

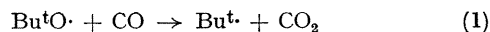
The Electron Spin Resonance Spectrum and Decarboxylation of the t-Butoxycarbonyl-radical in Solution

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Summary The t-butoxycarbonyl radical ($\text{Bu}^t\text{O}\dot{\text{C}}=\text{O}$), produced by photolysis of di-t-butyl peroxide in the presence of t-butyl formate, has been observed by e.s.r. spectroscopy and shown to be a σ -radical; the kinetics of the decarboxylation of $\text{Bu}^t\text{O}\dot{\text{C}}=\text{O}$ have been measured and the reaction shown to have a low A -factor ($10^{10.8} \text{ s}^{-1}$) for a unimolecular scission.

In the gas phase alkoxy-carbonyl radicals are thought to undergo a β -scission reaction giving carbon dioxide and an alkyl radical.¹ Recently, Lissi, Scaiano, and Villa² have examined the oxidation of carbon monoxide by t-butoxy-radicals in the gas phase [reaction (1)] and suggested that if a t-butoxycarbonyl radical was an intermediate it would be expected to decarboxylate rapidly at the temperatures employed (108–148°).



We report the observation in solution by e.s.r. spectroscopy of the t-butoxycarbonyl radical and the kinetics of its decarboxylation. When di-t-butyl peroxide is irradiated with u.v. light in the presence of t-butyl formate in the cavity of an e.s.r. spectrometer at -15° the two superimposed spectra shown in the Figure are observed. The single line *A* is assigned to the t-butoxycarbonyl radical with an isotropic g -factor of 2.0011; no definite further

splitting could be detected. The remaining lines are due to the t-butyl radical produced by decarboxylation of the alkoxy-carbonyl radical.

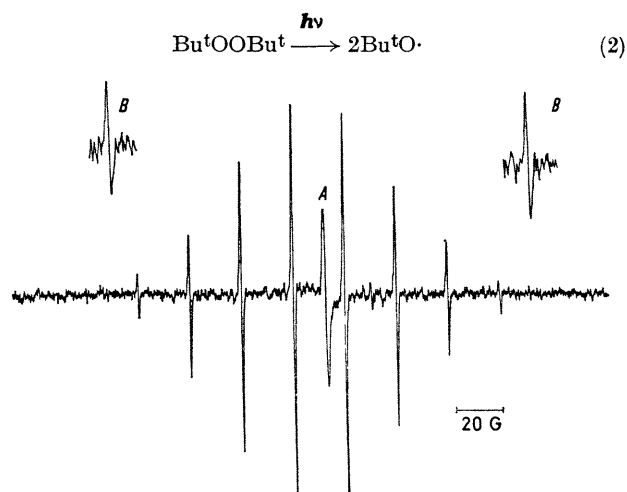
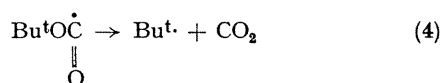
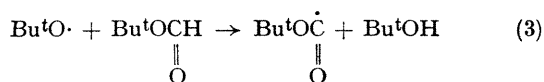


FIGURE. E.s.r. spectra obtained by photolysing a mixture of t-butyl formate and di-t-butyl peroxide (1:4 v/v) at -15° . Line *A* is due to the radical $\text{Bu}^t\text{O}^{12}\dot{\text{C}}=\text{O}$, lines *B* are from $\text{Bu}^t\text{O}^{13}\dot{\text{C}}=\text{O}$ recorded with increased modulation and gain at -60° .



Using the competitive technique which we have described previously³ k_3 was given by equation (5)

$$\log_{10} k_3 = (8.94 \pm 0.05) - \frac{(4780 \pm 105)}{4.575 T} \text{ M}^{-1} \text{ s}^{-1} \quad (5)$$

in the temperature range -70 to 0° .

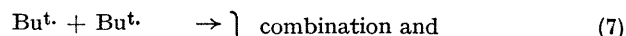
At -60° the signal from the t-butoxycarbonyl radical was sufficiently intense (see Figure) to enable hyperfine splitting from ^{13}C present in natural abundance in the carbonyl carbon to be observed. The large ^{13}C splitting [$a(^{13}\text{C}) = 183.5 \text{ G}$] in conjunction with the g -factor, which is lower than the free-spin value (2.0023), shows that the orbital containing the unpaired electron possesses appreciable s -character, t-butoxycarbonyl being a σ -radical.^{4,5†}

It may readily be shown that k_4 is given by equation (6)

$$k_4 = [\text{Bu}^t\cdot] \{2k_7[\text{Bu}^t\cdot] + k_8[\text{Bu}^t\text{O}\dot{\text{C}}\text{O}]\} / [\text{Bu}^t\text{O}\dot{\text{C}}\text{O}] \quad (6)$$

under steady state conditions where reactions (7) and (8)

refer to the removal of t-butyl radicals from the system.‡



The concentration of t-butoxy-radicals is relatively small and radical-radical reactions involving them need not be considered. The value of $2k_7$ is $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at ambient temperatures and there is good evidence that k_8 is close to $2k_7$ with a very small activation energy for both reactions.⁶ The concentrations of t-butoxycarbonyl and t-butyl radicals were measured by e.s.r. as a function of temperature from -65° to $+5^\circ$ and taking the above value for $2k_8$ and k_7 we obtain

$$\log_{10} k_4 = (10.81 \pm 0.05) - \frac{(7710 \pm 420)}{4.575 T} \text{ s}^{-1}$$

The low A factor for the decarboxylation of the t-butoxycarbonyl radical (which is exothermic by $22.3 \text{ kcal mol}^{-1}$) is not without precedent since the accepted value⁷ of A for the decarbonylation of the acetyl radical in the gas phase is $10^{10.3} \text{ s}^{-1}$.

We thank Professor A. G. Davies for useful discussions.

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† $a(^{13}\text{C})$ in $\text{Bu}^t\text{O}\dot{\text{C}}=\text{O}$ is intermediate between the values found for $\text{H}\dot{\text{C}}=\text{O}$ (134 G) and $\text{F}\dot{\text{C}}=\text{O}$ (286 G) in the solid state.⁶

‡ Photolysis of 2,2'-azoisobutane in the presence of t-butyl formate did not give rise to the e.s.r. spectrum of the t-butoxycarbonyl radical in the temperature range -30 to $+25^\circ$.

§ Thermodynamic data taken from refs. 7 and 8, assuming $D[\text{Bu}^t\text{OC}(\text{O})-\text{H}] = D[\text{MeOC}(\text{O})-\text{H}] = 92.7 \text{ kcal. mol}^{-1}$.

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