The Electron Spin Resonance Spectra and Decarboxylation of Alkoxycarbonyl Radicals [1]

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The e.s.r. spectrum of the t-butoxycarbonyl σ-radical, generated by u.v. irradiation of a liquid mixture of di-t-butyl peroxide and t-butyl formate, has been observed. Decarboxylation of this radical has been monitored by kinetic e.s.r. spectroscopy and the unimolecular rate constant for the reaction $\mathrm{Bu^tO\dot{C}O} \longrightarrow \mathrm{Bu^t\cdot} + \mathrm{CO_2}$ is given by $\log (k/\mathrm{s^{-1}}) = 13{\cdot}4 - 12{\cdot}1/\theta$ where $\theta = 2{\cdot}303\,RT/\mathrm{kcal\ mol^{-1}}$.

These kinetic parameters differ from those reported in an earlier communication because it was assumed that the rate constants for reaction of a t-butyl radical with a t-butyl radical or with a t-butoxycarbonyl radical had the same value. This assumption has been tested experimentally and shown to be incorrect.

Abstraction of hydrogen from the alkoxy-groups of alkyl carbonates gives radicals which do not decompose to form alkoxycarbonyl radicals.

THE use of e.s.r. spectroscopy in the study of transient radical intermediates produced in non-aqueous solution by irradiation of suitable mixtures with high-intensity u.v. light, constitutes an important advance in the spectroscopic and kinetic investigation of free-radical reactions.[2-4] Radicals have been formed mainly by

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[1] A preliminary account of some of this work has appeared; D. Griller and B. P. Roberts, *Chem. Comm.*, 1971, 1035.

[2] J. K. Kochi and P. J. Krusic, *Chem. Soc. Special Publ. No.* 24, 1970, p. 147.

[3] R. S. Cooke and G. S. Hammond, *Chem. Soc. Special Publ. No.* 24, 1970, p. 1.

[4] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

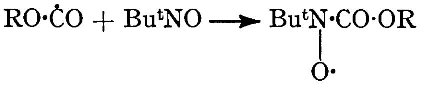
homolytic substitution at hydrogen [equation (2)] or at a metal centre by t-butoxyl radicals generated photolytically from di-t-butyl peroxide.

$$\mathrm{Bu^tO{\cdot}OBu^t} \xrightarrow{h\nu} \mathrm{2Bu^tO{\cdot}} \qquad (1)$$

$$\mathrm{Bu^tO{\cdot}} + \mathrm{RH} \longrightarrow \mathrm{Bu^tOH} + \mathrm{R{\cdot}} \qquad (2)$$

There is evidence for the existence of free alkoxycarbonyl radicals ($\mathrm{RO\dot{C}{=}O}$) in the gas phase although in many cases it is indirect since the observed reaction products were those derived from the alkyl radical formed by exothermic decarboxylation.[5] Alkoxycarbonyl radicals, produced in solution by hydrogen abstraction from methyl- or ethyl-formate, were trapped by 2-methyl-2-nitrosopropane to give the t-butyl alkoxycarbonyl nitroxide [equations (3) and (4), R = Me or Et].[6]

$$\mathrm{Bu^tO{\cdot}} + \mathrm{RO{\cdot}CHO} \longrightarrow \mathrm{Bu^tOH} + \mathrm{RO{\cdot}\dot{C}O} \qquad (3)$$



$$\mathrm{RO{\cdot}\dot{C}O} + \mathrm{Bu^tNO} \longrightarrow \mathrm{Bu^t}\underset{\mathrm{O{\cdot}}}{\underset{|}{\mathrm{N}}}\mathrm{{\cdot}CO{\cdot}OR} \qquad (4)$$

When t-butyl peroxybenzoate was irradiated with u.v. light in the presence of an alkyl formate, e.s.r. spectra attributed to alkoxycarbonyl radicals were observed, although there was no evidence of decarboxylation at the temperatures employed.[7]

In the reaction of trifluoromethyl hypofluorite with carbon monoxide in the gas phase, the trifluoromethoxycarbonyl radical was proposed as chain carrier.[8]

$$\mathrm{CF_3O{\cdot}} + \mathrm{CO} \longrightarrow \mathrm{CF_3O{\cdot}\dot{C}O} \qquad (5)$$

$$\mathrm{CF_3O{\cdot}\dot{C}O} + \mathrm{CF_3OF} \longrightarrow \mathrm{CF_3O{\cdot}CFO} + \mathrm{CF_3O{\cdot}} \qquad (6)$$

Recently Lissi, Scaiano, and Villa [9] studied the oxidation of carbon monoxide by t-butoxyl radicals in the gas phase [equation (7)]. In the temperature range 108—

$$\mathrm{Bu^tO{\cdot}} + \mathrm{CO} \longrightarrow \mathrm{Bu^{t}{\cdot}} + \mathrm{CO_2} \qquad (7)$$

148° the authors found that equation (8) holds, where $\theta = 2{\cdot}303\ RT/\mathrm{kcal\ mol^{-1}}$.

$$\log\,(k_7/\mathrm{l\ mol^{-1}\ s^{-1}}) = (7{\cdot}0 \pm 1{\cdot}8) - (10{\cdot}4 \pm 3{\cdot}4)/\theta \qquad (8)$$

The t-butoxycarbonyl radical appears to be a likely intermediate in reaction (7) and it seemed of interest to identify this radical in solution by e.s.r. spectroscopy and to examine its rate of decarboxylation. Alkoxycarbonyl radicals are expected to be σ-radicals (*i.e.* the unpaired electron is localised in an orbital with nonvanishing amplitude at the carbonyl-carbon nucleus) and, as has been pointed out,[10] organic σ-radicals have been little studied by e.s.r. in comparison with π-radicals.

EXPERIMENTAL

A Varian E-4 e.s.r. spectrometer was used in conjunction with a Mazda 1 K W ME/D mercury lamp with a lens system as described.[4] The intensity of light incident on the sample was varied by placing sheets of metal gauze of different transmittance in the light path. The standard variable-temperature accessory was calibrated using a Chromel–Alumel thermocouple and the heating effect of the radiation measured and compensated for. The field sweep of the spectrometer was calibrated using a solution of Fremy's salt in saturated aqueous sodium carbonate, $a(^{14}\mathrm{N})$ 13·091 G.[11] g-Factors were measured by comparison with Fremy's salt (g 2·00550) or with tetracene [12] in concentrated sulphuric acid (g 2·00260) contained in narrow glass capillaries immersed in the samples. Sample preparation and radical concentration measurements were carried out as described previously.[4]

t-Butyl formate was prepared by the method of Stevens and Van Es.[13] 1-Adamantyl formate was prepared similarly, b.p. 52° at 0·1 mmHg; n.m.r. ($\mathrm{CCl_4}$) τ 2·17 (s, CHO). The remaining esters of formic and carbonic acid were commercial samples purified by distillation. Phenyl formate, which should give the phenoxycarbonyl radical, was too readily hydrolysed to give unambiguous results. For the kinetic study of the decarboxylation of the t-butoxycarbonyl radical the following blank experiments were carried out. 2,2′-Azoisobutane was photolysed in the presence of t-butyl formate; only the signal from the t-butyl radical was observed with no trace of the t-butoxycarbonyl radical. The latter radical was not observed when t-butyl formate was photolysed in the absence of peroxide. In the other systems studied the spectra described in the text were observed only in the presence of di-t-butyl peroxide.

RESULTS AND DISCUSSION

Spectroscopic Studies.—The spectroscopic parameters of the radicals observed when solutions containing di-t-butyl peroxide and the substrate under study were irradiated with u.v. light whilst in the cavity of the e.s.r. spectrometer are given in Table 1.

t-Butyl formate. The formyl hydrogen is abstracted to produce the t-butoxycarbonyl radical, the e.s.r. spectrum of which consists of a single line with no resolvable fine structure (see Figure in ref. 1). The signal, which disappeared immediately the irradiation ceased, was sufficiently strong to enable $a(^{13}\mathrm{C})$ for the carbonyl carbon to be measured without isotopic enrichment. The values of both g and $a(^{13}\mathrm{C})$ show the σ-character of the radical.[10] Cochran, Adrian, and Bowers [14] have measured the ^{13}C-hyperfine splitting in $\mathrm{H\dot{C}O}$ and $\mathrm{F\dot{C}O}$ in the solid state. They obtained isotropic values of $a(\mathrm{H^{13}\dot{C}O})$ 134 G and $a(\mathrm{F^{13}\dot{C}O})$ 286 G and concluded that the large increase on going from $\mathrm{H\dot{C}O}$ to $\mathrm{F\dot{C}O}$ resulted mainly from an increase in the *s*-character

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[8] P. J. Aymonino, *Chem. Comm.*, 1965, 241; *Photochem. and Photobiol.*, 1968, **7**, 761. See also J. Heicklen, *Adv. in Photochem.*, 1969, **7**, 57.

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[10] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, 1970, **92**, 722.

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[12] B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191.

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of the orbital containing the unpaired electron, associated with a decreased angle $\widehat{FCO}$ compared with $\widehat{HCO}$. The t-butoxy-group is intermediate in electronegativity between H and F and might be expected to produce an intermediate angle in agreement with the observed coupling [$a(^{13}C)$ 183·5 G].

As the temperature was increased the signal due to the t-butoxycarbonyl radical decreased accompanied by an increase in the signal from the t-butyl radical formed by decarboxylation (see below).

1-*Adamantyl formate.* This compound was studied in the hope that decarboxylation of the 1-adamantyloxycarbonyl radical might yield the e.s.r. spectrum of the 1-adamantyl radical. The g-value and $a(^{13}C)$ show that 1-adamantyloxycarbonyl is a σ-radical. As the temperature was increased the spectrum of the alkoxycarbonyl radical decayed but the signal from the adamantyl radical did not appear. Adamantyloxycarbonyl would be expected to decarboxylate less readily than t-butoxycarbonyl[15] and, at +45°, when the spectrum of the latter had almost disappeared, that of the former was still strong. High temperatures would be needed to bring about the decarboxylation of the adamantyloxycarbonyl radical, but abstraction of hydrogen by the adamantyl radical from the parent formate would also be facilitated, leading to a chain decomposition of the ester.

TABLE 1

E.s.r. parameters for radicals resulting from hydrogen abstraction by t-butoxyl radicals

Substance	Solvent	Temp.	Radicals observed	g-factor	Hyperfine splittings (G)
$Bu^tO{\cdot}CHO$	P[a]	−60°	$Bu^tO{\cdot}\dot{C}O$[b]	2·0011	$a(^{13}C\text{-}1)$ 183·5
1-AdO·CHO	P	−60	1-AdO·$\dot{C}$O	2·0011	$a(^{13}C\text{-}1)$ 185·2
EtO·CHO	P	−20	EtO·$\dot{C}$O	2·0011	$a(\gamma H)$ not resolved
$(MeO)_2CO$	F[a]	−10	$\dot{C}H_2O{\cdot}CO{\cdot}OMe$		$a(\alpha H)$ 20·0 $a(\varepsilon H)$ 0·30
$(EtO)_2CO$	F	−40	$CH_3\dot{C}HO{\cdot}CO{\cdot}OEt$		$a(\alpha H)$ 18·9 $a(\beta H)$ 23·9 $a(\varepsilon H)$ 0·27
$(Bu^iO)_2CO$	F	−50	$Me_2\dot{C}CH_2O{\cdot}CO{\cdot}OBu^i$		$a(\beta CH_2)$ 12·6 $a(\beta Me)$ 23·0
			$Me_2CH\dot{C}HO{\cdot}CO{\cdot}OBu^i$		$a(\alpha H)$ 18·3 $a(\beta H)$ 24·5

[a] P ≡ Di-t-butyl peroxide; F ≡ $CFCl_2CF_2Cl$. [b] A small concentration of t-butyl radicals was also present at this temperature. See below and the Figure in ref. 1.

$$AdO{\cdot}\dot{C}O \longrightarrow Ad{\cdot} + CO_2 \qquad (9)$$

$$Ad{\cdot} + AdO{\cdot}CHO \longrightarrow AdH + AdO{\cdot}\dot{C}O \qquad (10)$$

Ethyl formate. Photolysis of di-t-butyl peroxide in the presence of this ester yielded the e.s.r. spectrum of the ethoxycarbonyl radical, a single line at g 2·0011. The spectrum of the radical $CH_3\dot{C}HOH$ produced by abstraction of hydrogen from traces of ethanol, which is both difficult to remove from ethyl formate and very reactive towards t-butoxyl radicals, was also detected. At high temperatures (+65°) the spectrum of the ethyl radical formed by decarboxylation of the ethoxycarbonyl radical was also apparent.

The reaction between hydroxyl radicals and ethyl formate in an aqueous flow system is reported[16] to give rise to the overlapping e.s.r. spectra of $CH_3\dot{C}H{\cdot}O{\cdot}CHO$ and the ethoxycarbonyl radical (g 2·0005 ± 0·0003).

Dimethyl and diethyl carbonate. These compounds were studied in order to determine whether the radicals produced by abstraction of hydrogen from the alkoxy-groups would undergo β-scission to give aldehyde and an alkoxycarbonyl radical. Abstraction of hydrogen occurred from the carbon adjacent to oxygen in the alkoxy-groups. Long-range coupling across the $^-O{\cdot}CO{\cdot}O^-$ group was observed in both cases. At high temperatures (55—90°) there was no evidence of radical decomposition to give alkoxycarbonyl or alkyl radicals [equation (11); R = H, R′ = Me; R = Me, R′ = Et].

$$R\dot{C}H{\cdot}O{\cdot}CO{\cdot}R' \longrightarrow RCHO + \dot{C}O{\cdot}OR' \longrightarrow R'{\cdot} + CO_2 \qquad (11)$$

At these temperatures a methyl radical was observed in the spectra from both carbonates and must thus be attributed to β-scission of the t-butoxyl radical facilitated by the polar medium.[17]

Di-isobutyl carbonate. The e.s.r. spectrum indicated that abstraction of hydrogen occurred from both the 1- and 2-positions of the isobutoxy-group. The radical produced by abstraction of the 2-methyne hydrogen predominated at −50° and the low β-hydrogen coupling constant in this radical is probably due to the existence of a preferred conformation with a dihedral angle of *ca.* 60° between the methyleneoxy C–H bonds and the plane containing the orbital of the unpaired electron. The magnitude of this β-hydrogen coupling constant was consistent with the observed second-order effects.[18]

Kinetic Studies.—When photolytically generated t-butoxyl radicals react with t-butyl formate (15% v/v solution in di-t-butyl peroxide) the t-butoxycarbonyl radical is formed and this subsequently decarboxylates

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[15] W. H. Chick and S. H. Ong, *Chem. Comm.*, 1969, 216.

[16] A. R. Metcalfe and W. A. Waters, *J. Chem. Soc.*, (*B*) 1967, 340.

[17] C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, 1964, **86**, 3368.

[18] R. W. Fessenden, *J. Chem. Phys.*, 1962, **37**, 747.

to give a t-butyl radical. By monitoring the concentrations of the two radicals as a function of temperature the kinetic parameters for the decarboxylation may be obtained.

$$\begin{array}{rll} \mathrm{Bu^tO\cdot + HCO{\cdot}OBu^t \longrightarrow Bu^tOH + \dot{C}O{\cdot}OBu^t} & & (12)\\ \mathrm{\dot{C}O{\cdot}OBu^t \longrightarrow CO_2 + Bu^{t\cdot}} & & (13)\\ \left.\begin{array}{r}\mathrm{\dot{C}O{\cdot}OBu^t + \dot{C}O{\cdot}OBu^t \longrightarrow}\\ \mathrm{\dot{C}O{\cdot}OBu^t + Bu^{t\cdot} \longrightarrow}\\ \mathrm{Bu^{t\cdot} + Bu^{t\cdot} \longrightarrow}\end{array}\right\} & \begin{array}{c}\text{non-radical}\\ \text{products}\end{array} & \begin{array}{c}(14)\\(15)\\(16)\end{array} \end{array}$$

Radical–radical reactions involving t-butoxyl radicals would be negligible because of the high rate of reaction (12).

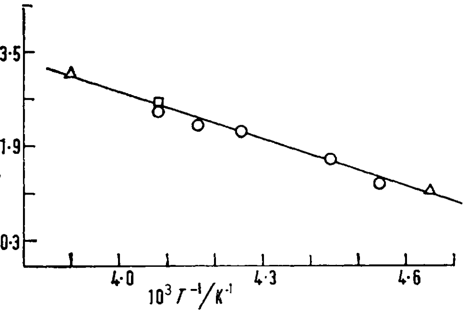
We have that,

$$d[\mathrm{Bu^{t\cdot}}]/dt = k_{13}[\mathrm{\dot{C}O{\cdot}OBu^t}] - 2k_{16}[\mathrm{Bu^{t\cdot}}]^2 - k_{15}[\mathrm{Bu^{t\cdot}}][\mathrm{\dot{C}O{\cdot}OBu^t}] \quad (17)$$

Under experimental conditions d[Bu$^{t\cdot}$]/dt is small with respect to terms on the right-hand side of equation (17) and equation (18) holds. At a given temperature the

$$1/[\mathrm{Bu^{t\cdot}}] = 2k_{16}[\mathrm{Bu^{t\cdot}}]/k_{13}[\mathrm{\dot{C}O{\cdot}OBu^t}] + k_{15}/k_{13} \quad (18)$$

radical concentrations were varied by reducing the incident light intensity progressively to *ca.* 9% of its maximum value. Plots of 1/[Bu$^{t\cdot}$] against [Bu$^{t\cdot}$]/[$\dot{\mathrm{C}}$O·OBu^t] gave straight lines from which the values of $2k_{16}/k_{13}$ and of k_{15}/k_{13} were determined. The process was repeated at different temperatures.



Arrhenius plot of data for the decarboxylation of the t-butoxycarbonyl radical in a 15% v/v solution of t-butyl formate in di-t-butyl peroxide. △ 3 points; □ 2 points; ○ 1 point

Reliable measurements [19,20] at ambient temperature give $2k_{16}$ as 2 × 10^9 l mol^{-1} s^{-1} in similar solvents to those used in this work. The variation of rate with temperature for such a diffusion-controlled reaction in solution may be estimated from the activation energy, E_{diff}, for diffusion in the medium.[21] Taking the value of $2k_{16}$ to be 2 × 10^9 l mol^{-1} s^{-1} at 30° and a reasonable estimate of E_{diff} of 2 ± 1 kcal mol^{-1}, the value of k_{13} was obtained as a function of temperature. An Arrhenius plot of the data obtained in di-t-butyl peroxide as solvent in the temperature range −17 to −58° is shown in the Figure.

Least-squares fitting of the data gives,

$$\log (k_{13}/\mathrm{s}^{-1}) = (13{\cdot}38 \pm 0{\cdot}02) - (12{\cdot}07 \pm 0{\cdot}35)/\theta \quad (19)$$

These kinetic parameters differ from those reported in our earlier communication,[1] in which the data were fitted to equation (18) making the assumption that $2k_{16} = k_{15} = 2 \times 10^9$ l mol^{-1} s^{-1} independent of temperature.[19,22]

The A-factor ($10^{13{\cdot}4}$ s^{-1}) for the decarboxylation of the t-butoxycarbonyl radical is in good agreement with the 'reasonable' value ($10^{13{\cdot}5}$ s^{-1}) assumed by Solly and Benson [23] for the decarboxylation of the methoxycarbonyl radical in the gas phase.

The present analysis allows us to estimate the cross-combination rate constant k_{15}. According to equation (18) the slope/intercept ratio from a plot of 1/[Bu$^{t\cdot}$] against [Bu$^{t\cdot}$]/[CO·OBu^t] is equal to $2k_{16}/k_{15}$, values of which are listed in Table 2.

TABLE 2

Variation of $2k_{16}/k_{15}$ with temperature

Temp.	$2k_{16}/k_{15}$	Temp.	$2k_{16}/k_{15}$
−28°	2·30	−53	4·81
−33	1·95	−58	3·33
−38	2·39	−58	2·44
−48	2·38	−58	2·10

At higher temperatures (> −28°) the slope/intercept ratio became much less reliable than the slope and so the temperature range of the former measurements is less than that of the latter. Whilst the spread of the data in Table 2 is quite large they do enable us to say that, in the temperature range −28 to −58°, $2k_{16}$ is about three times k_{15}, independent of temperature. The same temperature coefficient for both rate constants is to be expected for diffusion-controlled reactions in the same medium.[21]

Alkoxycarbonyl radicals are thermodynamically more stable with respect to decarboxylation than the isomeric acyloxyl radicals.

$$\mathrm{RO{\cdot}\dot{C}O} \xrightarrow{a} \mathrm{R\cdot} + \mathrm{CO_2} \xleftarrow{b} \mathrm{RCO_2\cdot} \quad (20)$$

Reaction (20*a*) is *ca.* 8 kcal mol^{-1} less exothermic than (20*b*).[24]

The acetoxyl radical is estimated [25] to undergo decarboxylation in solution [equation (20*b*), R = Me] with a rate constant of 1·6 × 10^9 s^{-1} at 60° with an activation energy of 6·6 kcal mol^{-1} and an A-factor of $10^{13{\cdot}5}$ s^{-1}. Indeed it seems unlikely that acetoxyl radicals can exist for long enough to diffuse out of the solvent cage in which they are generated. The decarboxylation of higher acyloxyl radicals is expected to be even more

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[23] R. K. Solly and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 427.

[24] P. Gray and J. C. J. Thynne, *Nature*, 1961, **191**, 1357.

[25] W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, 1962, **66**, 1591.

rapid than that of the acetoxyl radical, and the photolysis of diacyl peroxides at low temperatures has been proposed as a general method for the production of specific alkyl radicals for study by e.s.r. in solution.[26] In contrast, the rate constant for the decarboxylation of the t-butoxycarbonyl radical at 60° is $2{\cdot}9 \times 10^5$ s^{-1}, and the ethoxycarbonyl radical from ethyl formate decarboxylated much more slowly.

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