

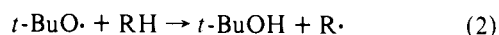
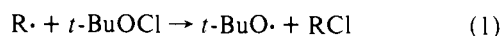
Hydrogen Abstraction by *tert*-Butoxy Radicals. A Laser Photolysis and Electron Spin Resonance Study

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Abstract: The absolute rates of reaction of *tert*-butoxy radicals with a variety of organic substrates in solution have been determined using laser flash photolysis techniques. The relative rates agree well with values obtained from studies of hydrocarbon halogenation by *tert*-butyl hypochlorite or by ESR in the case of ethers and alcohols, while the absolute rates are considerably higher than suggested by previous reports. The absolute rate constants reaffirm the similarity between the behavior of alkoxy radicals and carbonyl triplets. Di-*tert*-butyl peroxide photosensitizes the decomposition of carbon tetrachloride into trichloromethyl radicals and chlorine atoms. The process involves excited peroxide molecules, rather than *tert*-butoxy radicals.

The importance of alkoxy radicals in organic,²⁻⁴ biological,⁵ and atmospheric chemistry⁶ has motivated numerous studies of their reactions. These studies have frequently centered on the *tert*-butoxy radical, reflecting both the availability of several thermal and photochemical sources and the fact that the corresponding peroxide can be handled safely without any special precautions. Many reports have been concerned with the halogenation of organic substrates by *tert*-butyl hypochlorite, reactions 1 and 2.^{2,3,7-10}



When two different substrates R¹H and R²H are used, the relative yields of R¹Cl and R²Cl are a measure of the ratio k_2^2/k_2^1 ,² provided that chlorine chains and electron transfer reactions (vide infra) do not occur. The same reasoning can also be applied to the reaction of only one substrate having two or more reactive sites.^{7a} The pioneering work of Walling,⁷ Ingold,⁸ and Zavitsas⁹ has led to a large number of relative rate constants, as well as to the understanding of the mechanism of reaction and the conditions under which reliable measurements can be carried out.

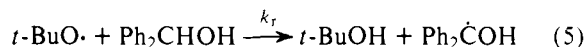
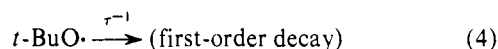
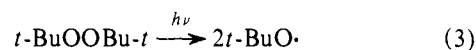
In spite of the large number of relative hydrogen abstraction rate constants which have been determined using the *tert*-butyl hypochlorite technique, the measurement of absolute values has so far been unsuccessful. Attempts to use ESR spectroscopy also have been unsuccessful. A direct measurement of *tert*-butoxy radical lifetimes has not been possible because *tert*-butoxy, like other alkoxy radicals, has so far escaped direct ESR identification.¹¹ Further, attempts to examine by ESR the formation of radicals produced from reactions of *tert*-butoxy radicals with the aim of detecting an induction period have been fruitless as a result of the short time scales associated with these processes and the difficulties in finding a suitable inert solvent.^{12,13}

In this study we have used a nanosecond laser flash photolysis technique and optical absorption spectroscopy to examine the reaction of *tert*-butoxy radicals produced in the photolysis of di-*tert*-butyl peroxide with a number of substrates.¹⁴ We have been able to obtain absolute abstraction rate constants which provide a solid base allowing the conversion of all the relative rate constants into absolute values. Several substrates have been carefully chosen so that absolute rates from previous competitive studies can be obtained in a "one-step" calculation rather than using numerous intermediate ratios. We have also examined the reactions of alcohols and ethers, for which we feel that the studies using the *tert*-butyl hypochlorite technique cannot be expected to be very accurate (vide infra). Further, we have confirmed several ratios of reactivities using ESR

spectroscopy and measured rates of self-termination of ketyl radicals in di-*tert*-butyl peroxide as solvent. This part of the study was carried out in order to provide reliable ESR standards for competitive studies of the reaction of *tert*-butoxy radicals and to evaluate the problems associated with this approach. In particular, the photochemistry of di-*tert*-butyl peroxide in carbon tetrachloride has been examined in some detail.

Results

A. Laser Photolysis Studies. All the laser photolysis experiments discussed in this paper have been carried out at room temperature in a 1:2 mixture of benzene and di-*tert*-butyl peroxide. Two types of approach were used. In the case of diphenylmethanol, the radical produced by hydrogen abstraction can be detected quite easily (λ_{max} 535 nm)¹⁵ and the mechanism can be represented by the reactions



The mechanism assumes that all the modes of decay of the *tert*-butoxy radical are first-order processes (whether true first order or pseudo-first-order). This assumption requires experimental confirmation at the high light intensities available in laser photolysis studies and will be discussed below. Further, the ketyl radical Ph₂ĊOH is regarded as a stable species in the time scale of our experiments. This can be confirmed experimentally from the shape of the plateau obtained in the oscilloscope traces. Under these conditions:

$$-d[t\text{-BuO}\cdot]/dt = (\tau^{-1} + k_r[\text{Ph}_2\text{CHOH}])(t\text{-BuO}\cdot) \quad (6)$$

$$d[\text{Ph}_2\dot{\text{C}}\text{OH}]/dt = k_r[\text{Ph}_2\text{CHOH}][t\text{-BuO}\cdot] \quad (7)$$

$$d[\text{Ph}_2\dot{\text{C}}\text{OH}] = \frac{-k_r[\text{Ph}_2\text{CHOH}]}{\tau^{-1} + k_r[\text{Ph}_2\text{CHOH}]} d[t\text{-BuO}\cdot] \quad (8)$$

and

$$\ln \frac{[\text{Ph}_2\dot{\text{C}}\text{OH}]_{\infty}}{[\text{Ph}_2\dot{\text{C}}\text{OH}]_t - [\text{Ph}_2\dot{\text{C}}\text{OH}]_{\infty}} = (\tau^{-1} + k_r[\text{Ph}_2\text{CHOH}])t \quad (9)$$

$$\ln \frac{A_{\infty}}{A_{\infty} - A_t} = k_{\text{expt}}t = (\tau^{-1} + k_r[\text{Ph}_2\text{CHOH}])t \quad (10)$$

where the subscripts ∞ and t refer to the plateau value and time t , respectively, and A refers to the optical density which was

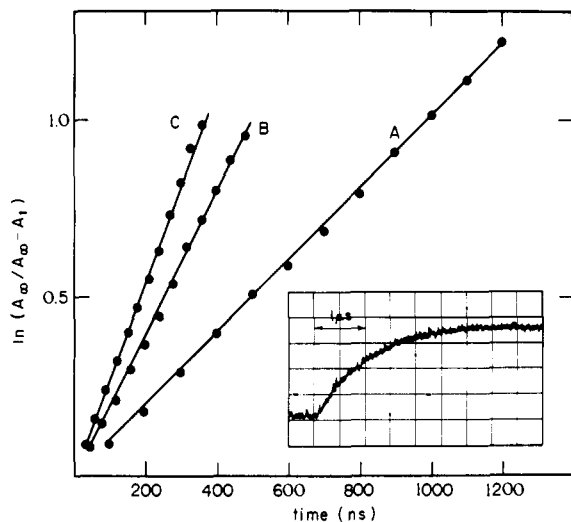


Figure 1. Evaluation of k_{expt} using eq 10 for three concentrations of diphenylmethanol: A, 0.069 M; B, 0.217 M; and C, 0.34 M. Only 12 points out of 50 used in the calculation are shown. Insert: typical oscilloscope trace for diphenylmethanol, 0.069 M.

determined from the corresponding oscilloscope traces. Figure 1 shows three plots which illustrate the evaluation of k_{expt} from the optical density. This approach also involves the assumption that the generation of the *tert*-butoxy radicals is a fast process compared with their decay. The short pulse duration (ca. 20–25 ns) and the fast decomposition of the excited peroxide (vide infra) make us feel confident that this assumption is correct. The experiments illustrated in Figure 1 were carried out under conditions where there is no contribution of second-order processes to the decay of the *tert*-butoxy radicals. The adequate range of pulse intensities was established by irradiating a solution of diphenylmethanol using the maximum available pulse intensity and under conditions of variable attenuation, defined as

$$\text{attenuation} = AT = \frac{\text{maximum power available}}{\text{power used in experiment}} \quad (11)$$

Then, the half-life, $t_{1/2}$, was measured and plotted vs. the attenuation (Figure 2). The mechanism of reactions 3–5 predicts a horizontal line at $t_{1/2} = \ln 2/k_{\text{expt}}$; however, we note that at low attenuation (i.e., high intensity) the plot deviates from this behavior. This is due to the occurrence of second-order processes, in particular, recombination of *tert*-butoxy radicals. The observation that *tert*-butoxy radicals can recombine in the presence of 0.2 M diphenylmethanol probably illustrates the type of radiation doses available better than the actual energy of ~ 80 mJ/pulse for $AT = 1$. All the experiments used for the evaluation of kinetic data were carried out in the plateau of Figure 2, and most of them in the region of attenuations indicated by the shaded segment. Similar types of studies were carried out for different concentrations of diphenylmethanol in order to ensure the validity of the approximation of first-order decay throughout the concentration range.

The value of k_r for diphenylmethanol was obtained from a plot of k_{expt} vs. $[\text{Ph}_2\text{CHOH}]$. From it we obtained $k_r = 6.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $\tau^{-1} = 5.7 \times 10^5 \text{ s}^{-1}$. The value of τ^{-1} is probably determined mainly by reaction 12, while reaction 13 can only be expected to have a minor contribution.^{7d,e}

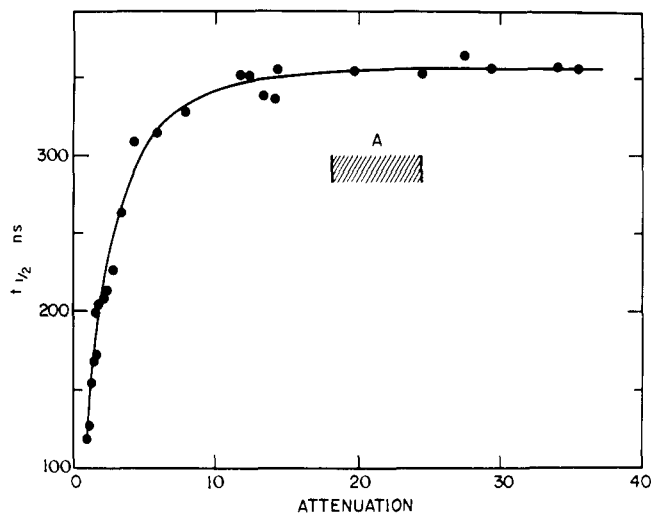
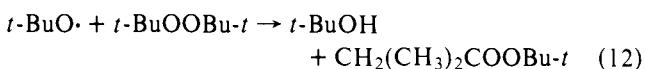
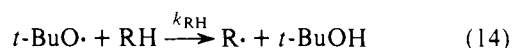


Figure 2. Plot of experimental half-life vs. laser pulse attenuation (see eq 11).

In principle the same technique could be applied to other substrates. The radicals produced in the hydrogen abstraction by *t*-BuO \cdot can also be detected in the case of toluene (e.g., benzyl¹⁶), 1-phenylethanol, and 1,3- and 1,4-cyclohexadiene, but they, in general, have very weak absorption in the visible region, while the UV bands are inadequate because of the absorption due to di-*tert*-butyl peroxide. The spectroscopy of the systems involving the cyclohexadienes will be discussed in detail elsewhere.¹⁷

An alternative approach, which we have used in all other systems, is to use the reaction with diphenylmethanol as a monitor for the reaction of *tert*-butoxy radicals with other substrates. For example, if we monitor the formation of the diphenylhydroxymethyl radical in a system containing diphenylmethanol and a second substrate RH (e.g., toluene) which yields R \cdot in reaction 14, the new rate equations are 15 and 16.



$$\ln \frac{A_\infty}{A_\infty - A_t} = k'_{\text{expt}} t \quad (15)$$

$$k'_{\text{expt}} = \tau^{-1} + k_r[\text{Ph}_2\text{CHOH}] + k_{\text{RH}}[\text{RH}] \quad (16a)$$

$$k'_{\text{expt}} = k_0 + k_{\text{RH}}[\text{RH}] \quad (16b)$$

where k'_{expt} refers to the buildup of the diphenylhydroxymethyl radical in the system.

The corresponding values of k_0 can be obtained from the data for diphenylmethanol presented above or in an independent experiment for that particular value of $[\text{Ph}_2\text{CHOH}]$. Figure 3 shows several representative plots leading to the evaluation of k'_{expt} . The values of k_{RH} are then obtained from plots of $(k'_{\text{expt}} - k_0)$ vs. the concentration of substrate (Figure 4). The excellent agreement obtained when several concentrations of diphenylmethanol are used provides further support to the mechanism proposed.

The laser photolysis experiments require reaction 5 to be the only source of diphenylhydroxymethyl radicals. The question can be raised as to whether the radicals produced in reactions 12, 13, and 14 can abstract from diphenylmethanol. These reactions probably take place; however, their contribution should be negligible in the time scale of our experiments. For example, methyl radicals are about three orders of magnitude less reactive than *tert*-butoxy radicals,¹⁸ and the radicals present in our system should be even less reactive than methyl.

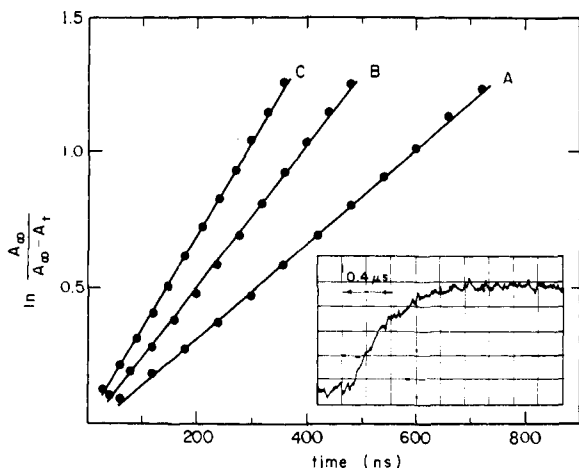


Figure 3. Evaluation of k'_{expt} for 1,7-octadiene, A, 0.067 M; B, 0.54 M; and C, 0.94 M. Concentration of diphenylmethanol (used as a probe) 0.133 M. Only 12 representative points out of 50 used for the calculation have been plotted in each case. Insert: oscilloscope trace for 1,7-octadiene, 0.94 M.

For some of the substrates examined the concentrations used are rather high. Such is the case of methanol and toluene where the concentration by volume approaches, or somewhat exceeds 25%. Since the value of τ is largely determined by reaction 12 the substrates actually replaced the benzene cosolvent, in order to maintain a constant concentration of di-*tert*-butyl peroxide of 67% by volume. Table I gives a summary of all the rate constants obtained. Typical errors should not exceed 10–15%, with the only exception being *tert*-butyl hydroperoxide, for which we were able to determine only one value of k'_{expt} . The problems in this system were associated with the production of benzophenone, which also produces diphenylhydroxymethyl radicals via photoreduction.

Another approach which can be used in order to test the validity of the values of k_0 and k_{RH} obtained is to plot the plateau absorbances as a Stern–Volmer relation, i.e.

$$\Phi_{\text{Ph}_2\dot{\text{C}}\text{OH}} = \Phi_{t\text{-BuO}\cdot} \frac{k_{\text{RH}}[\text{RH}]}{k_0 + k_{\text{RH}}[\text{RH}]} \quad (17)$$

The value of $\Phi_{\text{Ph}_2\dot{\text{C}}\text{OH}}$ is proportional to the plateau value of the optical density:¹⁹

$$\Phi_{\text{Ph}_2\dot{\text{C}}\text{OH}} = \alpha A_\infty \quad (18)$$

and

$$\frac{1}{A_\infty} = \frac{\alpha}{\Phi_{t\text{-BuO}\cdot}} \left(1 + \frac{k_0}{k_{\text{RH}}[\text{RH}]} \right) \quad (19)$$

This approach assumes that the experiments are carried out at constant pulse intensity. Since this is difficult to achieve with a ruby laser the energy of each pulse was measured using a suitable monitor system and the values of A_∞ normalized to constant pulse intensity. Figure 5 shows a Stern–Volmer plot using eq 19 and gives $k_{\text{RH}}/k_0 = 1.1 \text{ M}^{-1}$ vs. 1.2 M^{-1} (from the data in Table I).

Finally, we have observed that the plots of k'_{expt} vs. $[\text{RH}]$ for some alcohols tend to show negative curvature. This was particularly obvious in the case of 1-phenyl-1-ethanol, while there was no indication of curvature in the case of diphenylmethanol¹⁴ or 2-propanol. The value for 1-phenyl-1-ethanol given in Table I corresponds to the zero concentration extrapolation; the curvature mentioned above can be interpreted as a decrease of the activity coefficient with increasing substrate concentration.

B. ESR Studies. We have used ESR techniques in order to measure several ratios of reactivities. They not only confirm the results obtained in laser photolysis experiments, but in fact

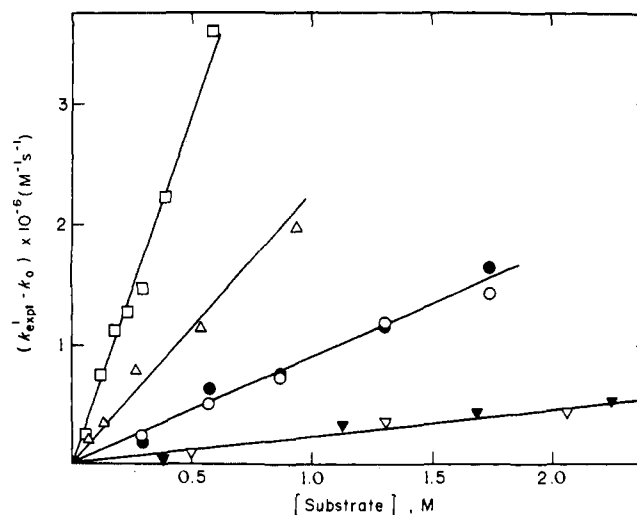


Figure 4. Evaluation of k_{RH} using eq 16b, for cyclohexene (partially), \square ; 1,7-octadiene, Δ ; cumene, \bullet and \circ (for $[\text{Ph}_2\dot{\text{C}}\text{OH}]$ 0.170 and 0.099 M, respectively) and toluene, \blacktriangledown and \triangledown (for $[\text{Ph}_2\dot{\text{C}}\text{OH}]$ 0.167 and 0.088 M, respectively).

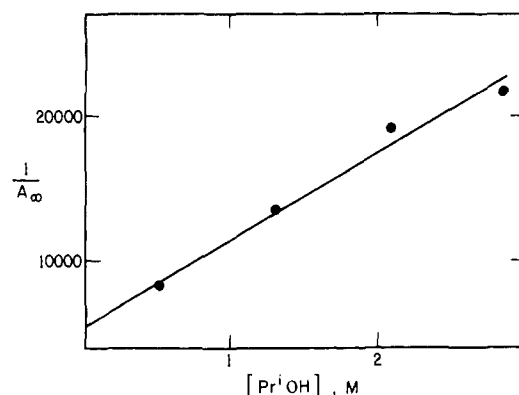


Figure 5. Stern–Volmer plot (eq 19) for 2-propanol. The optical densities have been normalized to constant pulse intensity and are given in arbitrary units. Typical values are in the range of 0.01–0.03.

provide more accurate values in the case of the less reactive substrates like methanol.

UV irradiation of a solution of two substrates, AH and BH, in neat di-*tert*-butyl peroxide leads to the formation of the radicals $\text{A}\cdot$ and $\text{B}\cdot$ via hydrogen abstraction by *tert*-butoxy radicals. The lifetime of the *tert*-butoxy radicals can be assumed to be controlled exclusively by the reactions with AH and BH. Hence, if the decay of $\text{A}\cdot$ and $\text{B}\cdot$ occurs in second-order processes, the rate laws for the stationary (designated by the subscript 0) radical concentrations are given by

$$k_{\text{AH}}[\text{AH}][t\text{-BuO}\cdot]_0 - k_{\text{AB}}[\text{A}\cdot]_0[\text{B}\cdot]_0 - 2k_{\text{AA}}[\text{A}\cdot]_0^2 = 0 \quad (20)$$

$$k_{\text{BH}}[\text{BH}][t\text{-BuO}\cdot]_0 - k_{\text{AB}}[\text{A}\cdot]_0[\text{B}\cdot]_0 - 2k_{\text{BB}}[\text{B}\cdot]_0^2 = 0 \quad (21)$$

where $2k_{\text{AA}}$, $2k_{\text{BB}}$, and k_{AB} are the self- and cross termination rate constants and k_{AH} and k_{BH} represent the rate constants for hydrogen abstraction from AH and BH. For diffusion-controlled radical termination the cross reaction might be approximated by

$$k_{\text{AB}} = 2(k_{\text{AA}}k_{\text{BB}})^{1/2} \quad (22)$$

and combination of eq 20–22 gives

$$\frac{k_{\text{AH}}}{k_{\text{BH}}} = \left(\frac{k_{\text{AA}}}{k_{\text{BB}}} \right)^{1/2} \frac{[\text{A}\cdot]_0 [\text{BH}]}{[\text{B}\cdot]_0 [\text{AH}]} \quad (23)$$

Table I. Rates of Hydrogen Abstraction Obtained Using Laser Flash Photolysis

substrate	max concn ^a	[Ph ₂ CHOH] ^a	$k_{RH} \times 10^{-5}$ ^b	$k_{RH}/k_{\text{toluene}}$		N_{runs}	³ benzophenone $k_{RH} \times 10^{-5}$ ^{b,c}
				this work	lit.		
toluene	2.82	0.080; 0.167	2.3	1.0	1.0	9	1.7
ethylbenzene	2.4	0.167	10.5	4.5	2.3, ² 3.2 ³	5	5.0
cumene ^d	1.72	0.099; 0.170	8.7	3.8	2.8, ² 6.8 ³	10	5.5
mesitylene	2.16	0.133	8.3	3.6	4.0 ^{7a,e}	4	9.3
cyclopentane	2.97	0.133	8.8	3.8	5.0, ² 4.5 ³	4	
cyclohexene	0.79	0.101	57	25	37 ³	8	
1,7-octadiene	0.94	0.133	23	10	11 ^{9c,f}	5	
1,3-cyclohexadiene	0.42	0.133	420	18		5	
1,4-cyclohexadiene	0.53	0.133	540	23		5	
methanol	7.4	0.133	2.9	1.3		2	
ethanol	2.74	0.133	11.0	4.8		3	5.6
2-propanol	2.87	0.134	18	7.8		4	13
2-propanol- <i>d</i> ₈	3.03	0.133	5.5	2.4		5	
1-phenylethanol	1.66	0.133	18 ^g	7.8		5	
diphenylmethanol ^h	0.52	variable	69	30		23	8.9
diisopropyl ether	1.98	0.133	12.0	5.2		9	
tetrahydrofuran	2.95	0.171	83	36	52 ²	5	
tetrahydrofuran- <i>d</i> ₈	0.90	0.133	30	13		3	
<i>tert</i> -butyl hydroperoxide	0.01	0.133	2500 ⁱ	109		1	

^a In M. ^b In M⁻¹s⁻¹. ^c Reactivity of triplet benzophenone, from ref 35. ^d See also ref 14. ^e Taken as 5/6 of the cyclohexane reactivity. ^f Taken as twice the reactivity of 1-octene. ^g Extrapolated to zero substrate concentration. ^h See ref 14 for a plot of the data. ⁱ Based on only one substrate concentration; see text.

Hence, relative hydrogen abstraction rate constants can be evaluated from relative stationary radical concentrations, provided that the value of k_{AA}/k_{BB} is known and the conditions mentioned above are fulfilled.

The values of k_{AA} and k_{BB} were obtained in modulation ESR (MESR)^{20,21} experiments with solutions containing only one substrate (referred to as AH). In these experiments the UV light intensity and hence the initiation of radical A· is modulated harmonically. This leads to an oscillatory radical concentration $[A\cdot](t)$ which in general contains the fundamental Fourier component at the light modulation frequency and higher harmonics. At sufficiently high modulation frequencies ω_L , the amplitude Z_1 and the phase angle ϕ_1 of the fundamental Fourier component are given by^{21,22}

$$Z_1 \approx \frac{I_0}{2} (\omega_L^2 + \tau_{LA}^{-2})^{-1/2} \quad (24)$$

$$\tan \phi_1 \approx -\omega_L \tau_{LA} \quad (25)$$

where I_0 is the peak-to-peak amplitude of the initiation rate and τ_{LA} is a time constant associated with the decay of A·. The relations 24 and 25 allow the determination of τ_{LA} from the frequency dependence of the fundamental amplitude Z_1 and phase ϕ_1 . Additional information about the decay law can be obtained from the amplitude Z_2 of the first harmonic Fourier component at $2\omega_L$. Z_2 has been shown to increase from $Z_2 = 0$ for pure first order to a maximum value for pure second-order decay kinetics. At a modulation frequency given by

$$\omega_L^2 \tau_{LA}^2 = 5 \times 10^{-2} \quad (26)$$

this maximum value amounts to $Z_2 = 0.136Z_1$ ²¹

We have used these features of MESR to evaluate the decay laws and rates of the radicals $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, and $(CH_3)_2CHO\dot{C}(CH_3)_2$ in di-*tert*-butyl peroxide solution. The method is exemplified in some detail for the $CH_3\dot{C}HOH$ radical. Figure 6A shows the frequency dependence of the amplitude h_L of one of the ESR absorption lines of $CH_3\dot{C}HOH$ at the light modulation frequency ω_L . Since h_L is proportional to Z_1 , there is a linear correlation between h_L^{-2} and ω_L^2 (eq 24) and τ_{LA}^2 for the radical A· is obtained from the slope-to-intercept ratio. Figure 6B illustrates

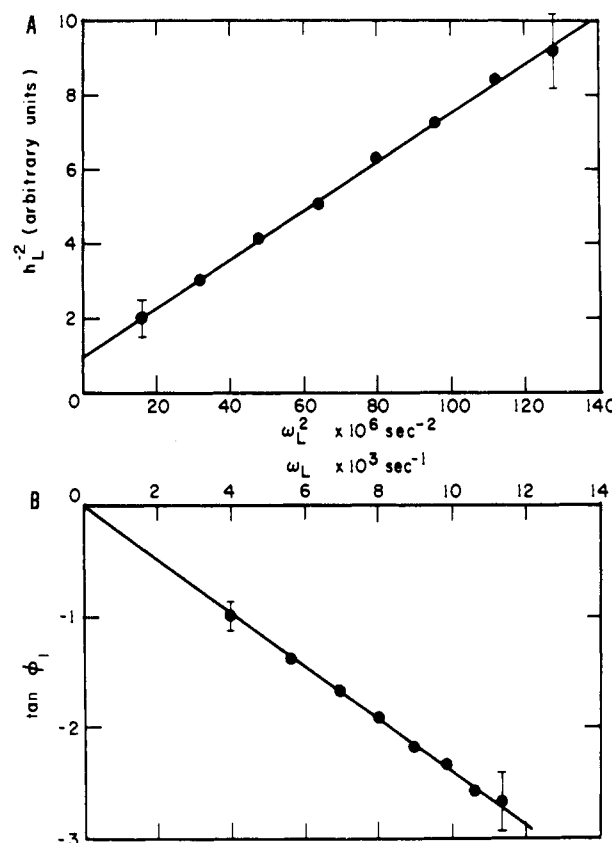


Figure 6. Frequency dependence of the fundamental MESR amplitude h_L (A) and phase ϕ_1 (B) for the $CH_3\dot{C}HOH$ radical.

the plot corresponding to eq 25, also for the case of the $CH_3\dot{C}HOH$ radical. From Figure 6A we obtain $\tau_{LA} = 2.45 \times 10^{-4}$ s and from Figure 6B $\tau_{LA} = 2.42 \times 10^{-4}$ s, in excellent agreement with each other.

Knowing τ_{LA} the decay law is determined by measuring the fundamental and first harmonic amplitudes at the modulation frequency given by eq 26. For $CH_3\dot{C}HOH$ we obtain $Z_2/Z_1 = 0.134 \pm 0.004$, which indicates a second-order decay law.

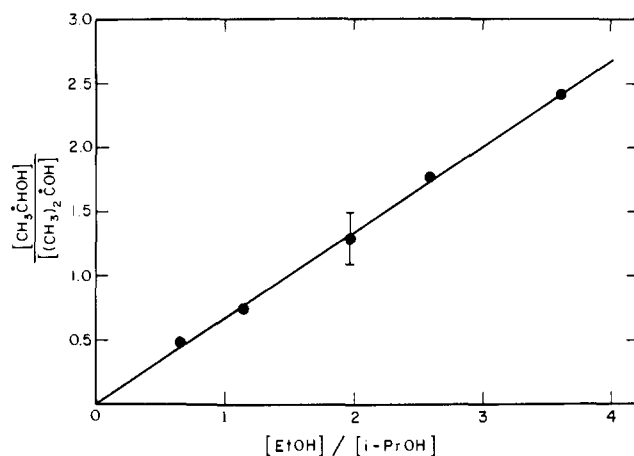


Figure 7. Dependence of the ratio of stationary radical concentration upon the concentration ratio of substrates; see eq 23.

In this case τ_{LA} is given by^{21,22}

$$\tau_{LA} = 4k_{AA}[A\cdot]_0 \quad (27)$$

and the termination rate constant can be evaluated from τ_{LA} and the stationary radical concentration $[A\cdot]_0$.

Table II contains the kinetic results for the radicals examined in this way. The second column gives the values of Z_2/Z_1 which prove the second-order nature of the decay process, and therefore the validity of the rate laws of eq 20 and 21 for the four radicals in di-*tert*-butyl peroxide solution. The termination rate constants given in Table II lie well in the range expected for diffusion-controlled radical terminations. The increase in $2k_{AA}$ by going from 2-hydroxy-2-propyl radicals to hydroxymethyl radicals indicates an increase of the diffusion coefficient with increasing ratios of the radii of the solvent and diffusing solute molecules.²³ The slightly higher rate constant for the ether radical compared to that of the smaller radical from 2-propanol may be due to a difference in the solution viscosities which result from the relatively high substrate concentrations (15% by volume). Since, in addition, the termination rate constants for hydroxymethyl in methanol²¹ and 2-hydroxy-2-propyl in 2-propanol²⁴ have been shown to be controlled by radical diffusion and since the rate constants in Table II lie fairly close together we feel confident that the assumption 22 holds approximately. Thus, relation 23 applies and can be used to evaluate relative hydrogen abstraction rates by *tert*-butoxy radical.

Table III gives the ratios of the hydrogen abstraction rate constants obtained using eq 23, the rates of radical terminations from Table II, and experimentally determined values of $[A\cdot]_0/[B\cdot]_0$.²⁵ The absolute values have been calculated using ethanol as a standard. Figure 7 shows the dependence of the ratio of the stationary radical concentrations in the ethanol-2-propanol system.

To complete this section we would like to comment on a series of experiments which we originally started to determine an absolute rate of hydrogen abstraction by *tert*-butoxy radical using our modulation ESR technique. In an attempt to measure the phase shift caused by the induction period between excitation of the peroxide and formation of radicals due to hydrogen abstraction by *tert*-butoxy radical we tried as an inert solvent carbon tetrachloride, which has been widely used in conjunction with the *tert*-butyl hypochlorite technique. To our surprise, we observed that UV irradiation of a solution of di-*tert*-butyl peroxide (15% by volume) in this solvent without any additional substrates leads to the characteristic ESR absorption pattern of trichloromethyl radicals which were not formed in detectable concentrations in the absence of di-*tert*-

Table II. Rates of Radical Recombination in Di-*tert*-butyl Peroxide at 21 °C

radical	Z_2/Z_1^a at $\omega_L^2\tau_{LA}^2 = 5 \times 10^{-2}$	$2k_{AA}$, $10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\cdot\text{CH}_2\text{OH}$	0.136	5.3 ± 0.4
$\text{CH}_3\dot{\text{C}}\text{HOH}$	0.134	4.4 ± 0.4
$(\text{CH}_3)_2\dot{\text{C}}\text{OH}$	0.133	3.9 ± 0.4
$(\text{CH}_3)_2\text{CHO}\dot{\text{C}}(\text{CH}_3)_2$	0.137	4.1 ± 0.6

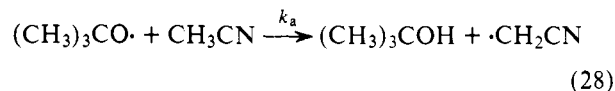
^a Error limit ± 0.004 .

Table III. Relative Rates of Hydrogen Abstraction Obtained by ESR Spectroscopy

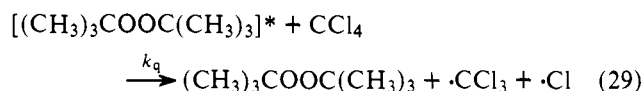
AH	BH	k_{AH}/k_{BH}	k_{BH}^a
EtOH	CH ₃ OH	3.2 ± 0.3	3.4×10^5
EtOH	(CH ₃) ₂ CHOH	0.71 ± 0.05	15.5×10^5
EtOH	[(CH ₃) ₂ CH] ₂ O	0.93 ± 0.07	11.8×10^5
(CH ₃) ₂ CHOD	(CD ₃) ₃ CDOD	2.5 ± 0.3	

^a In $\text{M}^{-1} \text{ s}^{-1}$, with ethanol (see Table I) as a standard.

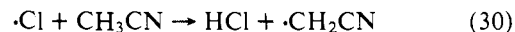
butyl peroxide (note that $\lambda \geq 275 \text{ nm}$). To trace their origin we carried out a series of stationary ESR experiments irradiating solutions of the peroxide in acetonitrile with variable amounts of carbon tetrachloride present. In the absence of CCl_4 the ESR spectrum shows the absorption of $\cdot\text{CH}_2\text{CN}(A\cdot)$ and methyl radical ($M\cdot$) indicating a competitive decay of *tert*-butoxy radical in the reactions 28 and 13.



With addition of increasing amounts of CCl_4 the stationary concentration of $M\cdot$ decreases while that of $A\cdot$ stays essentially constant. The data are given in Table IV. Since, according to gas-phase values, the chlorine abstraction from CCl_4 by methyl radical has a rate constant of only $7.5 \text{ M}^{-1} \text{ s}^{-1}$ (extrapolated to $T = 21 \text{ }^\circ\text{C}$) the most probable interpretation of these experimental results is the quenching of the photoexcited peroxide by CCl_4 :



An analogous reaction is known for the reaction of CCl_4 with excited ketones.²⁶ While reaction 29 can explain the observed decrease of methyl radical concentration with increasing $[\text{CCl}_4]$, the near constancy of $[A\cdot]_0$ is probably due to the abstraction reaction



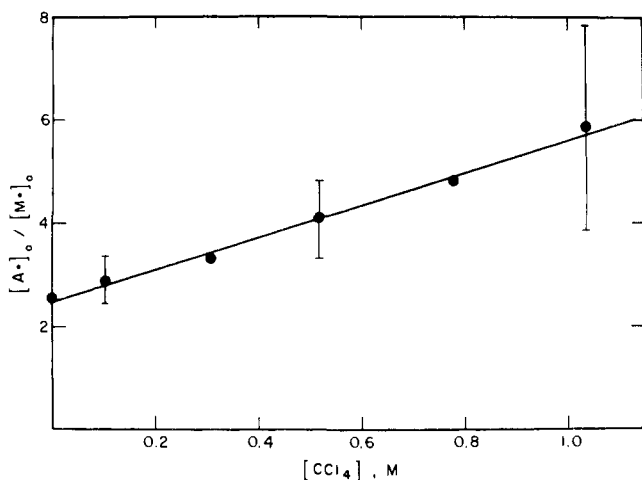
which regenerates $A\cdot$.

To estimate the quenching constant k_q we assume that the lifetimes of *tert*-butoxy radical and $\text{Cl}\cdot$ are dominated by reactions 28, 13, and 30, that the radicals $M\cdot$, $A\cdot$, and $\cdot\text{CCl}_3$ decay in second-order termination reactions, and that eq 22 holds for all cross terminations. A straightforward calculation then yields a Stern-Volmer relation

$$\frac{[A\cdot]_0}{[M\cdot]_0} = \left(\frac{k_M}{k_A}\right)^{1/2} \left\{ \frac{k_a[\text{CH}_3\text{CN}]}{k_s} + \left(1 + \frac{k_a[\text{CH}_3\text{CN}]}{k_s}\right) \frac{k_q}{2k_d} [\text{CCl}_4] \right\} \quad (31)$$

Table IV. Radical Concentrations in CH₃CN and Their Dependence on [CCl₄]

[CCl ₄], M	0	0.104	0.311	0.518	0.777	1.036
[·CH ₃] ₀ , M	1.9	1.7	1.4	1.1	0.9	0.7 × 10 ⁻⁷
[·CH ₂ CN] ₀ , M	4.8	4.9	4.6	4.5	4.3	4.1 × 10 ⁻⁷

**Figure 8.** Data on the photosensitized decomposition of carbon tetrachloride, according to eq 31.

where $[A\cdot]_0$ and $[M\cdot]_0$ are the stationary radical concentrations, k_M and k_A are the self-termination rate constants of the methyl and $\cdot\text{CH}_2\text{CN}$ radicals, and k_d is the rate constant for cleavage of the photoexcited peroxide into two *tert*-butoxy radicals. Figure 8 shows a plot of the concentration ratio $[A\cdot]_0/[M\cdot]_0$ taken from the data in Table IV vs. the carbon tetrachloride concentration. Linear regression yields an intercept value of 2.5. If we assume diffusion control for the self-termination rate constants of methyl and $\cdot\text{CH}_2\text{CN}$ radicals the ratio $(k_M/k_A)^{1/2}$ should be close to unity. Thus, the intercept directly reflects the ratio of the rates for hydrogen abstraction k_a to β -scission k_s in neat acetonitrile:

$$k_a[\text{CH}_3\text{CN}] \approx 2.5k_s \quad (32)$$

Using this value we obtain from the slope in Figure 8 according to eq 31

$$k_d/k_d \approx 1.8 \text{ M}^{-1}$$

If the upper, diffusion-controlled limit for the rate of quenching is taken as $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, then the minimum value for k_d^{-1} is $\sim 0.4 \text{ ns}$.

Discussion

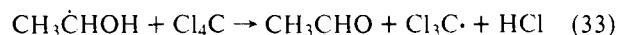
The data shown in Tables I and III include a number of values for alcohols and ethers measured directly and by competition with ethyl alcohol using ESR techniques. The agreement between both methods is good (discrepancy $\leq 15\%$). The rate constant for methanol obtained in ESR experiments is higher than the laser photolysis value. The difference might be a reflection of the higher concentration range used in laser photolysis experiments. In this case we think that the ESR value is a better one, the laser photolysis technique being more accurate for the faster substrates which can compete favorably with diphenylmethanol ($\sim 0.1 \text{ M}$).

Deuterium isotope effects are normal, with typical values (2-propanol and tetrahydrofuran) in the 2.4–3.2 range.

The time profiles obtained in laser photolysis experiments measure the lifetime of the precursor of the detectable species, i.e., $\tau(t\text{-BuO}\cdot)$. That is, the technique measures molecular reactivity rather than the reactivity of one particular site in the molecule (even in the case of diphenylmethanol where the radical is detected directly). In all the examples considered

therein the only site with significant reactivity corresponds to the lowest C–H bond dissociation energy.

The abundant literature on the reactions of *tert*-butoxy radicals provide a good basis for the understanding of their relative reactivities toward a variety of substrates.^{7–10,27} We have tried to include in our measurements substrates frequently used as references; such is the case for toluene^{2,3,28} and cyclopentane.²⁹ We have also examined a number of hydrocarbons for which the relative reactivities are fairly well known (see Table I) in order to verify the consistency of the ratios obtained by laser photolysis with those obtained using the *tert*-butyl hypochlorite technique. A reasonable agreement is usually observed, with a few exceptions, in particular diisopropyl ether, where our value does not agree well with previous measurements.^{7b} This is probably due to the fact that the radicals derived from ethers and alcohols are good electron donors, and their reactions with carbon tetrachloride (a common solvent for the *tert*-butyl hypochlorite technique) are well documented in hydroxylic solvents,³⁰ e.g., reaction 33.



In addition, acids have a strong effect on the inter-³¹ and intramolecular^{7d,e,32} reactions of *tert*-butoxy radicals.

A few rate constants deserve further comment. We are somewhat surprised by the low reactivity of diisopropyl ether as compared with 2-propanol, particularly if the increased number of hydrogen atoms is taken into account. The reactivity of mesitylene is over three times that of toluene; this is in line with previous studies indicating that methyl substitution of the aromatic ring enhances the reactivity.^{7b,8c,33} Other comparisons are also included in Table I; no literature values for alcohols and ethers have been included because of the problems discussed above.

The high reactivity of hydroperoxides had been predicted by Howard⁴ and Ingold.²⁸ We emphasize at this point the need to eliminate hydroperoxide impurities from both the *tert*-butoxy radical source as well as the substrate. Even minor concentrations of hydroperoxides can totally invalidate the results.

All the absolute rate constants measured or estimated in the past are considerably lower than those reported in this paper. The only report which estimated a value reasonably close to those measured by laser techniques is that of Lorand and Wallace,³⁴ who obtained $k_{\text{RH}} \approx 0.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for toluene from a study of the decomposition of *tert*-butyl triphenylperacetate in neat toluene. Using their results and our rate for toluene it is possible to calculate the rate of reaction between *tert*-butoxy radical and triphenylmethyl radicals as $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The reactivity of *tert*-butoxy radicals is very similar to that of carbonyl triplets,³⁵ a similarity which was pointed out by Walling and Gibian³⁶ and Padwa³⁷ and is widely recognized. A comparison of rates of hydrogen abstraction by benzophenone triplet is given in Table I. In another case, acetone triplets³⁸ react with alcohols somewhat slower than *tert*-butoxy radicals and as a result are more selective.

tert-Butoxy radicals have so far escaped direct ESR detection. The report by Weiner and Hammond³⁹ indicating that they had detected *tert*-butoxy radicals in the photolysis of pure peroxide has been seriously questioned by Symons on spectroscopic grounds.⁴⁰ Our evidence confirms Symons' doubts about the identity of the radical; the species detected had a lifetime of a few milliseconds, while under their experimental

conditions the maximum lifetime for *tert*-butoxy radicals would be in the neighborhood of 1 μ s. Further, the longest lifetime for which one can expect a clean second-order decay would be around 100 ns, well beyond the time resolution of conventional ESR techniques. The difficulties in finding an inert solvent and the low extinction coefficient of di-*tert*-butyl peroxide make this problem essentially insolvable at the present time.

Finally, we want to comment on our observation that the photolysis of di-*tert*-butyl peroxide in carbon tetrachloride produces trichloromethyl radicals. We felt that it was important to clarify the origin of these radicals, particularly in view of the fact that carbon tetrachloride has been a popular solvent in studies using the *tert*-butyl hypochlorite technique. Our study (see eq 28–33) indicates that a precursor of the *tert*-butoxy radicals is in fact responsible for this effect, quite probably the excited singlet state; this species must have a lifetime of at least 0.4 ns.⁴¹ On the other hand, our laser photolysis experiments do not show any induction period suggesting that the precursor of the *tert*-butoxy radicals must have a lifetime of less than 20 ns.⁴² Such an upper limit is also consistent with the observation that di-*tert*-butyl peroxide does not fluoresce at room temperature. In summary, our results indicate that the trichloromethyl radicals produced in the photochemistry of the di-*tert*-butyl peroxide–carbon tetrachloride system do not result from reactions of *tert*-butoxy radicals, but rather from the quenching by carbon tetrachloride of an excited state of the peroxide with a lifetime between 0.4 and 20 ns.

Conclusions

The reactions of *tert*-butoxy radicals are considerably faster than suggested by previous studies. It is noteworthy that a similar observation has been recently reported from this laboratory in the case of the phenyl radical.⁴³ In fact, the reasons why both alkoxy and phenyl radicals eluded the determination of absolute rates for a long time are similar; the high reactivity of these radicals requires a suitable fast technique in most organic media, or an inert solvent in which the lifetime becomes long enough for adequate monitoring. The absolute rates reported in this study (Table I) provide a basis allowing the conversion of relative values from earlier reports into absolute rate constants.

Carbon tetrachloride undergoes sensitized photodecomposition when irradiated in mixtures with di-*tert*-butyl peroxide. The effect should be attributed to the interaction of photoexcited peroxide with carbon tetrachloride.

Experimental Section

Materials. Di-*tert*-butyl peroxide (MCB) was distilled and treated in an alumina column. This purification was found suitable for all experiments, and peroxide from other sources (Fluka or K & K) gave the same results. Benzene (Aldrich, Gold Label) was used as received. Carbon tetrachloride (Mallinckrodt) was fractionally distilled twice. Aliphatic alcohols (spectroquality) were used as received as was 2-propanol-*d*₈ (Aldrich). All hydrocarbons were routinely distilled and treated on an alumina column and their purity was checked by VPC.

Diphenylmethanol (Aldrich or MCB) was sublimed twice, the elimination of traces of benzophenone being the main consideration. Only freshly prepared samples were used. In fact, the elimination of benzophenone is extremely important, because its extinction coefficient (at 337.1 nm) is considerably higher than that of di-*tert*-butyl peroxide and its photoreduction yields the same radical as reaction 5. In addition the samples were never pulsed more than six to eight times in order to avoid the accumulation of benzophenone via radical disproportionation. Fortunately, the presence of benzophenone is so obvious in the oscilloscope traces that the problem can be readily recognized.

Laser Photolysis. The pulses from a frequency doubled, Q-switched ruby laser (347.1 nm) were used for excitation. The pulses were at-

tenuated using glass plates. The monitoring system consisted of a 450-W xenon lamp, a Bausch & Lomb high-intensity monochromator, and a RCA-1P28 photomultiplier tube. The lamp was pulsed so as to increase the output by a factor of 200–400 during 1–2 ms. All kinetic measurements were carried out at 535 nm, but a spectroscopic study confirmed the identity of the diphenylhydroxymethyl radical, the characteristics of which are well known from the photoreduction of benzophenone.¹⁵ The rise time of the detection system was less than 5 ns.

The values of k_{expt} and k'_{expt} were usually derived from four to eight oscilloscope traces. In order to achieve this, the information from the photographs was transformed into digital format and transmitted to a PDP-11 computer using a photodigitizer. The corresponding calculations were preceded by signal averaging of the data.

ESR Experiments. Oxygen-free di-*tert*-butyl peroxide solutions containing 15% by volume substrates were passed in a continuous flow (flow rate of 0.24 mL/min) through a flat quartz cell (0.4 mm optical path length) inside an ESR cavity where they were irradiated with the filtered light ($275 \text{ nm} \leq \lambda \leq 340 \text{ nm}$) of a 1-kW Xe-Hg short arc lamp (Hanovia 977 B-1). A Varian V-4501 ESR spectrometer equipped with circulator and bias arm was used. Absolute radical concentrations were obtained from stationary ESR spectra via simulation and double integration and comparison with a calibrated standard (Varian strong pitch sample).

For the determination of radical lifetimes we used modulation ESR spectroscopy. The UV light was chopped with a suitable rotating sector device to produce a harmonically modulated radical initiation. Radical lifetimes and decay laws were evaluated from amplitudes and phases of the oscillating radical concentration which were monitored by phase sensitive detection (Ithaco Lock-in Analyzer, Model 393-03) of the fundamental Fourier component and its first harmonic. Details of the experimental technique and the calibration procedures were essentially as described elsewhere.²¹

All measurements have been made at a temperature of (21 ± 2) °C.

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A Pulse Radiolysis Study of the Triplet Sensitized Production of Singlet Oxygen: Determination of Energy Transfer Efficiencies

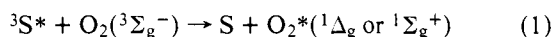
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Abstract: The technique of pulse radiolysis has been used to produce aromatic and aromatic carbonyl triplet states in liquid benzene. The quenching of such triplets by $\text{O}_2(^3\Sigma_g^-)$ leads to the production of singlet oxygen ($^1\Delta_g$), the subsequent reactivity of which has been followed by time-resolved observation of the bleaching of diphenylisobenzofuran (DPBF). Measurement of quenching rate constants together with sensitizer triplet and DPBF bleaching yields has allowed the efficiency of the process for energy transfer to oxygen to be determined. This efficiency varies considerably from sensitizer to sensitizer and appears to be inversely related to the sensitizer intersystem crossing efficiency.

Introduction

Singlet oxygen $\text{O}_2(^1\Delta_g)$ is now accepted as an important participant in the overall process termed photodynamic action. It seems likely that the major process by which it is formed in biological systems involves energy transfer from a triplet sensitizer ($^3\text{S}^*$) according to



and indeed this process is the most common means of its production in the laboratory. It has been generally assumed that this process takes place with unit efficiency; i.e., for each triplet quenching act a molecule of $\text{O}_2(^1\Delta_g \text{ or } ^1\Sigma_g^+)$ is produced and in solution any $^1\Sigma_g^+$ states produced rapidly decay to $\text{O}_2(^1\Delta_g)$. A systematic investigation of the validity of this overall picture has so far been lacking. We have established a method for the investigation of $\text{O}_2(^1\Delta_g)$ reactivity based on the pulse radiolysis technique and have addressed ourselves to the particular question of the efficiency of step 1.

The interaction between ground-state molecular oxygen and the electronically excited triplet states of organic molecules has been the subject of a number of recent studies.²⁻⁷ In the quenching by oxygen of aromatic hydrocarbon triplets⁶ the highest rate constants observed were for those sensitizers

having triplet energies close to but greater than the singlet energy of $\text{O}_2(^1\Delta_g)$. Further, the maximum rate constant measured was only some 10% of the diffusion-limited value in the liquid matrix. An encounter complex between $\text{O}_2(^3\Sigma_g^-)$ and a triplet state can have either singlet, triplet, or quintet multiplicity.⁸ The quintet encounter complex can only decay to starting materials and hence the maximum attainable quenching rate constant should be $1/5$ of the diffusion-controlled value. That values of $1/5$ of diffusion control or lower were found led to the conclusion⁶ that the major decay route was from the singlet complex, the products of which are ground-state (singlet) aromatic and excited singlet oxygen. This conclusion supported the suggestion of Algar and Stevens,³ based on a photooxidation study, that all of the quenched sensitizer triplets give rise to $\text{O}_2(^1\Delta_g)$. In addition, Stevens⁹ names the encounter complex an "oxicplex" and assigns structural and spectroscopic properties to it.

In this work we have made direct measurements of the decay kinetics and yield of $\text{O}_2(^1\Delta_g)$ in benzene solution as a function of sensitizer. Triplet sensitizer states have been generated by energy transfer from matrix triplet and singlet states produced by pulse radiolysis.

When a high energy electron beam is incident on a target