

The C-3 hydrocarbons were determined by inserting decomposition vials equipped with break-seal directly into the helium line at the inlet of the g.l.c. instrument. Since carbon dioxide was found to interfere, a quantity of Ascarite was placed between the vial and the g.l.c. inlet.

Cyclohexanecarboxylic acid and isobutyric acid were determined quantitatively both by g.l.c. and infrared analysis, using their carbonyl stretching absorption bands at 1695 and 1700 cm^{-1} . Both acids were identified qualitatively by comparison of the infrared spectra of authentic samples with those of samples which had been obtained by extraction of decomposition mixtures with 10% sodium bicarbonate solution.

Kinetics Runs. The procedures used in the regular kinetics runs have been described.⁵

The high-pressure equipment employed in these experiments consisted of three main components: a commercial hydraulic hand pump (Blackhawk P-39), a high-pressure intensifier unit, and a reaction autoclave. The intensifier unit and autoclave were of

standard design (see Acknowledgment). The autoclave was immersed in an oil bath whose temperature was controlled to $\pm 0.05^\circ$. The intensifier allowed a maximum working pressure of 10,000 kg./cm^2 .

For the reactions under pressure, carefully degassed samples were transferred to 5-ml. syringes under a nitrogen atmosphere. After filling, each syringe was capped and placed in the autoclave (hexane was used as the pressure transmitting fluid in the autoclave). After its heating period, the pressure was released, and the syringe was removed. A portion of the sample was subsequently weighed and assayed iodometrically.

Acknowledgment. The authors are indebted to the grant agencies which made this work possible.¹ We are also indebted to Dr. Allen D. King, who designed the pressure intensifier and autoclave which were used in the high-pressure experiments,^{3,3} and whose help made the results in Table IV possible.

(33) These items were built in the machine shop, Physics Department, University of Georgia.

The Self-Reactions of *t*-Butylperoxy Radicals

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*Contribution from the California Research Corporation,
Richmond, California. Received April 10, 1965*

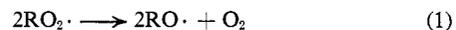
*The self-reactions of *t*-butylperoxy radicals were studied by e.s.r. techniques. It was found that the reaction $2\text{RO}_2 \cdot \rightarrow 2\text{RO} \cdot + \text{O}_2$ has an activation energy of 15.5 ± 1.3 kcal./mole and in benzene proceeds five times as rapidly as the reaction $2\text{RO}_2 \cdot \rightarrow \text{ROOR} + \text{O}_2$ at 22° . The latter reaction appears to be the normal chain-terminating step in systems where *t*-butoxy radical can readily regenerate the peroxy radical. It has a rate constant in benzene of $3.9 \pm 0.5 \times 10^2$ l. mole⁻¹ sec.⁻¹ at 22° and an activation energy of 10.2 ± 1 kcal./mole. The data are suggestive that these two reactions proceed via the fast equilibrium, $\text{RO}_2 \cdot + \text{RO}_2 \cdot \rightleftharpoons \text{ROOOOR}$, involving the tetroxide as an intermediate, although the evidence is not conclusive. If the tetroxide mechanism is correct, it is suggested that the chain-terminating reaction will yield oxygen in the excited $^1\Delta_g$ or $^1\Sigma_g^+$ states rather than the normal $^3\Sigma_g^-$ ground state to avoid change in multiplicity.*

One of the most intriguing problems in free-radical chemistry concerns the detailed mechanism of the self-reactions of tertiary alkylperoxy radicals. Among the reactive radicals which are important intermediates in the oxidation of hydrocarbons, they show uniquely long lifetimes, reflecting a relatively slow self-reaction resulting in radical chain termination. While iodine atoms and methyl radicals exhibit diffusion limited bimolecular association rate constants in solution of about 10^{10} l. mole⁻¹ sec.⁻¹ and the secondary tetralylperoxy radical exhibits a bimolecular chain termination rate constant of about 10^7 l. mole⁻¹ sec.⁻¹, the rate

constant of the much studied cumylperoxy radical is about 10^5 l. mole⁻¹ sec.⁻¹, and, as discussed in this paper, the value for *t*-butylperoxy radicals is in the order of 10^3 l. mole⁻¹ sec.⁻¹. In the former cases the activation energies are essentially nil.

It is thoroughly established from many studies that chain termination in autoxidation reactions is second order in peroxy radical concentration. *A priori* this does not necessarily mean that self-reaction constitutes a radical destroying process in itself. It does imply, however, that the self-reaction is, or is directly related to, the rate-controlling process leading to a termination event.

Detailed study of cumene autoxidation by product analysis¹ and isotopic oxygen exchange² demonstrate that a frequent primary step must involve the head-to-head interaction product, ROOOOR or its nonbonded equivalent, either as a transition state or as an unstable intermediate. The isotopic exchange experiments of Bartlett and Traylor show that for every chain-terminating event at 60° cumylperoxy radicals interact several times without chain termination as in reaction 1. Bartlett and Traylor were unable to



specifically define the chain-termination process in their studies, but suggested a variety of interactions involving fragmentation species of the cumyloxy radical.

(1) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

(2) P. D. Bartlett and T. G. Traylor, *ibid.*, **85**, 2407 (1963).

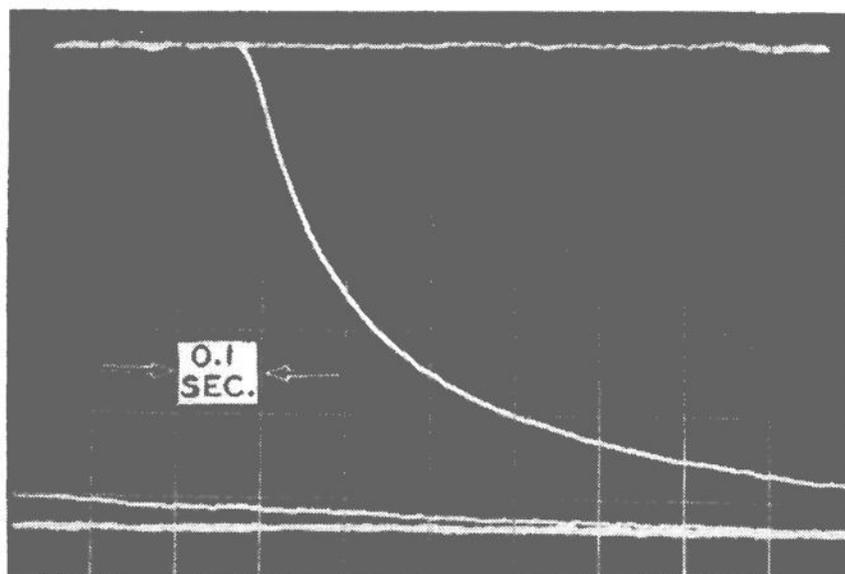
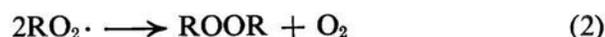


Figure 1. E.s.r. decay curve, $1.7 \times 10^{-3} M$ *t*-butylperoxy radical in methanol ($0.023 M$ Ce^{+4}) at 22° .

Reaction 2 has been frequently used as a convenient



representation of the termination process for peroxy radicals, but experimental evidence for its occurrence has been lacking. However, from a study of the chain decomposition of *t*-butyl hydroperoxide induced by *t*-butyl peroxyoxalate at 45° , Hiatt and co-workers³ have recently provided strong evidence that reaction 2 is the terminating process of *t*-butylperoxy radicals in this type of system. They also furnish good evidence for reaction 1, which from their studies proceeds about ten times as rapidly as reaction 2 at 45° .

In an attempt to elucidate in more detail the nature of these reactions and any others which may be taking place, the self-reactions of *t*-butylperoxy radicals have been studied primarily by observing their kinetic behavior with e.s.r.

Experimental

E.s.r. Decay Studies. A Varian X-band spectrometer equipped with dual cavity and 100-kc. modulation was used. The radicals were generated in two ways: by reaction of ceric ammonium nitrate with *t*-butyl hydroperoxide in a stopped-flow system, and by photolysis of the hydroperoxide. In the stopped-flow experiments, an efficient mixer similar in design to that of Dixon and Norman⁴ was fed from nitrogen-pressured reactant vessels. The outlet of the mixer fed a highly fluted tube of 0.5-cc. volume which ensured complete mixing of the solution before it entered the flat, e.s.r. measurement cell. Measurements were made at a constant flow rate which allowed the flowing solution to enter the measurement zone 0.075 sec. after leaving the mixer. Under all conditions studied, every evidence indicated that the reaction was complete before the solution entered the measurement zone. Radical concentrations were varied by changing the concentration of reactants, although a very large excess of either ceric or hydroperoxide was present in each case to ensure rapid and complete reaction. The spin-lattice relaxation time of *t*-butylperoxy radical is not known but is probably in the order of 10^{-6} sec. With the 0.075-sec. delay between the mixer outlet and

(3) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964).

(4) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

measurement zone, there could be no chance that thermal equilibrium of the spin system was not established. A manually operated valve, which was not limiting in any of these measurements, served for stopping flow. Initial radical concentrations were monitored during steady-state flow on a standard Varian recorder and the decay was recorded on a Tektronics 564 storage oscilloscope. The decay trace, an illustrative example of which is given in Figure 1, was photographed and then analyzed. Variable, noise-filter networks were used depending upon the radical concentration. The network time constant was always maintained at least ten times as fast as the decay process being studied and thus had no measurable effect upon the decay characteristics. In-place calibration of the system was done with freshly prepared solutions of DPPH of known concentration in methanol, appropriate integrations being performed in all cases. A standard sample, always present in the dual cavity, allowed correction to be made for variations in spectrometer sensitivity due to solvent-induced variations in cavity Q.

In the photolysis experiments, hydroperoxide was introduced into the cell *via* the flow system. A mercury lamp was manually switched off after steady-state conditions were reached, and the decay was monitored as above.

Steady-State Measurements during Chain Decomposition of Hydroperoxide. Determinations of the steady-state concentration of peroxy radicals in the chain decomposition of the hydroperoxides were made with the equipment and in the manner previously described.⁵ Chain decomposition was initiated at known rates with azobisisobutyronitrile (AIBN) in the presence of oxygen in benzene.

Oxygen Evolution during the Chain Decomposition of Hydroperoxide. The rate of oxygen evolution during AIBN-induced decomposition of hydroperoxide in the presence of oxygen was determined with the same equipment previously used for studying autoxidation rates.⁶

Materials. C.P. solvents and reagent grade ceric ammonium nitrate were used as received. Eastman AIBN was recrystallized from methanol. Lucidol *t*-butyl hydroperoxide, used as received, was assayed by iodometric titration. Cumene hydroperoxide was purified *via* the sodium salt.

Results

Chain Decomposition of Hydroperoxide. The study of oxygen evolution during AIBN-initiated chain decomposition of *t*-butyl hydroperoxide confirmed the results previously given by Hiatt and co-workers who monitored hydroperoxide disappearance. In full agreement with their results, the rate of oxygen evolution was observed to be first order in AIBN concentration over an eightfold range. It was independent of the concentration of hydroperoxide over the range studied, 0.21 to 1.56 *M*. Figure 2 shows an illustrative example of the data, oxygen evolved *vs.* time at constant AIBN concentration and two hydroperoxide concentrations. The ratio, oxygen evolution rate (moles l^{-1} sec^{-1}) to the known initiation rate (moles l^{-1} sec^{-1}), was

(5) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 591 (1963).

(6) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2930 (1962).

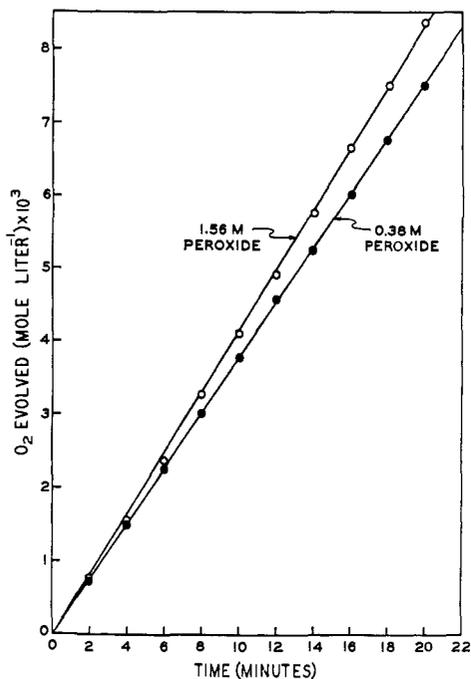


Figure 2. Oxygen evolution against time in AIBN-catalyzed decomposition of *t*-butylhydroperoxide; [AIBN] = 0.13 M; 57°.

found to be 9.0 at 65°, 7.0 at 57.2°, 5.8 at 50.0°, 5.1 at 45.0°, and 4.0 at 36.0°. These contain an additive correction factor of 0.36, since the apparent ratio for AIBN in the initiation step (all measurements based upon volume change) is -0.36 with an efficiency factor for AIBN initiation of 0.68.

Similar experiments with cumene hydroperoxide showed similar dependence of rate upon AIBN and hydroperoxide concentrations. The ratios, oxygen evolution rate to initiation rate, were close to those observed for *t*-butyl hydroperoxide: 3.2 at 38.0°, 4.3 at 45.0°, and 5.2 at 57.2°.

Ce⁺-t-Butyl Hydroperoxide Stopped Flow by E.s.r.
In these experiments the observed half-lives for *t*-butylperoxy radical decay varied over a wide range (0.1 to about 7 sec.) as the initial radical concentration varied from about 3×10^{-3} to about 3×10^{-5} M. Consequently, the establishment of a kinetic order of decay greater than first is certain. This behavior was observed in methanol containing large excess of Ce^{+4} as well as with a large excess of hydroperoxide over Ce^{+4} , thus eliminating either methanol or Ce^{+4} as being involved in the rate-controlling decay process. In the low-concentration range each individual experiment gave reasonably good, second-order plots over the concentration range which could be studied in any one decay experiment. Figure 3, curve 1, shows a second-order plot of 7.9×10^{-5} M *t*-butylperoxy radical generated by reaction of 0.023 M ceric ammonium nitrate with 4×10^{-4} M hydroperoxide.

In Table I, the apparent second-order decay constant for low initial radical concentrations studied under several extreme reactant conditions are presented. The data have been analyzed by the relation

$$\frac{-d[RO_2\cdot]}{dt} = 2k[RO_2\cdot]^2$$

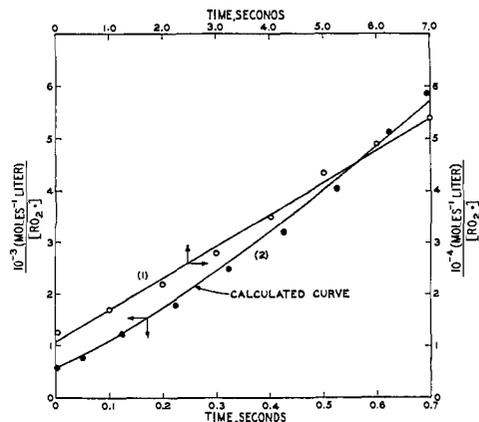


Figure 3. Second-order decay plots at 22°; initial radical concentration: (1) 7.9×10^{-5} M; (2) 1.7×10^{-3} M.

It should be kept in mind that at the moment no mechanistic conclusions are implied by the analysis used.

Table I. Decay Constants for *t*-Butylperoxy Radicals with Initial Concentrations in the Range 4×10^{-5} to 8×10^{-5} M at 22°

Conditions	Decay constant $\times 10^{-3}$, l. mole ⁻¹ sec. ⁻¹
0.023 M Ce^{+4} , 4×10^{-4} M <i>t</i> -butyl hydroperoxide in methanol	8.2 ± 2
1.11 M <i>t</i> -butyl hydroperoxide, 4×10^{-4} M Ce^{+4} in methanol	11.0 ± 2
Photolysis (neat hydroperoxide)	4.2 ± 0.7
0.023 M Ce^{+4} , 4×10^{-4} M <i>t</i> -butyl hydroperoxide in water	25 ± 5

While second-order decay was observed at low radical concentrations (as noted above this was also true in photolysis experiments), decay in the higher concentration range, the order of 10^{-3} M, was no longer pure second order but appeared more accurately represented as a combination of first- and second-order processes. In Figure 3, curve 2, the second-order plot for radical decay at an initial concentration of 1.7×10^{-3} M illustrates this point. While the deviation from second order is not great, this behavior was consistently and repeatedly observed. Unfortunately, radical concentrations higher than about 3×10^{-3} M, where one might hope to observe pure, first-order decay, could not be reliably studied with the present technique. While the proof, by these experiments, that radical decay does become first order at high concentration levels is not conclusive, this fact is indicated, and emphasis will be placed upon this possibility in the Discussion section.

The decay characteristics of *t*-butylperoxy radicals at initial concentrations near 3×10^{-3} M were also studied at temperatures of about 5°. The equipment is not well suited to temperatures other than room temperature, but by prechilling the two reactant solutions and measuring the solution temperature as it left the exit of the e.s.r. cell a rough determination of the temperature coefficient could be made. Under the above-stated conditions, the second-order decay plot resembled that of curve 2 in Figure 3, and the linear

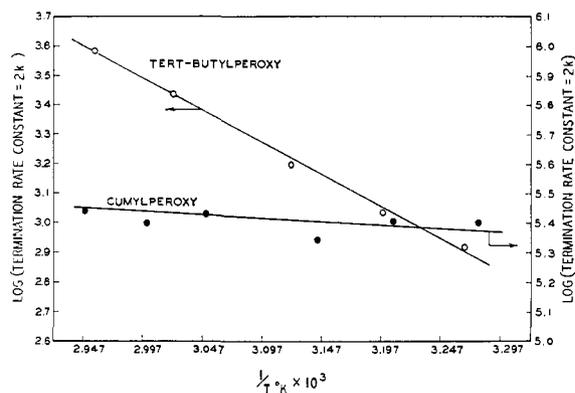


Figure 4. Log (termination rate constant $2k$) vs. $1/T$ ($^{\circ}\text{K}$).

part of the curve corresponded to a second-order decay constant of $9 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. Consequently, an approximate 18-kcal. activation energy is associated with the decay process. A similar value is indicated by results given in the next section.

*Steady-State Determination of *t*-Butylperoxy Radical Concentration during Chain Decomposition of Hydroperoxide.* These experiments, done in benzene under oxygen with AIBN initiation, were analyzed by the normal steady-state expression

$$[\text{RO}_2\cdot]_{\text{ss}} = \left(\frac{R_i}{2k}\right)^{1/2}$$

where R_i is the AIBN initiation rate. Once again no mechanistic significance is necessarily to be attached to the quantitative value of $2k$ derived. It is true, however, that the measurement must give a bona fide value of the radical termination rate even though the mechanistic route to this value may, at the moment, be undetermined. Three completely independent sets of determinations were made at four temperatures between 36.0 and 65.0° . The activation energy of k was found to be $10.2 \pm 1 \text{ kcal./mole}$, and the 22° value of $2k$ was $3.9 \pm 0.5 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. A typical plot of $\log 2k$ vs. $1/T$ ($^{\circ}\text{K}$.) is shown in Figure 4. The experiments were conducted with *t*-butyl hydroperoxide concentrations of both 1.56 and 0.38 and an AIBN concentration of 0.1 M . Throughout these studies the initiation rate by AIBN at 0.1 M was taken to be $7.7 \times 10^{-7} \text{ mole l.}^{-1} \text{ sec.}^{-1}$ at 57.2° , an established value.⁶ The initiation rate at other temperatures was obtained by extrapolation from this value using an activation energy of 30.9 kcal. which appears correct to within $\pm 0.2 \text{ kcal.}$ ^{7,8} The measured, steady-state radical concentrations were the order of 10^{-5} M .

Steady-State Determination of Cumylperoxy Radical Concentration during Chain Decomposition of Hydroperoxide and Autoxidation of Cumene. Because of the unexpectedly large activation energy associated with the self-termination reaction of *t*-butylperoxy radicals indicated above, the same equipment and procedures were used to study cumylperoxy radical self-termination. The rotating sector results of Melville and Richards⁹ have shown the activation energy of the

(7) M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3712 (1955).

(8) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

(9) H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).

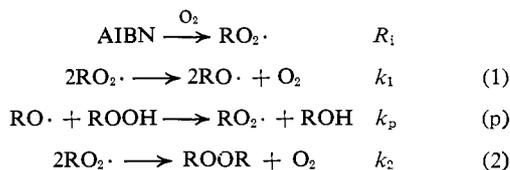
latter reaction to be essentially zero, a result which was roughly confirmed by e.s.r. measurement of the steady-state cumylperoxy radical concentration during the autoxidation of cumene at known initiation rates.⁵ A more careful repeat of these experiments in the present study, over the temperature range 38 to 73° , shows the activation energy of this reaction to be $0 \pm 1 \text{ kcal./mole}$. In addition, the steady-state cumylperoxy radical concentrations existing during the AIBN-catalyzed decomposition of cumene hydroperoxide, exactly analogous to the *t*-butyl hydroperoxide experiments described above, were determined over the temperature range 32 to 68° . These experiments yielded an activation energy of $2.0 \pm 1 \text{ kcal./mole}$ for the chain-termination reaction of cumylperoxy radicals; data are shown in Figure 4. Consequently, it would appear that the large activation energy indicated above for the termination reaction of *t*-butylperoxy radicals is reliable.

Miscellaneous. The stated reliabilities of the various results given represent the mean deviation of several completely independent determinations done at different times. The largest uncertainty arises from determining the absolute radical concentrations. At any given time with all equipment in place, the experimental observations could be repeated with reasonably good precision, about $\pm 10\%$. The repeatability between different sets of duplicate experiments was only good to about $\pm 50\%$, however.

Within experimental error the g -value of *t*-butylperoxy radical was the same in methanol containing excess Ce^{+4} as it was in benzene with radicals generated by oxidation of hydroperoxide, $g = 2.0146 \pm 0.0001$. The line width, which is anomalously large, varied only slightly. At no time did the spectrum give indication that a radical other than *t*-butylperoxy was present. Large concentrations (0.01 M) of the paramagnetic ion Ce^{+3} did not influence the decay kinetics either in Ce^{+4} -hydroperoxide cases nor in the photolysis experiments.

Discussion

The kinetic results of Hiatt and co-workers on the chain decomposition of *t*-butyl hydroperoxide strongly suggest that chain termination results directly from the self-reaction of *t*-butylperoxy radicals. The results presented here, which are capable of greater accuracy than the technique used by these authors, confirm their observations and prove conclusively that chain termination occurs in this manner. The possibility that either free *t*-butoxy radicals or fragmentation species derived therefrom are involved in the termination event is excluded by the lack of dependence of rate upon hydroperoxide concentration. The mechanism under discussion is as follows.



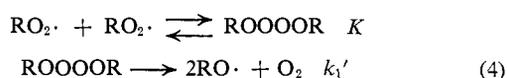
The steady-state rate of oxygen evolution is given by eq. 3, where the ratio k_1/k_2 gives the relative occurrence of the nonterminating reaction of *t*-butylperoxy radicals

$$\frac{d[\text{O}_2]}{dt} = \frac{R_1}{2} \left(1 + \frac{k_1}{k_2} \right) \quad (3)$$

to that which results in chain termination. From the data given in the Results section, k_1/k_2 is seen to have the value of 13.0 at 57.2° and to decrease with temperature with a difference in activation energies of reactions 1 and 2 of 5.3 ± 0.3 kcal./mole. The value of k_1/k_2 at 22°, the temperature of the stopped-flow experiments, is then 5.0; and it is expected that the e.s.r. decay data, when taken under conditions such that peroxy radicals cannot be regenerated, would correspond essentially to the value of $2k_1$.

From determinations of the steady-state radical concentration during chain decomposition of the hydroperoxide, which give a measure only of reaction 2, uninfluenced by reaction 1, $2k_2$ is seen to have the value 3.9×10^2 l. mole⁻¹ sec.⁻¹ at 22°. Consequently, the e.s.r. decay experiments might be expected to have values the order of 10^3 l. mole⁻¹ sec.⁻¹ when run under conditions such that *t*-butylperoxy radicals cannot be regenerated from hydroperoxide by reaction with *t*-butoxy radicals. Reference to Table I shows that the decay constants reported there have approximately the expected values within the limits of experimental error and in view of the different solvent media employed. The effect of solvent appears large (a 20-fold variation between benzene and water). However, the decay constant observed with Ce⁴⁺-produced radicals in excess hydroperoxide in methanol does not show the expected drop to the value of $2k_2$. This may arise from the competitive reaction of *t*-butoxy radicals with methanol, the resulting radicals decaying rapidly in processes not influencing the rate-controlling self-reaction of *t*-butylperoxy radicals.

One of the most important results of the decay experiments is the possible trend toward first-order kinetics at high concentration. It must be admitted that the evidence is not conclusive, only suggestive. Nevertheless, the trend has a ready explanation if it is assumed that *t*-butylperoxy radicals are in rapid equilibrium with the tetroxide, existing as a true intermediate, and if the decomposition of the tetroxide determines the subsequent chemistry. This mechanism for radical decay is given in eq. 4, where a fast disappearance of *t*-butoxy radicals in a manner not involving *t*-butylperoxy radicals is assumed, and leads to the kinetic relationship for peroxy radical decay given by eq. 5.



$$t = \left\{ \frac{1}{2k_1'K[\text{RO}_2\cdot]_t} - \frac{1}{2k_1'K[\text{RO}_2\cdot]_0} \right\} + \frac{4.6}{k_1'} \log \frac{[\text{RO}_2\cdot]_0}{[\text{RO}_2\cdot]_t} \quad (5)$$

By this formulation the apparent second-order decay constants given previously in Table I and those identified as $2k_1$ in the preceding sections become identically $2k_1'K$. Equation 5 has been used to fit the data of Figure 3, curve 2, with the values $K = 158$ l. mole⁻¹ and $k_1' = 30$ sec.⁻¹; $2k_1'K = 9.5 \times 10^3$ l. mole⁻¹ sec.⁻¹. The solid line in Figure 3, curve 2, is calculated with these parameters and fits the data nicely. Equally good fit was obtained with a number of decay experi-

ments having initial radical concentrations of 3×10^{-3} to 1×10^{-3} mole l.⁻¹. While eq. 5 with the above stated parameters gives good fit of the experimental data, our inability to actually observe first-order decay and the lack of sensitivity of the data to this criterion render the analysis indicative rather than conclusive.

In support of the idea that *t*-butylperoxy radical interaction proceeds through the tetroxide, it should be noted that Milas and Djokic¹⁰ have reported the isolation of di-*t*-butyl tetroxide as a crystalline material at -78°. At temperatures of -30 to 0°, the material is reported to decompose to equivalent amounts of oxygen and di-*t*-butyl peroxide. Further circumstantial support for this idea is available from the observation of Ingold and Morton who recently reported, without comment, that the low-temperature decay of *t*-butylperoxy radicals produced by photolysis and studied by e.s.r. is first order.¹¹

However, Benson,¹² on the basis of estimated heats of reaction, has recently argued that the tetroxide cannot have sufficient stability to be isolated at -78° due to an estimated rapidity of reaction 1, to which he assigns a ΔH of -2 ± 10 kcal. and makes the reasonable assumption that $\Delta E_{\text{act}} \approx \Delta H$ for this reaction. The present results are in conflict with this conclusion, however, since by two completely independent procedures the activation energy of eq. 1 is observed to be 15-18 kcal. By these data, the lifetime of the tetroxide at -78° would be several hours, at least with respect to reactions 1 and 2. Benson estimates the heat of the dimerization reaction of *t*-butylperoxy radicals to give tetroxide to be -4 ± 12 kcal., indicating only weak stability of the latter with respect to the former. The present results agree with this idea since the slight deviation from second-order decay kinetics observed at high radical concentrations shows no temperature dependence (although the decay rate does).

One additional fact must be incorporated into this over-all picture, namely, that Ingold and Morton observed a lifetime for *t*-butylperoxy radicals at -78° of only several minutes and an activation energy of only several kilocalories/mole. If all of the experimental data under discussion are assumed to be correct, one must conclude that an additional interaction of *t*-butylperoxy radicals other than reactions 1 and 2 takes place with low probability and small activation energy. A possibility might be a head-to-tail interaction to give di-*t*-butyl peroxide and O₂ (³Σ_g⁻) from radicals of like spin or the peroxide and O₂ (¹Δ_g) from radicals of unlike spin.

It is difficult to understand the difference in activation energies for what appear to be comparable reactions of *t*-butylperoxy and cumylperoxy radicals. As noted in the Results section, the AIBN-catalyzed decomposition of cumene hydroperoxide appears quantitatively similar to that for *t*-butyl hydroperoxide even though the activation energies differ. At low temperatures a change in mechanism for *t*-butylperoxy radicals is clearly indicated by the results of Ingold and Morton. If this mechanism is identified with that

(10) N. A. Milas and S. M. Djokic, *Chem. Ind. (London)*, 405, (1962).

(11) K. U. Ingold and J. A. Morton, *J. Am. Chem. Soc.*, **86**, 3400 (1964).

(12) S. W. Benson, *ibid.*, **86**, 3922 (1964).

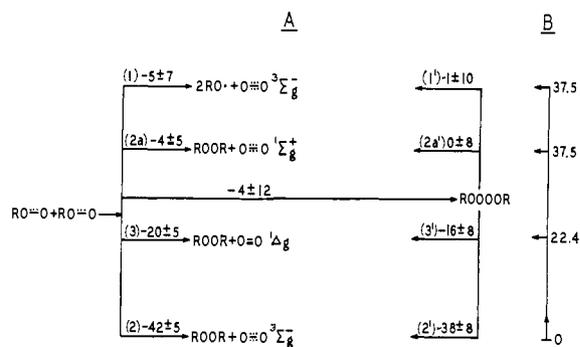


Figure 5. (A) Gas phase heats of reaction of *t*-butylperoxy radicals in kilocalories based upon estimates given in ref. 12. (B) Reaction heats relative to most exothermic possibility. Differences taken from accurately known dissociation energy of di-*t*-butyl peroxide and various electronic states of oxygen.

prevailing for cumene at higher temperatures one is faced with accounting for an extraordinarily small pre-exponential factor.

On purely empirical grounds, the tetroxide mechanism is appealing. Figure 5 lists the various reactions which have been under discussion, together with heats derived from Benson's estimates. If the self-reaction of *t*-butylperoxy radicals proceeds in this fashion, an interesting consideration arises concerning the chain-termination reaction. Decomposition of tetroxide to peroxide and oxygen in its ground state ($^3\Sigma_g^-$) reaction 2, energetically the most favored, is unlikely since it involves a change in multiplicity. This same feature should prevent solvent cage recombination of the *t*-butoxy radicals of reaction 1 (Figure 5), decomposition of tetroxide to ground-state oxygen, and butoxy radicals, where only about 10^{-9} sec. are available for geminate pair recombination. Since the spin-lattice relaxation time of radicals such as *t*-butoxy is probably the order of 10^{-6} sec., cage recombination should not occur. Consequently, if the tetroxide is a true intermediate, reaction 3 producing peroxide and singlet oxygen ($^1\Delta_g$) would be expected to be the preferred chain-terminating reaction. Reaction 2a to yield di-*t*-butylperoxide and oxygen ($^1\Sigma_g^+$) also appears energetically feasible. The spin-conservation restriction is, of course, removed if *t*-butylperoxy radicals react *via* a transition state in which the radicals have similar spins in eq. 1 or in either the head-to-head or head-to-tail formulation of eq. 2.

Frequently, it is very convenient to be able to estimate the heats of radical reactions from individual bond dissociation energies and the assumption that these remain

constant. In the cases of present interest these assumptions work well except for those reactions in which oxygen is a product. Thus, if the energy of a three-electron bond is taken as one-half that of the normal single bond,¹³ the estimated heats of reaction for this type of reaction agree very well with the more elaborate estimates of Benson as shown in Table II. When ground-state oxygen is a reaction product, an additional heat term must be included to account for the coupling interaction of the two three-electron bonds.¹³ It is this interaction which makes the $^3\Sigma_g^-$ state of oxygen more stable than the $^1\Delta_g$ state and the $^1\Sigma_g^+$ state less stable by about the same amount. Both Pauling¹⁴ and Walsh¹⁵ consider that this interaction term should amount to about 19 kcal./mole, namely about one-half the difference in the $^3\Sigma_g^- - ^1\Sigma_g^+$ states of the oxygen molecule (38 kcal./mole). If this value is used, however, the estimated heats disagree with those of Benson, in cases where oxygen is a product, by just about 19 kcal. From an empirical point of view the best check of the proper value to use is provided by the reaction



since the heats of formation of the two radicals involved appear to be firmly established by experiment.^{16,17} Good agreement is provided by the simple estimate, $\Delta H = 10$ kcal. vs. 8 ± 5 kcal. from the experimental heats of formation of the radicals, if the interaction energy is taken as 38 rather than 19 kcal./mole. The simple estimates given in Table II use this value.

Table II. Estimated Heats of Reaction

	ΔH , kcal.	
	Simple estimate	Ref. 12
$\text{ROOOOR} \rightarrow \text{RO}\cdot + \text{RO}\cdots\text{O}$	19	21 ± 6
$\text{ROOOOR} \rightarrow 2\text{RO}\cdots\text{O}$	0	-4 ± 12
$\text{ROOOOR} \rightarrow 2\text{RO}\cdot + \text{O}\cdots\text{O} (^3\Sigma_g^-)$	0	-2 ± 10
$\text{ROOOOR} \rightarrow \text{ROOR} + \text{O}\cdots\text{O} (^3\Sigma_g^-)$	-38	-38 ± 8

Acknowledgment. The author is grateful to Mr. M. C. Burns for assistance with the experiments and to Dr. R. Hiatt for an account of his work prior to its publication.

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