_{14}/k_{25} \approx 1.6 \times 10^{17}$ molecule cm⁻³ extrapolated from the lower-temperature determinations of this ratio, a simplified steady-state analysis [neglecting reaction (1)] predicts quantum yields of 2-4 for the major products when reaction (26) is the dominant process for removing CH₃O. Our observations with excess t-BuO₂H are consistent with this and the observed dependence on the O₂:t-BuO₂H ratio is consistent with the value $k_{21}/k_{26} \approx 0.4$ derived above.

The results at the different temperatures are summarised in table 2. From this table and a further discussion (q.v.) of the changing non-terminating/terminating ratio in the peroxy combinations reactions (1) and (3), we can draw the following kinetic conclusions.

Analysis of the alcohol and hydroperoxide yields (q.v.) provides values of 1.0 and 1.7 for k_{18a}/k_{18b} at 333 and 373 K, respectively. Simple Arrhenius extrapolation of these figures yields $k_{18a}/k_{18b} \approx 0.6$ at 298 K, this value being preferred to that of 1.5 implied by our independent approximate measurements of k_{14}/k_{25} and $k_{14}k_{18a}/k_{25}k_{18}$ (table 2). These estimates were derived assuming a similar temperature dependence for the ratios k_{18a}/k_{18b} and k_{1a}/k_{1b} . Thus, our results are consistent with a general picture in which the recombination of peroxy radicals (primary-primary, or primary-tertiary) is largely terminating (by ca. 2:1) at room temperature, but becomes increasingly non-terminating channel dominant. Extrapolation of these conclusions to a temperature (> 500 K) typical of cool-flame/auto-ignition phenomena provides additional evidence that non-terminating recombination reactions between peroxy radicals are likely to be of major importance where these radicals are present in high concentration.

We find the ratio k_{14}/k_{25} increases by a factor of *ca*. 20 from 298-333 K. This corresponds to an activation energy of 17 kcal mol⁻¹, which is comparable with the preferred value^{12, 13} of 16.5 kcal mol⁻¹ given in the literature for the thermal decomposition of the t-BuO radical, reaction (14). The same Arrhenius parameters for k_{14} yield a value of 25 s⁻¹ for this rate constant at room temperature and this leads to an estimate of $k_{25} \approx 5 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ from our experimental measurement of k_{14}/k_{25} . More recent data for $k_{14}[k_{14} = 10^{15.5} \exp(-17.0 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$ at high pressure] given by Batt¹⁴ would lead to a much higher value for k_{25} (*ca*. 2×10^{-12} cm³ molecule⁻¹ s⁻¹).

Also, our measurement of k_{21}/k_{26} (< 0.4) at 373 K can be used to estimate k_{26} at this temperature. Recent work^{15, 16} gives $k_{21} \approx 2.6 \times 10^{-15}$ cm⁻³ molecule⁻¹ s⁻¹ at 373 K, and we therefore obtain $k_{26} > 7 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. The published range of error in the rate of reaction (21) is wide and it could be considerably faster (or slower). Furthermore it is difficult to accept a value for k_{25} (t-BuO + t-BuO₂H) substantially higher than that for k_{26} (CH₃O + t-BuO₂H). However, the estimate of 0.4 for k_{21}/k_{26} was derived by neglecting the further terminating reaction (16) and kinetic studies in the presence of added isobutane (reported in greater detail in Part 2) suggest that this reaction is significant at low oxygen pressures and with the t-BuO₂ concentrations present in our experiments. Our estimate of k_{16} is very tentatively placed¹⁷ at ca. 4×11^{-11} cm³ molecule⁻¹ s⁻¹, but this value would imply that our lower

limit for k_{26} is substantially lower than the actual value, perhaps by an order of magnitude or more. Thus the evidence taken together points to a value of at least 10^{-14} and probably nearer 10⁻¹³ cm³ molecule⁻¹ s⁻¹ as a characteristic rate constant describing the abstraction of the hydroperoxidic hydrogen atom by alkoxy radicals in the temperature range 298-373 K. These values are as fast or faster than those reported by Howard and Ingold¹⁸ for a series of analogous reactions in the liquid phase at 303 K. The high value of this rate constant, together with the observed temperature dependence of k_{14}/k_{25} , implies a near-zero activation energy for this class of abstraction reaction, which clearly must be given careful consideration in modelling combustion systems where hydroperoxide is a likely product. Finally, we note that the self-consistent scheme presented above can only be constructed by accepting a value of k_{21} close to the high values favoured in the most recent determinations.^{15, 16} The much lower values suggested by the earlier work of Heicklen and co-workers19, 20 would lead to the anomalous situation of the methoxy abstraction reaction (26) being some orders of magnitude slower than the corresponding process with t-butoxy radicals [reaction (25)].

Our results (table 1) show a pronounced increase in the yield of hydroperoxide relative to that of the alcohols (t-BuOH and MeOH) with increasing temperature, and this is indicative of an increase in the non-terminating/terminating ratios in reactions (1) and (18) with increasing temperature. Unfortunately, the results do not of themselves permit k_{1a}/k_{1b} and k_{18a}/k_{18b} to be determined independently. The steady-state analysis (see Appendix) leads to the following expression relating k_{1a}/k_{1b} and k_{18a}/k_{18b} to the observed product yields.

$$[t-BuO_{2}H] = \frac{k_{18a}}{k_{18b}}[t-BuOH] + \frac{k_{1a}}{2k_{1b}}[MeOH].$$
 (i)

At room temperature k_{1a}/k_{1b} has been estimated³ to be 0.5, and in view of the low methanol yield, the assumption [t-BuO₂H]/[t-BuOH] $\approx k_{18a}/k_{18b}$ is justified. (Thomas and Calvert's results¹⁰ suggest a value of 1 for this ratio, but in view of the discrepancies with the present work this result should be accepted with caution.) As the temperature is raised the methanol yield does not increase; however, it is probable that the increased yield of [t-BuO₂H] is due to increases in both k_{18a}/k_{18b} and k_{1a}/k_{1b} . Thus, the same approximation is unlikely to be valid over the temperature range of the present experiments. A more reasonable assumption is that the non-terminating/ terminating ratios for these similar reactions increase by comparable amounts with increasing temperature. The roughly constant methanol yield [resulting from the terminating channel of reaction (1)] then implies an increasing overall contribution from reaction (1) as the temperature is raised, which is as expected on the basis of the kinetic arguments presented in part 2 of the Results section. Our data can be fitted by values of k_{18a}/k_{18b} of ca. 1.0 at 333 K and ca. 1.7 at 373 K. The corresponding values of k_{1a}/k_{1b} from eqn (i) are ca. 0.85 and ca. 1.3, respectively. A simple Arrhenius extrapolation of these ratios to room temperature yields $k_{18a}/k_{18b} \approx 0.6$ and $k_{1a}/k_{1b} \approx 0.5$, the latter value being in good agreement with the experimental determination.

CONCLUSIONS

(1) The initial combination reaction between t-butylperoxy radicals leads predominantly to t-butoxy radicals, and the major products (acetone, t-butanol, t-butyl hydroperoxide, methanol and formaldehyde) derive from decomposition of the t-butoxy radical and further reaction of its decomposition products. (2) There is a direct termination route from the combination of t-butylperoxy radicals which leads to di-t-butyl peroxide. This route corresponds to *ca*. 0.14 of the total recombination rate at 298 K, although this fraction falls rapidly with increasing temperature. (3) Abstraction reactions between alkoxy radicals (CH₃O· and t-BuO·) and t-butyl hydroperoxide play an important part in the overall reaction and complicate interpretation of the results. These reactions exhibit very low activation energies and proceed with a rate constant of 10^{-13} cm³ molecule⁻¹ s⁻¹ at 298-373 K. (4) Our results over the temperature range 298-373 K are consistent with a mechanism in which recombination between methylperoxy and t-butylperoxy radicals and between two methylperoxy radicals is predominantly terminating at room temperature but becomes increasingly non-terminating as the temperature rises. These observations are consistent with the tenet that bimolecular combinations between peroxy radicals are important, chain-propagating reactions in spontaneous gas-phase oxidation processes.

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APPENDIX

We assume that addition of O_2 to t-Bu[•] and to CH_3 · [reactions (6) and (8)] is fast and irreversible. Further, reaction (22) is considered to be the only removal process for HO_2 · (t-Bu O_2 · radicals are present in high concentration), so that the sequence (21) and (22) is equivalent to reaction (16), but catalysed by O_2 . Then, under conditions where reaction (14) is the only effective removal process for t-BuO[•] and CH₃O[•] is removed by either reaction (16) or (21), the following kinetic expressions are applicable:

$$\frac{d[CH_{3}O_{2}\cdot]}{dt} = k_{14}[t-BuO\cdot] - k_{18}[CH_{3}O_{2}\cdot][t-BuO_{2}\cdot] - 2k_{1}[CH_{3}O_{2}\cdot]^{2}$$
$$\frac{d[CH_{3}O\cdot]}{dt} = k_{18a}[CH_{3}O_{2}\cdot][t-BuO_{2}\cdot] + 2k_{1a}[CH_{3}O_{2}\cdot]^{2}$$
$$-[CH_{3}O\cdot]\{k_{16}[t-BuO_{2}\cdot] + k_{21}[O_{2}]\}$$
$$\frac{d[t-BuO\cdot]}{dt} = 2k_{13a}[t-BuO_{2}\cdot]^{2} - k_{14}[t-BuO\cdot] + k_{18a}[CH_{3}O_{2}\cdot][t-BuO_{2}\cdot].$$

The lifetimes of these radicals are very short compared with that of $[t-BuO_2^{+}]$ and we therefore place them in steady state during the recombination process. The following solutions for the radical concentrations are then obtained

$$[CH_{3}O_{2}^{\cdot}] = \frac{k_{18b}}{4k_{1}}(\phi - 1)[t - BuO_{2}^{\cdot}]$$

$$[CH_{3}O^{\cdot}] = \frac{\left\{\frac{(\phi - 1)}{4k_{1}}k_{18b}\left(\frac{k_{18a}}{k_{18b}} - \frac{k_{1a}}{k_{1}}\right) + 2k_{13a}\frac{k_{1a}}{k_{1}}\right\}[t - BuO_{2}^{\cdot}]^{2}}{k_{16}[t - BuO_{2}^{\cdot}] + k_{21}[O_{2}]}$$

$$[t - BuO^{\cdot}] = \left(2k_{13a} + \frac{k_{18a}k_{18b}}{4k_{1}}(\phi - 1)\right)\frac{[t - BuO_{2}^{\cdot}]^{2}}{k_{14}}$$

$$= \left(1 + \frac{16k_{1}k_{13a}}{k_{13}}\right)^{\frac{1}{2}}.$$

where $\phi = \left(1 + \frac{16k_1k_1}{k_{18b}}\right)^{-1}$

11

d*t*

Defining the overall termination rate coefficient, k_{t} , such that

$$-\frac{\mathrm{d}[\mathrm{t}-\mathrm{BuO}_{2}\cdot]}{\mathrm{d}t} = 2k_{t}[\mathrm{t}-\mathrm{BuO}_{2}\cdot]^{2}$$

we obtain [neglecting reaction (13b)]

$$k_{1} = k_{13a} \left(1 + \frac{k_{1a}}{k_{1}} \right) + \frac{k_{18b}}{8k_{1}} (\phi - 1) \left(k_{18} + k_{18a} - \frac{k_{18b}k_{1a}}{k_{1}} \right)$$

The rates of product formation are given by:

$$\frac{d[acetone]}{dt} = \left(2k_{13a} + \frac{k_{18a}k_{18b}}{4k_1}(\phi - 1)\right)[t - BuO_2 \cdot]^2$$

$$\frac{d[t - BuOH]}{dt} = \frac{k_{18b}^2}{4k_1}(\phi - 1)[t - BuO_2 \cdot]^2$$

$$\frac{d[t - BuO_2H]}{dt} = \left\{\frac{(\phi - 1)}{4k_1}k_{18b}^2 \left(\frac{k_{18a}}{k_{18b}} - \frac{k_{1a}}{k_1}\right) + 2k_{13a}\frac{k_{1a}}{k_1}\right\}[t - BuO_2 \cdot]^2$$

$$\frac{d[CH_3OH]}{dt} = \frac{k_{1b}k_{18b}^2}{16k_1^2}(\phi - 1)^2[t - BuO_2 \cdot]^2.$$

Each expression is second order in t-BuO₂, and so the relative product yields are independent of radical concentration. During an extended period of photolysis, with t-BuO₂ itself in steady state, we have:

$$2P = 2k_t [t-BuO_2 \cdot]^2$$

where P is the photolysis rate, and the following relationships may be shown:

$$\frac{d}{dt}[acetone + t-BuO_{2}H + t-BuOH] = 2P$$
$$\frac{d}{dt}[acetone - CH_{3}OH] = P.$$

Note that the conditions under which reaction (1) may be neglected are:

when
$$(\phi - 1) = \frac{8k_1k_{13a}}{k_{18b}^2}$$
 and $k_t = 2k_{13} + \frac{k_{18a}}{k_{18b}}$

and the product quantum yields are given by:

$$\frac{d[acetone]}{dt} = P$$
$$\frac{d[t-BuOH]}{dt} = \frac{k_{18\,b}}{k_{18}}P$$
$$\frac{d[t-BuO_2H]}{dt} = \frac{k_{18\,a}}{k_{18}}P.$$

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