Laser Flash Photolysis–Electron Spin Resonance Kinetic Studies of Homolytic Reactions in Solution

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Laser flash photolytic (308 nm) generation coupled with time-resolved e.s.r. spectroscopic detection of radical intermediates has been used to obtain absolute rate coefficients and activation parameters for a number of uni- and bi-molecular homolytic reactions [(A)—(F)] in solution. The results accord well with

$$\mathrm{Bu^tO\dot{C}O \longrightarrow Bu^{t\cdot} + CO_2} \qquad (A)$$

$$\mathrm{(EtO)_3\dot{P}OBu^t \longrightarrow Bu^{t\cdot} + (EtO)_3PO} \qquad (B)$$

$$\mathrm{Bu^tO^\cdot + cyclo\text{-}C_5H_{10} \longrightarrow cyclo\text{-}C_5H_9^\cdot + Bu^tOH} \qquad (C)$$

$$\mathrm{Bu^tO^\cdot + Bu^tOMe \longrightarrow Bu^tO\dot{C}H_2 + Bu^tOH} \qquad (D)$$

$$\mathrm{Me_3SiO^\cdot + cyclo\text{-}C_5H_{10} \longrightarrow cyclo\text{-}C_5H_9^\cdot + Me_3SiOH} \qquad (E)$$

$$\mathrm{Me_3SiO^\cdot + Bu^tOMe \longrightarrow Bu^tO\dot{C}H_2 + Me_3SiOH} \qquad (F)$$

those obtained previously for some of these reactions using other techniques. The data for reaction (C) are in excellent agreement with those obtained by laser flash photolysis coupled with optical detection of transients, but differ markedly from results obtained previously by a flash photolysis/e.s.r. technique. The kinetic results for the hydrogen transfers (E) and (F) represent the first absolute rate data for reactions of trialkylsiloxyl radicals. The trimethylsiloxyl radical is more reactive in hydrogen abstraction and also more electrophilic than $\mathrm{Bu^tO^\cdot}$; these differences are attributable to the π-acceptor properties of the $\mathrm{Me_3Si}$ group.

Knowledge of absolute rate coefficients and activation parameters is necessary for a proper understanding of chemical reactivity. In recent years there has been a sharp increase of interest in the determination of absolute rate coefficients for free-radical reactions which take place in the liquid phase and this has resulted in the publication of a series of comprehensive compilations of the available kinetic data.[1]

The most important experimental methods for measurement of absolute rate coefficients are based on the time-resolved detection of reactant and/or product free radicals using optical absorption or electron spin resonance spectroscopy. Laser flash photolytic generation coupled with nanosecond-response optical detection has proved to be a very powerful technique, particularly in the hands of Scaiano[2] and of Ingold.[3] However, one drawback with this method can be the difficulty of assigning optical absorptions to particular radicals or the absence of suitable absorption bands. Such difficulties are generally avoided when e.s.r. spectroscopic detection is employed, although response times are necessarily longer than with optical methods and thus very rapid transformations cannot be studied. The majority of these investigations[4–10] have been concerned with determination of absolute rate coefficients for radical–radical reactions [equation (1)] when, because the rate cannot exceed that of diffusive encounter of the reactants in solution, radical lifetimes ($1/2k_t[\mathrm{R^\cdot}]$) are $\geqslant$ 0.5—1 ms under normal

$$\mathrm{R^\cdot + R^\cdot} \xrightarrow{2k_t} \text{molecular products} \qquad (1)$$

conditions, thus permitting the use of relatively slow-response e.s.r. spectrometers. More recently, Fischer[11] has also shown that absolute rate coefficients for competing pseudo-first-order radical–molecule reactions [equation (2)] can be extracted from very precise measurements of radical concentration *versus* time profiles even when the major decay pathway is still self-reaction.

$$\mathrm{R^\cdot + M} \longrightarrow \text{products} \qquad (2)$$

However, the most direct e.s.r. method for kinetic study of such radical–molecule reactions and of unimolecular transformations [equation (3)] in the liquid phase is to follow $[\mathrm{R^\cdot}]$ as a function of time under conditions where reaction (1) does not

$$\mathrm{R^\cdot \longrightarrow S^\cdot} \qquad (3)$$

compete significantly. Such an approach, which in solvents of normal viscosity requires a rapid-response e.s.r. detection system, has received only very limited attention.[12–15] For this technique to be successful, the photochemical generation of reactant radicals must be effectively instantaneous, which dictates the use of pulsed laser light sources, and in the present paper we describe the application of this laser flash photolysis/e.s.r. (LFPESR) technique for the direct determination of absolute rate coefficients for a number of established free-radical reactions.

Our apparatus is less sophisticated than that described by McLauchlan *et al.*,[16] which operates without field modulation and has a shorter response time. A number of other groups have also made use of rapid-response time-resolved e.s.r. spectroscopy in fundamental investigations of chemically induced dynamic electron polarisation (CIDEP) effects and relaxation phenomena for radicals generated mainly from triplet-state precursors. These investigations, which have been reviewed,[17] were generally not concerned with the measurement of rate coefficients for chemical reactions.

Results and Discussion

The primary radical sources were di-t-butyl peroxide (DTBP) and bis(trimethylsilyl) peroxide (TMSP), which were photolysed at 308 nm with pulses of light from a xenon chloride excimer laser [equation (4; R = Bu^t or Me$_3$Si)]. Repetition rates of up

$$\mathrm{ROOR} \xrightarrow{h\nu} 2\mathrm{RO}^{\bullet} \qquad (4)$$

to 100 Hz were available, the pulse width was *ca.* 10 ns, and pulse energies of up to 40 mJ were obtainable, although for kinetic work much lower energies (*ca.* 1—5 mJ) were usually required. Under these conditions the production of oxyl radicals (RO$^{\bullet}$) is effectively instantaneous[18,19] and the subsequent reactions of these species may be studied by monitoring the build-up of product radicals in the sample. Alternatively, the t-butoxyl radical can be converted (again instantaneously on the timescale of the LFPESR experiments) into a wide variety of other types of radical, the subsequent transformations of which may then be monitored. In all such experiments the growth or decay of the radical of interest is kinetically first-order and the rate coefficient obtained should thus not be affected by any non-uniformity in the distribution of radicals within the cylindrical sample tube.[20]

The general procedure followed was to sweep and record the normal e.s.r. spectrum while running the laser at 100 Hz and thus to select the magnetic field corresponding to the maximum of a suitable hyperfine line. The spectrometer was then 'locked' to this line, using a field-frequency interlock device, so that the resonance condition would be maintained despite any small drift in microwave frequency. The applied magnetic field was modulated at 1 MHz and after phase-sensitive detection[21] the output was passed to a Nicolet LAS 12/70 signal-processing system which incorporates a 20 MHz digitiser. The laser and computer were triggered by a pulse-sequencing unit such that the laser fired at a pre-set time after the computer was triggered. Generally, the sequence was repeated at 50 Hz until 10^4 peak height *versus* time profiles had been collected, and the averaged curves were then plotted using an X–Y recorder and analysed to obtain the rate coefficients. The laser flash intensity was progressively attenuated using Pyrex glass filters and metal mesh screens until the measured first-order rate coefficients showed no dependence on light intensity, at which point second-order radical–radical reactions[2,13] and CIDEP effects (see later) could be neglected.

Sample depletion was not normally a problem under the conditions employed and it was generally not necessary to pass the sample solution through the photolysis cell.

Decarboxylation of the t-Butoxycarbonyl Radical.—We have shown previously[22] that t-butoxyl radicals rapidly abstract hydrogen from t-butyl formate to give t-butoxycarbonyl radicals, decarboxylation of which to give t-butyl radicals can be monitored by e.s.r. spectroscopy [equations (5) and (6)]. By

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{Bu^tOCHO} \longrightarrow \mathrm{Bu^tO\dot{C}O} + \mathrm{Bu^tOH} \qquad (5)$$

$$\mathrm{Bu^tO\dot{C}O} \xrightarrow{k_6} \mathrm{Bu^{t\bullet}} + \mathrm{CO_2} \qquad (6)$$

measuring the relative concentrations of Bu^{t}O$\dot{C}$O and Bu$^{t\bullet}$ during continuous photochemical generation of the former, we have determined k_6 relative to the rate coefficient for self-reaction of Bu$^{t\bullet}$.[22] However, this steady-state e.s.r. (SSESR) method is indirect and can be subject to various errors[23] and therefore we considered that the direct measurement of k_6 using the LFPESR technique would be appropriate.

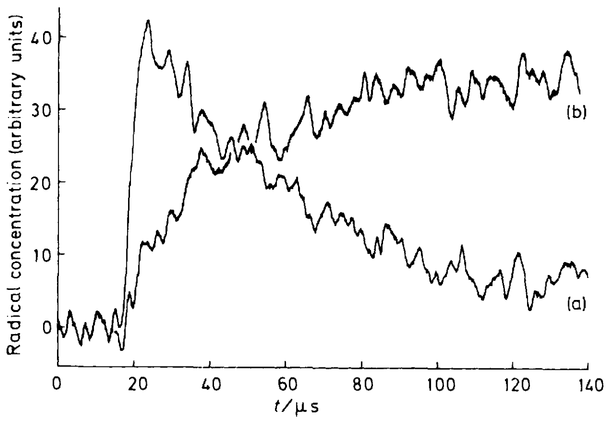

Figure. (a) Decay curve for the t-butoxycarbonyl radical generated by flash photolysis of DTBP and t-butyl formate in octane at 266 K; (b) growth curve for the t-butyl radical produced by β-scission of Bu^{t}O$\dot{C}$O under the same conditions

The concentration of Bu^{t}O$\dot{C}$O following flash photolysis was monitored *via* its single-line e.s.r. spectrum (g = 2.0011). Lines 5 and 6 of the t-butyl radical (modulated so that the second-order fine structure was only partially resolved) were monitored and rate coefficients were shown to be independent of the choice of line. The growth of Bu$^{t\bullet}$ and decay of Bu^{t}O$\dot{C}$O following flash generation of the latter in octane solvent at 266 K are illustrated in the Figure. Under conditions such that radical–radical reactions are unimportant, equation (7) holds and values of k_6 can be obtained from straight-line plots of ln[h(Bu^{t}O$\dot{C}$O)] or ln[h^{∞}(Bu$^{t\bullet}$) − h(Bu$^{t\bullet}$)] against time, where the peak height h is assumed to be proportional to radical concentration and the label ∞ refers to the 'plateau' concentration of Bu$^{t\bullet}$ (10^{-6}—10^{-7}M).

$$\mathrm{d[Bu^{t\bullet}]/d}t = -\mathrm{d[Bu^tO\dot{C}O]/d}t = k_6[\mathrm{Bu^tO\dot{C}O}] = k_6\{[\mathrm{Bu^{t\bullet}}]_{\infty} - [\mathrm{Bu^{t\bullet}}]\} \qquad (7)$$

Results from representative experiments in solvents of different viscosities are given in Table 1; rate coefficients obtained by monitoring Bu^{t}O$\dot{C}$O or Bu$^{t\bullet}$ are in good accord. An Arrhenius plot of the data obtained between 240 and 286 K gives a good straight line defined by equation (8), in which R = 8.314 × 10^{-3} kJ mol^{-1} K^{-1}, and the activation parameters are in reasonable agreement with those (A = $10^{14.1}$ s^{-1}, E_a = 50.5 kJ mol^{-1}) determined previously by the SSESR method.[22,24] All

$$\log_{10}(k_6/\mathrm{s^{-1}}) = (13.2 \pm 0.3) - (45.2 \pm 1.5)/2.303RT \qquad (8)$$

the activation parameters obtained in this work are collected in Table 2.

β-*Scission of the t-Butoxy(triethoxy)phosphoranyl Radical* (**1**).—The phosphoranyl radical (**1**) is produced during photolysis of DTBP in the presence of triethyl phosphite [equation (9)];[25] under those conditions addition of t-butoxyl radicals to phosphorus takes place at close to the encounter-controlled rate,[26] and the e.s.r. spectrum of the product appears as a widely spaced doublet which results from coupling to ^{31}P [a(P) = 889.9 G, g = 2.0021 at 208 K in cyclopropane].[27] β-Cleavage of (**1**) to give t-butyl radicals [equation (10)] has been

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{(EtO)_3P} \longrightarrow \underset{(\mathbf{1})}{\mathrm{(EtO)_3\dot{P}OBu^t}} \qquad (9)$$

Table 1. Representative results obtained for the β-scission of the t-butoxycarbonyl radical

T/K	[Bu^{t}OCHO]/M[a]	Solvent[b]	Laser flash intensity[c]	Bu^{t}OĊO decay k_6/s^{-1}	Bu$^{t\bullet}$ growth k_6/s^{-1}	$k_6^{\text{calc.}}$/s^{-1} [d]
244.4	1.43	A	10	3.16×10^3		3.48×10^3
251.2	1.43		10	5.42×10^3		6.35×10^3
252.3	1.19		10	6.70×10^3		6.97×10^3
253.3	1.19		30	8.55×10^3		7.59×10^3
259.8	1.19		30	1.46×10^4		1.30×10^4
263.5	1.19		30	1.64×10^4		1.74×10^4
278.3	1.43		10	4.75×10^4		5.22×10^4
279.5	1.43		30	4.88×10^4		5.68×10^4
284.5	1.43		100	8.35×10^4		8.00×10^4
265.3	1.43	B	10		2.59×10^4	2.00×10^4
265.3	1.43		30	2.48×10^4		2.00×10^4
267.1	1.43		100	2.82×10^4		2.30×10^4
267.2	2.46		100	2.65×10^4		2.32×10^4
267.5	2.46		10		2.86×10^4	2.37×10^4
265.5	1.43	C	30	2.00×10^4		
267.4	1.43		30		2.17×10^4	
259.2	1.43	D	10		1.55×10^4	
276.8	1.43		10		5.98×10^4	

[a] At room temperature. [b] A = cyclopropane–DTBP (4:1 v/v); B = octane–DTBP (4:1 v/v); C = liquid paraffin–DTBP (1:1 v/v); D = neat DTBP. [c] Arbitrary units. [d] Calculated from the Arrhenius parameters given in Table 2.

Table 2. Arrhenius parameters for reactions studied by the LFPESR technique and comparisons with previous work

Reaction	Solvent[a]	Temp. range (K)	$\log_{10}$ (A/ s^{-1} or dm^3 mol^{-1} s^{-1})	E_a/kJ mol^{-1}	k (293 K)/ s^{-1} or dm^3 mol^{-1} s^{-1}	Ref.
$\mathrm{Bu^tO\dot{C}O} \longrightarrow \mathrm{Bu^{t\bullet}} + \mathrm{CO_2}$	A,B	240—286	13.2 ± 0.3	45.2 ± 1.5	1.39×10^5	This work
	C	215—256	14.1 ± 0.5	50.5 ± 2.0	1.25×10^5	*b*
$(\mathrm{EtO})_3\dot{\mathrm{P}}\mathrm{OBu^t} \longrightarrow \mathrm{Bu^{t\bullet}} + (\mathrm{EtO})_3\mathrm{P{=}O}$	A	223—270	12.9 ± 0.5	41.8 ± 2.0	2.81×10^5	This work
	D	237—350	11.5 ± 0.5	34.3 ± 2.0	2.43×10^5	*c*
	A	193—223	10.6 ± 1.0	32.2 ± 4.0	7.25×10^4	*d*
$\mathrm{Bu^tO^\bullet} + \text{cyclo-}\mathrm{C_5H_{10}} \longrightarrow \text{cyclo-}\mathrm{C_5H_9^\bullet} + \mathrm{Bu^tOH}$	A	149—216	8.7 ± 0.3	14.8 ± 1.5	1.15×10^6	This work
	E	150—208	8.6 ± 0.3	14.7 ± 1.5	9.54×10^5	This work
	F	236—344	8.47 ± 0.45	14.5 ± 2.5	7.68×10^5	*e*
	C,G	253—303	10.1 ± 0.2	25.5 ± 1.3	3.59×10^5	*f*
$\mathrm{Me_3SiO^\bullet} + \text{cyclo-}\mathrm{C_5H_{10}} \longrightarrow \text{cyclo-}\mathrm{C_5H_9^\bullet} + \mathrm{Me_3SiOH}$	A	151—178	8.3 ± 0.5	11.6 ± 2.0	1.71×10^6	This work
$\mathrm{Bu^tO^\bullet} + \mathrm{Bu^tOMe} \longrightarrow \mathrm{Bu^tO\dot{C}H_2} + \mathrm{Bu^tOH}$	A	150—190	8.1 ± 0.5	12.6 ± 2.0	7.15×10^5	This work
	C,G	253—303	9.3 ± 0.2	21.8 ± 1.3	2.60×10^5	*f*
$\mathrm{Me_3SiO^\bullet} + \mathrm{Bu^tOMe} \longrightarrow \mathrm{Bu^tO\dot{C}H_2} + \mathrm{Me_3SiOH}$	A	162	8.1[g]	$\leqslant 8.7$	$\geqslant 3.5 \times 10^6$	This work

[a] A = cyclopropane–DTBP or –TMSP (4:1 v/v); B = octane–DTBP (4:1 v/v); C = neat DTBP; D = iso-octane–DTBP (3:7 v/v); E = $\mathrm{CF_2Cl_2}$–DTBP (4:1 v/v); F = benzene–DTBP (1:2 v/v); G = benzene–DTBP (4:1 v/v). [b] Refs. 22 and 24. [c] Ref. 26. [d] Ref. 28*b*. [e] Ref. 31. [f] Ref. 13. [g] Assumed value; see text.

studied previously[28] by the kinetic e.s.r. method at low temperatures, such that phosphoranyl radical decay is relatively slow and can be monitored with an unmodified commercial spectrometer employing 100 kHz field modulation. However,

$$(\mathrm{EtO})_3\dot{\mathrm{P}}\mathrm{OBu^t} \xrightarrow{k_{10}} \mathrm{Bu^{t\bullet}} + (\mathrm{EtO})_3\mathrm{P{=}O} \qquad (10)$$

this was only possible because (**1**) undergoes self-reaction relatively slowly and, even so, ambiguities still arise over the extent to which reaction of (**1**) with Bu$^{t\bullet}$ contributes to decay of the former radical. The SSESR technique has also been applied to this system and k_{10} was measured relative to $2k_t$ for Bu$^{t\bullet}$.[28a,29] Most recently, laser flash photolysis coupled with optical detection of (**1**) has been used to measure k_{10}, although u.v. absorption by the phosphoranyl was rather weak in the accessible wavelength region.[26]

Against this background we have examined the β-scission of (**1**) directly, using the LFPESR technique, by monitoring both the decay of the phosphoranyl radical* and the growth of Bu$^{t\bullet}$ under conditions where radical–radical reactions are unimportant. Furthermore, because of the very large phosphorus hyperfine splitting, this system was considered to provide an important test for the involvement of CIDEP effects[17,30] in perturbing the decay profile of the phosphoranyl radical, such effects might be expected to manifest themselves as a difference in the values of k_{10} obtained by monitoring the high- and low-field lines in the spectrum of (**1**) (see later for further discussion of this point).

The β-scission of (**1**) was studied between 223 and 270 K with [(EtO)$_3$P] in the range 0.6—1.2M; even for relatively large pulse energies (and thus radical concentrations) the rate coefficients obtained from the high- and low-field hyperfine lines were the same within experimental error. Most data were collected by monitoring the decay of (**1**), although at higher temperatures

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* Because of the large phosphorus hyperfine splitting, the field-frequency interlock could not be used when monitoring the decay of (**1**). However, the lines are relatively broad and drift was not a problem.

(>*ca.* 250 K) the rate coefficients obtained from the growth of $\mathrm{Bu^{t\bullet}}$ were in good agreement. However, at lower temperatures the half-life for the growth of $\mathrm{Bu^{t\bullet}}$ was shorter than that for the decay of (**1**) and the difference became more marked as the temperature was decreased. The origin of this effect is unclear, although it may possibly be connected with the chemical non-equivalence of apical and equatorial sites in the trigonal bipyramidal phosphoranyl radical.[27] The activation parameters obtained from the decay of (**1**) and the growth of $\mathrm{Bu^{t\bullet}}$ above 250 K are given in Table 2; they are in fair agreement with those obtained by the laser flash photolysis/optical detection technique[26] but differ appreciably from those determined previously by monitoring the decay of the e.s.r. spectrum of (**1**) at lower temperatures.

Since the formation of (**1**) is effectively instantaneous for phosphite concentrations in the region of 1M,[26] reaction (9) could be used to measure the response time of our LFPESR apparatus. Between 220 and 240 K, the instrument-limited time taken for the peak height of (**1**) to increase from 10 to 90% of its final value was *ca.* 2.5 μs; the rise was non-exponential.[21]

Hydrogen Abstraction from Cyclopentane.—The LFPESR technique is, of course, equally applicable to the study of bimolecular radical–molecule reactions under pseudo-first-order conditions. Hydrogen-atom abstraction from cyclopentane by t-butoxyl radicals [equation (11)] was chosen for

$$\mathrm{Bu^tO^\bullet + cyclo\text{-}C_5H_{10} \xrightarrow{k_{11}} cyclo\text{-}C_5H_9{}^\bullet + Bu^tOH} \quad (11)$$

investigation because this reaction has often been used as a standard in competition studies and because very different activation parameters have been obtained using laser flash photolysis/optical detection[18,31] or flash photolysis/e.s.r.[13,14] techniques (see Table 2).

Solutions of cyclopentane (1—5M) and DTBP (*ca.* 15% v/v) in cyclopropane or $\mathrm{CF_2Cl_2}$ were subjected to laser photolysis and the central α-proton 'doublet' [$m_I(4H_\beta) = 0$, $m_I(H_\alpha) = \pm 0.5$] of the cyclopentyl radical was used to monitor concentration, with the spectrometer locked to the strongest line within either multiplet arising from γ-proton and second-order splittings. The sample volume was measured as a function of temperature so that the concentration of cyclopentane could be precisely determined at any temperature. Under conditions such that radical–radical reactions are unimportant and when all the t-butoxyl radicals generated during the flash are consumed in reaction (11), the growth curve for $\mathrm{cyclo\text{-}C_5H_9{}^\bullet}$ may be analysed to obtain the pseudo-first-order rate coefficient $k_{11}[\mathrm{cyclo\text{-}C_5H_{10}}]$. For low laser pulse energies and cyclopentane concentrations above 0.5M, scavenging of $\mathrm{Bu^tO^\bullet}$ may be assumed to be complete.[13,14] Data from six separate runs in cyclopropane solvent containing different concentrations of cyclopentane in the temperature range 149—216 K yielded the results given in Table 2. The value of k_{11} was essentially unchanged in $\mathrm{CF_2Cl_2}$ solvent.

Our activation parameters are in excellent agreement with those determined by Wong, Griller, and Scaiano using the laser flash photolysis/optical detection method,[31] but differ considerably from those obtained by a flash photolysis/e.s.r. method[13] similar to our own except for the longer duration of the flash and the slower response of the spectrometer. We consider that the latter activation parameters, which imply improbably small rate coefficients at low temperatures, are likely to be in error.

Photolysis of TMSP in the presence of cyclopentane also affords the cyclopentyl radical [equation (12)];[32] the rate coefficient k_{12} was determined in cyclopropane by the same method used to obtain k_{11}. Because e.s.r. spectra were weaker than those derived from DTBP and since $\mathrm{Me_3SiO^\bullet}$ turned out to be more reactive than $\mathrm{Bu^tO^\bullet}$ (see Table 2), the accessible temperature range was rather small. Although the errors were relatively large, this work provides the first absolute rate coefficients for a reaction of a trialkylsiloxyl radical.

$$\mathrm{Me_3SiO^\bullet + cyclo\text{-}C_5H_{10} \xrightarrow{k_{12}} cyclo\text{-}C_5H_9{}^\bullet + Me_3SiOH} \quad (12)$$

We have found previously that replacement of the alkyl groups in a dialkylaminyl radical by $\mathrm{Me_3Si}$ ligands greatly increases the reactivity of the aminyl towards hydrogen-atom abstraction and we have attributed this difference to the greater strength of the N–H bond in $\mathrm{(Me_3Si)_2NH}$ than in a dialkylamine.[33] Similar factors probably operate with $\mathrm{Me_3COH}$ and $\mathrm{Me_3SiOH}$, the O–H bond in the latter being the stronger, and are likely to be responsible for the higher reactivity of $\mathrm{Me_3SiO^\bullet}$. Polar effects are probably also important, since $\mathrm{Me_3SiO^\bullet}$ should be more electrophilic than $\mathrm{Bu^tO^\bullet}$ on account of the greater π-acceptor capability of the trialkylsilyl group.[33,34]

Hydrogen Abstraction from t-Butyl Methyl Ether.—The reactions of t-butoxyl and trimethylsiloxyl radicals with t-butyl methyl ether were investigated by the LFPESR technique, by monitoring the growth of the t-butoxymethyl radical[35] [equations (13) and (14)]; the results are given in Table 2. The

$$\mathrm{Bu^tO^\bullet + Bu^tOMe \xrightarrow{k_{13}} Bu^tO\dot{C}H_2 + Bu^tOH} \quad (13)$$

$$\mathrm{Me_3SiO^\bullet + Bu^tOMe \xrightarrow{k_{14}} Bu^tO\dot{C}H_2 + Me_3SiOH} \quad (14)$$

rate coefficient k_{13} has been measured previously[13] using the flash photolysis/e.s.r. method; however, as for hydrogen abstraction from cyclopentane, the activation parameters obtained differ appreciably from those determined in our work. The relatively large activation energy (21.8 kJ mol^{-1}) reported previously would correspond to much smaller values of k_{13} than found by experiment in our (lower) temperature range.

Within the time response of our apparatus, it was only possible to place a lower limit on the value of k_{14} (2.0×10^5 dm^3 mol^{-1} s^{-1}) at the lowest temperature (162 K) accessible in cyclopropane solvent. If we assume an A factor of $10^{8.1}$ dm^3 mol^{-1} s^{-1}, this implies an activation energy of $\leqslant 8.7$ kJ mol^{-1}.

Whilst $\mathrm{Me_3SiO^\bullet}$ reacts more rapidly than $\mathrm{Bu^tO^\bullet}$ with both cyclopentane and t-butyl methyl ether, the latter is particularly reactive towards the siloxyl radical. This behaviour can be attributed to the greater electrophilicity of the siloxyl radical,[33,34] since charge-separated structures of the type (**2**) will make an appreciable contribution to the transition state for hydrogen abstraction from the ether on account of the relatively high stability of the oxonium ion. Such a polar effect should

$$\mathrm{RO^- \; H^\bullet \; H_2C{=}\overset{+}{O}Bu^t} \quad (\mathbf{2})$$

reduce the activation energy for attack of $\mathrm{Me_3SiO^\bullet}$ on $\mathrm{Bu^tOMe}$ more than for attack by $\mathrm{Bu^tO^\bullet}$.

Timescales.—Although the LFPESR apparatus may be used for measurement of rate coefficients for radical–radical reactions which can be diffusion-controlled or slower, this was not a primary objective in this work. We are concerned with unimolecular radical transformations and radical–molecule reactions (which are pseudo-first-order under the conditions of the experiment). The 'time window' available for study of such processes is limited on the one hand by the response of the e.s.r. spectrometer and polarisation effects and, at the other extreme, by the occurrence of second-order radical–radical reactions which limit the lifetime of the species of interest. The latter limit will depend on the radical concentration, spectrometer sensitivity, and the rate coefficient for radical–radical reaction, which may be as large as that corresponding to encounter control. Operationally with our apparatus and with non-persistent radicals, these constraints generally limit the measurable first- (or pseudo-first-) order coefficients to the range *ca.* 2×10^3—4×10^5 s^{-1}. However, since the sample temperature can be readily varied over a very wide range (−150 to +100 °C is realistic) this restricted time window still permits the study of reactions with widely differing activation energies. On the basis of an *A* factor of 10^{13} s^{-1}, unimolecular transformations with activation energies between *ca.* 20 and 70 kJ mol^{-1} can be studied. It is also feasible to extend this time window by working in more viscous solvents, since this will slow diffusion-controlled radical–radical reactions without affecting the rate of unimolecular decay.

CIDEP Effects.—Since the time dependence of the intensity of an e.s.r. spectrum is only related simply to radical concentration if a Boltzmann distribution between upper and lower spin states is maintained throughout the observation period, it is necessary to establish that CIDEP effects[17] are unimportant under our conditions. Spin polarisation may occur by two pathways: the radical-pair mechanism (RPM) and the triplet mechanism.[17] Since under our conditions DTBP[18,19] and, very probably, TMSP decompose from excited singlet states, only the RPM need be considered. Any polarisation present in our systems will develop during encounters between freely diffusing radicals (F-pairs). The number of such encounters that a radical undergoes during its lifetime will depend on the total radical concentration, whereas the first-order rate coefficient (*k*) for chemical transformation of the radical will be independent of the total radical concentration. Hence, if *k* is shown to be independent of the laser pulse energy, we can safely assume that the rate coefficient is not corrupted by CIDEP effects.

Furthermore, an important characteristic of RPM polarisation is that it varies with the position of the hyperfine component in a multi-line spectrum, changing from emission to enhanced absorption on going from low to high applied magnetic field. The polarisation developed in F-pairs of radicals which have the same *g* factor is equal and opposite for 'mirror image' lines on either side of the spectrum centre.[17,30] Hence, if the same value of *k* is obtained from measurements on a particular hyperfine line and on its mirror image, then CIDEP effects may be assumed to be unimportant. For most systems, lines close to or at the centre of the spectrum were chosen since the extent of polarisation increases with the distance away from the latter point.

Conclusion.—The LFPESR technique appears to be generally useful for the direct measurement of rate coefficients for radical reactions in solution and should prove complementary to the more rapid response laser flash photolysis methods which employ optical detection of transient radicals.

Experimental

Materials.—Most reagents and solvents were commercial products which were re-distilled before use, except for cyclopropane and CF_2Cl_2 which were used as received. Bis(trimethylsilyl) peroxide was prepared by a published procedure.[36] Samples were sealed in evacuated Suprasil quartz tubes (4 mm o.d. × 3 mm i.d.).

For pseudo-first-order reactions, when it was necessary to know reagent concentrations precisely, total volumes of the sealed samples were determined using a silicone rubber O-ring, which fitted tightly around the outside of the tube, to mark the liquid level at a known temperature. After being opened and emptied, the tube was filled to the mark with mercury, the weight of which was then used to calculate the volume of the original sample. The coefficient of cubical expansion of the solution was determined in a separate experiment using a graduated sample tube; the volume of the solution was measured at a series of temperatures within the experimental range. The corrections for the temperature dependence of reagent concentration are relatively small compared with other errors involved in LFPESR experiments.

Apparatus.—A Varian E-109 spectrometer was used along with an E-500 gaussmeter and an E-272B field-frequency lock accessory. The spectrometer could be operated with the normal 100 kHz field modulation and modified detection circuitry to give more rapid response,[37] or with a 1 MHz field modulation system as described by Smith, Blankenship, and Klein.[21]

An Oxford Lasers KX-80 rare gas halide excimer laser was used for photolysis. Every precaution was taken to avoid transmission of radiofrequency interference from the laser to the spectrometer; all cables were carefully shielded and the laser was electrically isolated from the rest of the apparatus by using an optical fibre trigger lead. The upright rectangular laser beam (8 mm × 25 mm) was directed through a slit which reduced its width to *ca.* 4 mm and then through the 75% transmission grid of the microwave cavity onto the sample supported in the Dewar insert of a standard variable-temperature unit. With high pulse energies, an optically induced 'spike' sometimes corrupted data for the first few microseconds after the laser flash, but for the pulse energies usually employed this spike was not a problem provided that solid material was not present suspended in the liquid samples and that the laser beam was positioned so as to pass parallel to the cavity sidewalls and to illuminate mainly the sample tube.

A Nicolet LAS 12/70 signal-processing system was used for collection and averaging of data and hard copies were obtained with a Hewlett-Packard HP 7044A X–Y plotter. The laser and signal averager were triggered by a home-built sequence timer which provided a variable pre-set delay between trigger pulses.

During kinetic runs the sample temperature was monitored with a thermocouple positioned in the Dewar insert just outside the photolysis region. After the run, this thermocouple was calibrated against a second thermocouple immersed in the sample solution* and positioned in the photolysis region. Under normal conditions, with the laser running at 50 Hz and delivering *ca.* 2 mJ per pulse, u.v. absorption by the sample caused its temperature to rise by *ca.* 2—3 °C.

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* When the solvent was cyclopropane or CF_2Cl_2 this was replaced by pentane so that an open sample tube could be used.

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