An Electron Spin Resonance Study of Some Trapped Primary Radicals

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The spin trapping technique has been employed, in conjunction with e.s.r. spectroscopy, to study the free radicals produced during the thermal decomposition of two common initiators of free radical polymerisation, benzoyl peroxide and azobisisobutyronitrile.

One of the common initiators of free radical polymerisations is benzoyl peroxide which dissociates thermally according to the reactions (1) and (2). In the presence of suitable unsaturated substances, the benzoyloxyl radical produced in (1) and the phenyl radical produced in (2) can initiate polymerisation giving rise to polymers with benzoyloxy and phenyl end-groups.[1] When benzoyl peroxide is decomposed in an inert solvent, such as benzene at 60 °C, most of the benzoyloxyl radicals produced in (1) subsequently dissociate as in (2); the yield of carbon dioxide can be depressed by the presence in the solution of certain additives.[2] The additives fall into two classes *viz.* those, such as monomers, that function by addition according to reaction (3) and those that act as hydrogen donors [reaction (4)]. The yields of carbon dioxide produced during decomposition of benzoyl peroxide can conveniently be determined using peroxide suitably labelled with carbon-14. The reactivities of various additives towards the benzoyloxyl radical can be compared applying standard treatments to the competition between (1) and (3) or (4).

$$(C_6H_5COO)_2 \xrightarrow{\Delta} 2C_6H_5COO\cdot \qquad (1)$$

$$C_6H_5COO\cdot \longrightarrow C_6H_5\cdot + CO_2 \qquad (2)$$

$$C_6H_5COO\cdot + X \longrightarrow C_6H_5COOX\cdot \qquad (3)$$

$$C_6H_5COO\cdot + YH \longrightarrow C_6H_5COOH + Y\cdot \qquad (4)$$

Recently there has been considerable interest in spin trapping particularly as, in conjunction with e.s.r. spectroscopy, the technique leads to information about free radicals normally present in only very low concentration.[3] As a preliminary investigation into the application of this technique we previously studied the influence of various trapping agents on the yield of carbon dioxide during the thermal decomposition of benzoyl peroxide.[4] It was evident that these trapping agents reacted readily with the benzoyloxyl radical because, even at comparatively low concentrations, they depressed the yield of carbon dioxide.

We have now extended our investigations to include a study of the e.s.r. spectra of the radicals trapped in these systems. We have also studied another common initiator of free radical polymerisations, azobisisobutyronitrile.

Experimental

Materials.—Benzene (May and Baker Ltd.) was purified as described[5] and dried over a 4X Linde molecular sieve. Benzoyl peroxide (B.D.H.) was precipitated from chloroform solution by the addition of an equal volume of light petroleum (b.p. 60—80°) and dried under vacuum before use. Azobisisobutyronitrile (Aldrich) was recrystallised several times from chloroform before use. 2-Methyl-2-nitrosopropane (MNP), *N*-t-butyl-α-phenylnitrone (PBN) (both Lancaster Synthesis), and nitrosobenzene (NB) (Aldrich) were all used as supplied.

Procedure.—Benzene solutions of the initiators and of the spin traps were degassed employing the usual freeze–thaw procedure and mixed immediately before sealing, under vacuum, in an e.s.r. sample tube. The concentration of the initiator in these experiments was *ca.* 10^{-2} mol dm^{-3} but the concentration of the spin trap ranged from 10^{-3} to 0.5 mol dm^{-3}. All reactions were studied in benzene solution *in situ* in the e.s.r. spectrometer at 333 K. Precautions were taken to exclude light during those experiments involving the use of MNP as trapping agent and an e.s.r. spectrum attributable to the photochemical decomposition product of MNP, di-t-butyl nitroxide,[6] was not observed in these experiments.

Spectroscopic Measurements.—All e.s.r. spectra were recorded on a Varian E3 spectrometer with 100 kHz magnetic field modulation. The magnetic field sweep was calibrated using Fremy's salt.[7] The temperature of the samples was controlled by means of a Varian E 4557 variable temperature unit. Computer simulations of e.s.r. spectra were obtained using a Data General Nova computer on line to the e.s.r. spectrometer and the splitting constants quoted from these simulations are considered to be accurate to ±2 μT.

Results and Discussion

Benzoyl Peroxide.—We describe first the results of our experiments involving benzoyl peroxide. Our earlier experiments indicated 2-methyl-2-nitrosopropane (MNP) was the most active of the trapping agents examined for the depression of carbon dioxide yields and nitrosobenzene (NB) the least active in this respect.[4] The possibility of obtaining the e.s.r. spectrum of trapped phenyl radicals should therefore be greatest in those experiments in which NB acts as the trapping agent.

E.s.r. spectra were recorded in a series of experiments in which the concentration of NB was varied over a wide range. In each experiment only a single species was observed [see Figure 1(A)] and its concentration increased with time. The successful computer simulation of this spectrum [see Figure 1(B)] requires *a*(N) 960, *a*(6H) 179, and *a*(4H) 80 μT and can clearly be assigned to the diphenyl nitroxide radical formed by the trapping of the phenyl radical. These splitting constants agree well with those for the same nitroxide in benzene solution formed by the reaction of t-butyl hydroperoxide with triphenylhydrazine.[8] There is no evidence, in these spectra, for a second species which could correspond to the trapped benzoyloxyl radical.

Similar experiments were performed employing *N*-t-butyl-

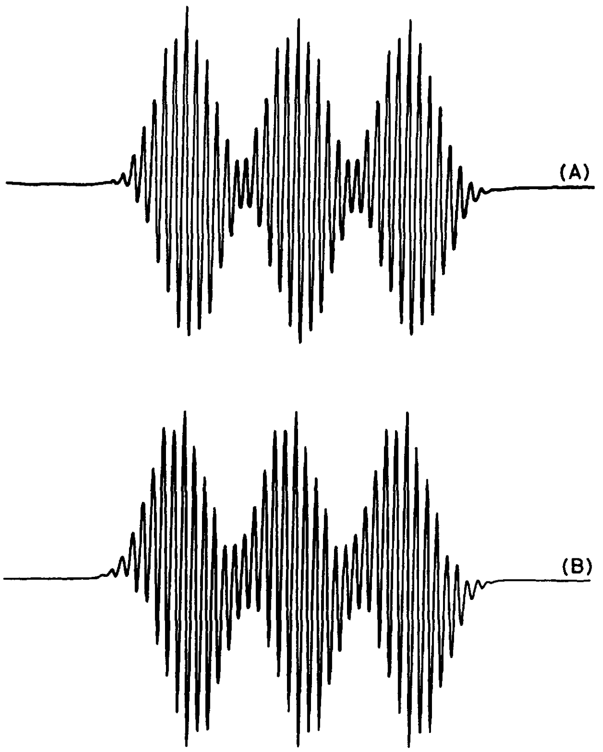

Figure 1. (A) The e.s.r. spectrum of the phenyl radical trapped by nitrosobenzene in benzene at 333 K together with its computer simulation (B) using the splitting constants given in the text

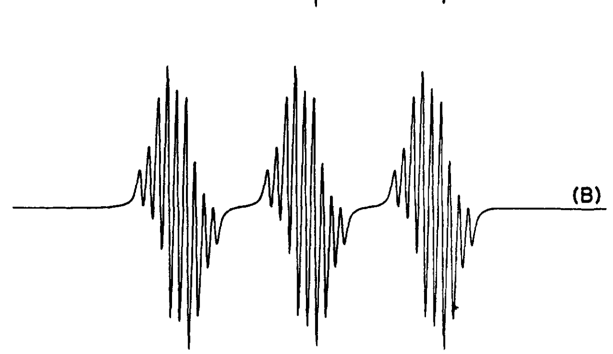

Figure 2. (A) The e.s.r. spectrum of the phenyl radical trapped by 2-methyl-2-nitrosopropane in benzene at 333 K together with its computer simulation (B) using the splitting constants given in the text

α-phenylnitrone (PBN) as the trapping agent. This system has been widely studied by other workers and our experiments give results consistent with those previously reported.[9,10] The principal species present in the e.s.r. spectrum is a 1 : 1 : 1 triplet of 1 : 1 doublets which grows in intensity during the course of the reaction and has been assigned to the nitrone adduct of the benzoyloxyl radical [a(N) 1 307 and a(β-H) 144 μT].[11] It might have been expected that PBN would also trap the phenyl radical. This adduct has been prepared in good yield by the addition of organolithium and Grignard compounds to the nitrone followed by oxidation and has splitting constants significantly different from those observed in these experiments [*i.e.* a(N) 1 441 and a(β-H) 221 μT].[12] However, Janzen *et al.*[10] have reported that the velocity constant for the addition of the phenyl radical to PBN is considerably smaller than those for other typical spin trapping reactions.

Of the three trapping agents studied MNP would be expected to trap the benzoyloxyl radical in good yield since, as described above, the trapping agent has the greatest influence on the carbon dioxide yield. Only one trapped species was observed [see Figure 2(A)] which corresponds, rather unexpectedly, to the trapped phenyl radical [a(N) 1 245, a(3H) 180, and a(2H) 87 μT, see computer simulation, Figure 2(B)]. It appears, therefore, that although MNP depresses the carbon dioxide yield indicating reaction with the benzoyloxyl radical, the resulting nitroxide is relatively unstable. Nitroxide radicals derived from MNP are often less persistent than many other nitroxides due to the formation of diamagnetic species by loss of either the trapped radical or the t-butyl radical.[13]

Azobisisobutyronitrile.—Azobisisobutyronitrile is another widely used initiator of free radical polymerisation; its thermal decomposition is thought to be free of complications, proceeding by reaction (5)[14] where R = $(CH_3)_2(CN)C$.

$$R{-}N{=}N{-}R \longrightarrow 2R\cdot + N_2 \qquad (5)$$

We describe first the results of our experiments employing NB as trapping agent. E.s.r. spectra were recorded for a range of NB concentrations. A characteristic e.s.r. spectrum was obtained [see Figure 3(A)] which grew gradually in intensity during the period of the measurements. The successful computer simulation of this spectrum is consistent with the trapping of the cyanopropyl radical [a(N) 1 154, a(3H) 218, and a(2H) 86 μT]. The same nitroxide has been reported in experiments involving the photochemical reaction of NB with $(CH_3)_2C(CN)NO$ in *o*-dimethylbenzene.[15] A comparison of the splitting constants in these experiments with those reported here confirms the nature of the trapped radical.

It has been suggested that the trapping of the cyanopropyl radical by PBN may be sterically hindered.[16] The PBN concentration was varied as before and again e.s.r. spectra corresponding to the PBN-trapped cyanopropyl radical [a(N) 1 405 and a(β-H) 310 μT] were obtained but only at reasonably high PBN concentrations. We find that the concentration of the trapped species is indeed very considerably smaller than in the corresponding experiment with benzoyl peroxide. The concentration of the trapped species is also very much less than in the experiment in which the cyanopropyl radical is trapped by MNP. These observations support the view that the trapping of the cyanopropyl radical by PBN is indeed sterically hindered.

Finally the experiment was repeated employing MNP as trapping agent. In this experiment a simple three-line e.s.r. spectrum was obtained [a(N) 1 475 μT] with intensity increasing with time. This spectrum has been reported previously as a minor component obtained during the thermal decomposition of azobisisobutyronitrile in the presence of MNP and styrene[17] and is assigned to t-butyl cyanopropyl nitroxide.

Studies of the products formed during the thermal decomposition of azobisisobutyronitrile have suggested the possible

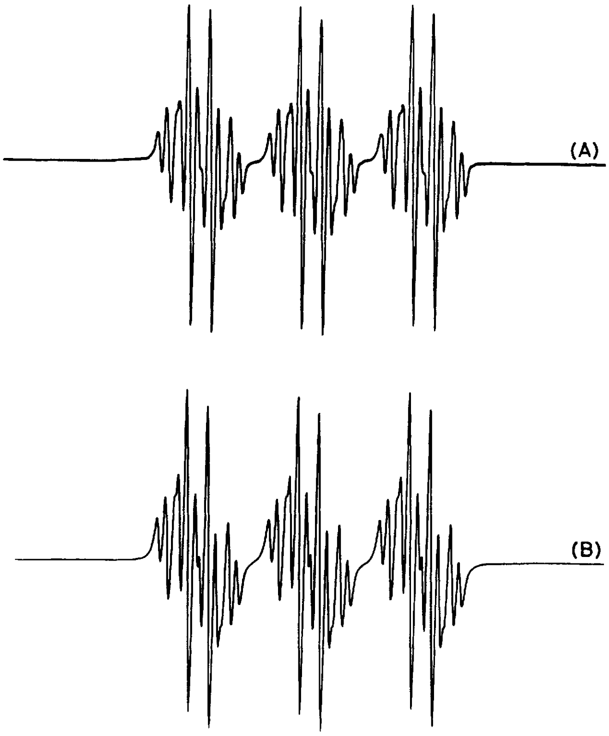

Figure 3. (A) The e.s.r. spectrum of the cyanopropyl radical trapped by nitrosobenzene in benzene at 333 K together with its computer simulation (B) using the splitting constants given in the text

presence of the dimethylketenimine radical, $(CH_3)_2C{:}C{:}N\cdot$.[18] It might be difficult to identify this radical with certainty when trapped by PBN, but when trapped by either MNB or NB the resulting e.s.r. spectra should be significantly different from that of the trapped cyanopropyl radical. However, a careful examination of the appropriate e.s.r. spectra failed to reveal evidence for trapped ketenimine radical. It could be, of course, that even if this radical is a significant product of the thermal decomposition of azobisisobutyronitrile, the efficiency of its reaction with these trapping agents is relatively low.

E.s.r. Spectra.—The nature of the various e.s.r. spectra follows closely that expected for the various trapped radicals. For example, the simplest spectrum obtained, that of t-butyl cyanopropyl nitroxide, gives a three-line 1 : 1 : 1 hyperfine pattern. Hyperfine splitting is not observed from the methyl protons or from the nitrogen of the CN group and the magnitude of the nitrogen splitting constant is very similar to that of di-t-butyl nitroxide [a(N) 1 503 μT]. This principal nitrogen splitting constant is significantly reduced in the two related radicals, *viz.* phenyl cyanopropyl and phenyl t-butyl nitroxide as a consequence of the delocalisation of spin density into the aromatic ring and is further reduced in diphenyl nitroxide due to the presence of a second aryl substituent. Unfortunately the two PBN adducts give similar six-line spectra with hyperfine splittings from the principal nitrogen and β-proton only. There is, however, a significant difference in the latter splitting constant for these two nitroxides.

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