Electron Spin Resonance Detection of Radical-pairs formed by γ-Radiolysis of Crystalline Diaryl Carbonates

By A. DAVIS,* J. H. GOLDEN,* J. A. MCRAE,† and M. C. R. SYMONS†

(*Explosives Research and Development Establishment, Ministry of Technology, Waltham Abbey, Essex, †Department of Chemistry, The University, Leicester)

WE have found that important stable products of the γ-radiolysis of diaryl carbonates are the corresponding *o*-hydroxydiphenyl ethers and carbon monoxide. When phenyl *p*-tolyl carbonate is irradiated only the mixed ether is formed, showing that the reaction is effectively intramolecular. This could be either a rearrangement or due to a cage-effect subsequent to process (1)

$$(RO)_2CO \rightarrow CO + 2RO \qquad (1)$$

An electron spin resonance study of γ-irradiated diaryl carbonate powders at 77°K shows unambiguously that process (1) does occur.

The spectrum obtained from di-*p*-tolyl carbonate is given in Figure 1. Those from diphenyl and phenyl *p*-tolyl carbonates were almost identical. The central feature is caused by a relatively small concentration of unpaired radicals and the remaining four lines are the parallel and perpendicular features associated with a triplet state. The splitting between the outer features gives an effective "magnetic" separation of 5·9 Å between the trapped radicals. The significance of this result is indicated in Figure 2 for the two possible configurations.

Our interpretation is strongly supported by the appearance of a weak resonance absorption at half-field which is assigned to the forbidden $\Delta m_s = 2$ transition. On warming, the triplet-state resonance is lost with no parallel increase in the intensity of the central line. Thus, as the chemical analysis indicates, cage recombination occurs before the radicals can diffuse through the crystal. In order for narrow lines to be obtained, such pairwise trapping must be very precise.[1,2] Elimination of small molecules would seem to be ideal for the required precision and electron spin resonance should be of general utility in probing such reactions in the solid state. Indeed a re-interpretation[3] of

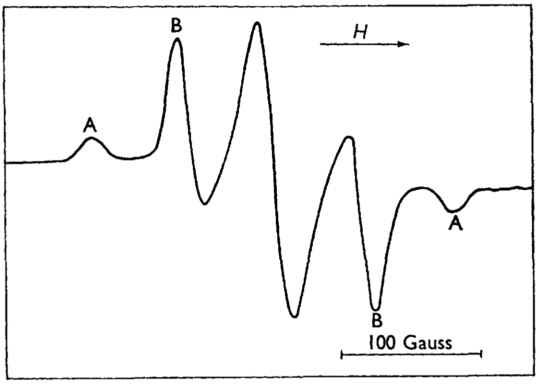

FIGURE 1. *Electron spin resonance spectrum of di-*p*-tolyl carbonate after γ-irradiation at* 77°K:
A–A = 268 gauss ∥ splitting; B–B = 138 gauss ⊥ splitting; g = 2·0053 for both central radical and triplet radicals

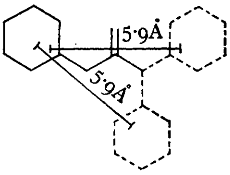

FIGURE 2. *Diagram showing the positions of the effective spin moments for* cis- *and* trans-*configurations of diphenyl carbonate*

the spectrum of azobisisobutyronitrile after photolysis[4] at 77° K has shown that radical pairs are formed at the expected distance apart if nitrogen molecules are eliminated. In this case hyperfine coupling was detected and can be interpreted in terms of rapid spin exchange.

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