

A Study of the 'Head' Addition of Benzoyloxyl Radicals to Vinyl Acetate

Jeremy Lane and Brian J. Tabner*

The Department of Chemistry, The University of Lancaster, Lancaster LA1 4YA

The radicals formed by the addition of the benzoyloxyl radical to vinyl acetate have been studied employing 2-methyl-2-nitrosopropane and 2,4,6-tri-*t*-butylnitrosobenzene as spin traps. The resulting e.s.r. spectrum of the radicals obtained using the latter spin trap indicates that a significant proportion (*i.e.* 3:10) of the benzoyloxyl radicals add to the substituted carbon atom of the C=C bond ('head' addition).

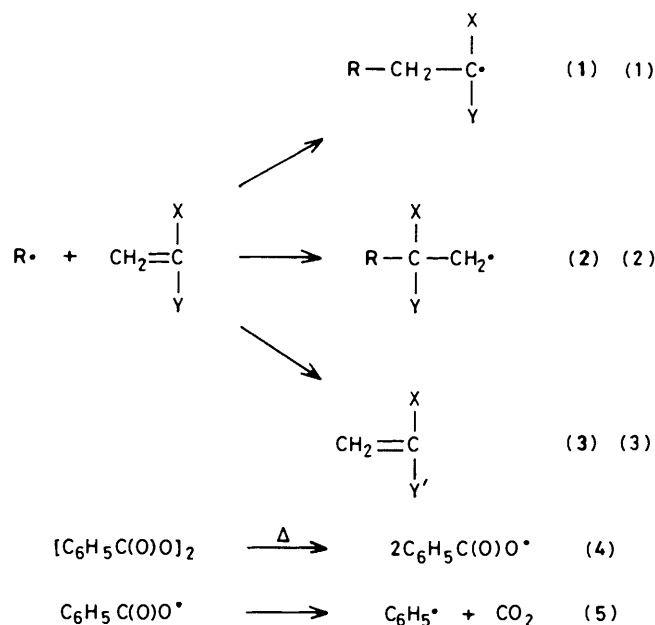
Information on the initiation of free radical polymerisation, by the addition of an appropriate radical to a suitable vinyl monomer, is of considerable importance. Clearly three reactions are possible under these conditions. It is usually assumed that reaction (1) predominates over (2) to the virtual exclusion of the latter. Reaction (3) (reaction with the substituent) is important only in a relatively small number of monomers such as methyl methacrylate and styrene.¹ Any possible competition between reactions (1) and (2) might be expected to vary with the nature of the monomer.

The spin trapping technique has recently aroused much interest as it allows information to be obtained on radicals normally present in only very low steady-state concentrations.² Potentially, therefore, it provides a useful means of detecting radical (2) in a typical polymerisation system. The optimum condition for such a system would be one in which (i) the initiating radical was relatively unselective in its site of addition leading to the formation of both radical (1), by 'tail' addition, and radical (2), by 'head' addition, (ii) the monomer was susceptible to 'head' addition, and (iii) the spin trap was sufficiently reactive to trap radicals (1) and (2) before further addition of monomer could occur. Some recently published results indicate that the first two of these conditions are satisfied, at least in part, by the addition of benzoyloxyl radicals to vinyl acetate.¹ Benzoyloxyl radicals are produced during the thermal dissociation of benzoyl peroxide according to reactions (4) and (5). Both the benzoyloxyl and phenyl radicals produced in these reactions are capable of initiating polymerisation.³

We report here the results of our investigations on this system employing 2-methyl-2-nitrosopropane and 2,4,6-tri-*t*-butylnitrosobenzene as spin traps. The former was selected as a suitable spin trap for these experiments because it traps carbon-centred radicals with a reasonably high efficiency but not oxygen-centred radicals, thus reducing the complexity of the observed spectra. However, as described in the text below, experiments employing 2,4,6-tri-*t*-butylnitrosobenzene as a spin trap were found to be more successful in detecting the presence of a radical (2).

Experimental

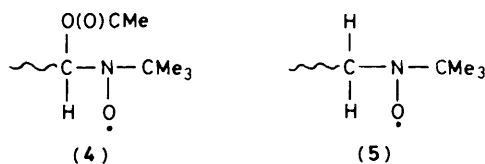
Materials.—Benzene (May and Baker) was purified by washing three times with concentrated sulphuric acid, followed by three washings with water and then three washings with 5% NaOH. After a further series of washings with water it was dried over MgSO₄ and CaH₂ and after distillation was stored over a 4X Linde molecular sieve. Benzoyl peroxide (Laporte Industries Ltd.) was purified by repeated precipitation from chloroform solution by the addition of an equal volume of light petroleum (b.p. 60–80 °C) and dried under vacuum before use. The spin traps, 2-methyl-2-nitrosopropane (Lancaster Synthesis) and 2,4,6-tri-*t*-butylnitrosobenzene (Aldrich), were used as supplied.



Styrene (B.D.H.) was purified as described⁴ and then dried over MgSO₄ and CaH₂. It was then distilled under nitrogen (b.p. 40–42 °C at 17 mmHg). Vinyl acetate (B.D.H.) was purified as described.⁴

Procedure.—Benzene solutions of the initiator and spin trap and of the monomer 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 and that of the spin traps was 10⁻¹–5 × 10⁻¹ mol dm⁻³. The concentration of the monomer was in the range 2.5–10% (by volume). All reactions were studied in benzene solution *in situ* in the e.s.r. spectrometer at 333 K. Precautions were taken to exclude light as far as was possible during the course of all 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.⁵ 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 1220 computer on line to the spectrometer and the hyperfine splitting constants quoted from these simulations are considered to be accurate to ± 2 μT, but are less accurate for the



minor species in multi-component spectra. The computer simulations assume that the principal nitrogen hyperfine lines have the same linewidth. It is apparent from the experimental spectra, however, that this is not the case. However, computer simulations of the e.s.r. spectra to take this linewidth variation into account were not attempted due to the complexity of the simulation of multi-component spectra.

Results and Discussion

Recent results obtained from a study of the reaction of benzoyloxyl radicals with a variety of monomers in the presence of nitroxides indicate that the polymerisation of styrene, vinyl acetate, methyl methacrylate, and methyl acrylate can all be initiated by the head addition of the benzoyloxyl radical.¹ However, the percentage initiation *via* head addition is relatively small (*ca.* 5%) with styrene, methyl methacrylate, and methyl acrylate, but is much more significant (*ca.* 20%) with vinyl acetate. Vinyl acetate was therefore selected for our experiments as the monomer for which the possibility of forming and subsequently trapping radical [2; X = H, Y = O(O)CMe] appears to be greatest.

Radicals (1) and (2) [X = H, Y = O(O)CMe] formed by the addition of the initiating radical to vinyl acetate, when trapped by 2-methyl-2-nitrosopropane (MNP), should give rise to e.s.r.-distinguishable species (4) and (5) with hyperfine coupling to one and to two β -protons respectively.

It is possible that the proportions of addition products (4) and (5) could be dependent on the chain length of the growing polymer. In order to optimise the conditions necessary for the observation of the trapped radical (5) there is, therefore, a requirement for an efficient trapping agent and for a relatively low monomer concentration. Our experiments with MNP as spin trap give an e.s.r. spectrum with $a(N)$ 1259 and $a(H)$ 118 μ T, assigned to radical (4), with a very small additional spectrum just observable. However, a decrease in the monomer concentration results only in the appearance of the spectrum of PhN(O[•])CMe₃ [formed by the trapping of phenyl radicals produced in reaction (5)]. There was no apparent change in the relative intensity of the very weak secondary spectrum which may possibly be assigned to radical (5).

Despite the obvious advantages of employing MNP in these experiments we turned to the alternative spin trap 2,4,6-tri-*t*-butylnitrosobenzene (TNB). This spin trap behaves similarly to MNP. For example, when benzoyl peroxide is thermally decomposed in its presence but in the absence of a monomer, it does not trap the benzoyloxyl radical but does trap the phenyl radical [see Figure 1(a)]. The resulting spectra are complicated by additional hyperfine coupling due to interaction with two *meta*-protons, but remain sensitive to the nature of the trapped radical. In addition this spin trap has been successful in trapping a wide range of carbon-centred radicals.⁶

The thermal decomposition of benzoyl peroxide in the presence of vinyl acetate and TNB leads to complicated e.s.r. spectra a typical example of which is illustrated in Figure 2(a). An examination of the spectra obtained with various vinyl acetate and spin trap concentrations leads to the conclusion that this spectrum is a superimposition of spectra arising from four trapped radicals. One of these is undoubtedly that of the trapped phenyl radical [$a(N)$ 969, $a(o-H)$ 281, $a(m-H)$ 94, $a(p-H)$

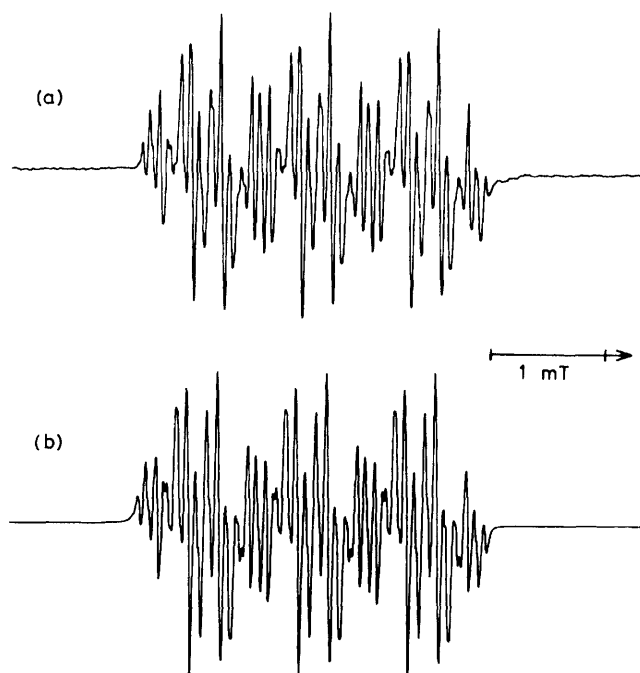
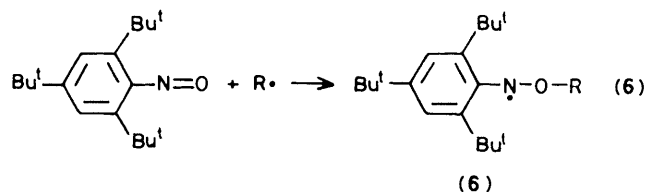


Figure 1. Experimental e.s.r. spectrum of the phenyl radical trapped by TNB in benzene at 333 K (a), and its computer simulation (b) based upon the splitting constants quoted in the text



263, and $a(m'-H)$ 65 μ T] and another is undoubtedly that formed by the trapping of radical (1) [X = H, Y = O(O)CMe] [$a(N)$ 1 227, $a(H)$ 1 578, and $a(m-H)$ 70 μ T]. One of the two other remaining species has a lower g -value than any of the other radicals in this system which is indicative of the formation of an anilino radical [reaction (6)].⁶

In order to examine the possible formation of an anilino radical in these systems similar experiments were undertaken with styrene (which is less prone to head addition¹) as the monomer. The resulting e.s.r. spectrum is illustrated in Figure 3(a) which more clearly results from the superimposition of two spectra. The major species [$a(N)$ 1 337, $a(H)$ 1 739, $a(m-H)$ 76 μ T, and g 2.0063] can be assigned to the radical formed by the trapping by TNB of radical (1; X = H, Y = Ph) and the minor species [$a(N)$ 1 050, $a(H)$ 172, $a(m-H)$ 172 μ T, and g 2.0039] can be assigned to the anilino radical [6; R = CH(Ph)CH₂~]. Both of these radicals result as a consequence of tail addition. This conclusion is consistent with the conclusion of Terabe and Konaka⁷ that addition to TNB occurs at the nitrogen atom with primary alkyl radicals (in our case the radical formed by head addition to vinyl acetate) and at the oxygen atom with tertiary alkyl radicals, with addition occurring at both atoms with secondary alkyl radicals (in our case the radical formed by tail addition to vinyl acetate). With this additional information, the third species in the experiments with vinyl acetate [$a(N)$ 1 032, $a(H)$ 65, and $a(m-H)$ 194 μ T] can be assigned to the corresponding anilino radical [6; R = CH(MeO₂C)CH₂~].

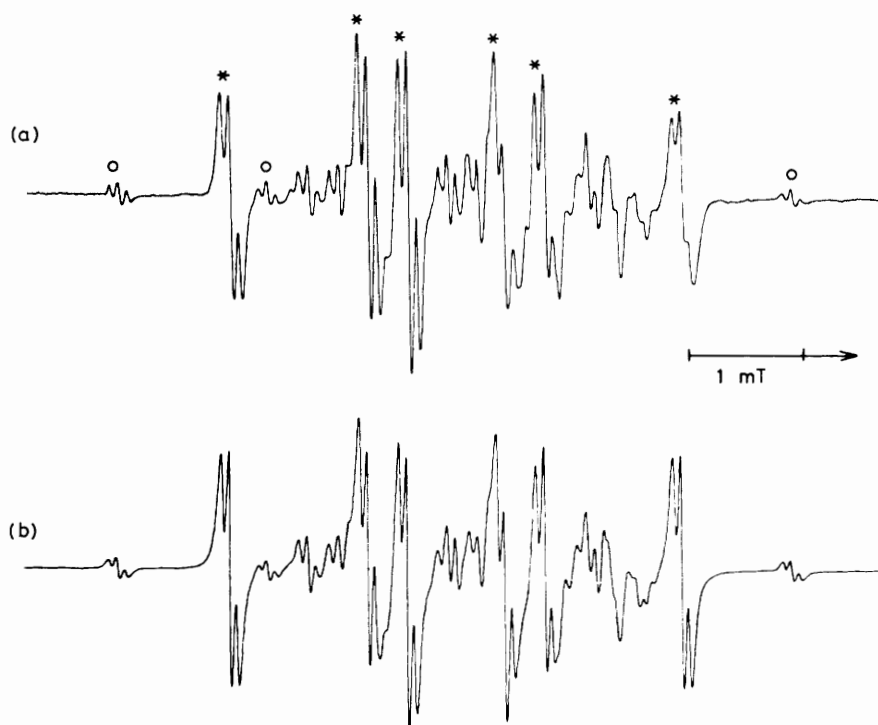


Figure 2. Experimental e.s.r. spectrum obtained during the decomposition of benzoyl peroxide in the presence of TNB and vinyl acetate in benzene at 333 K (a). The hyperfine lines arising from radical [1; X = H, Y = O(O)CMe], trapped by TNB, are indicated by * and those arising from radical [2; X = H, Y = O(O)CMe], trapped by TNB, where they do not overlap with lines arising from other species, are indicated by o. The computer simulation (b), for the mixture of the four species described in the text, is based on the splitting constants quoted

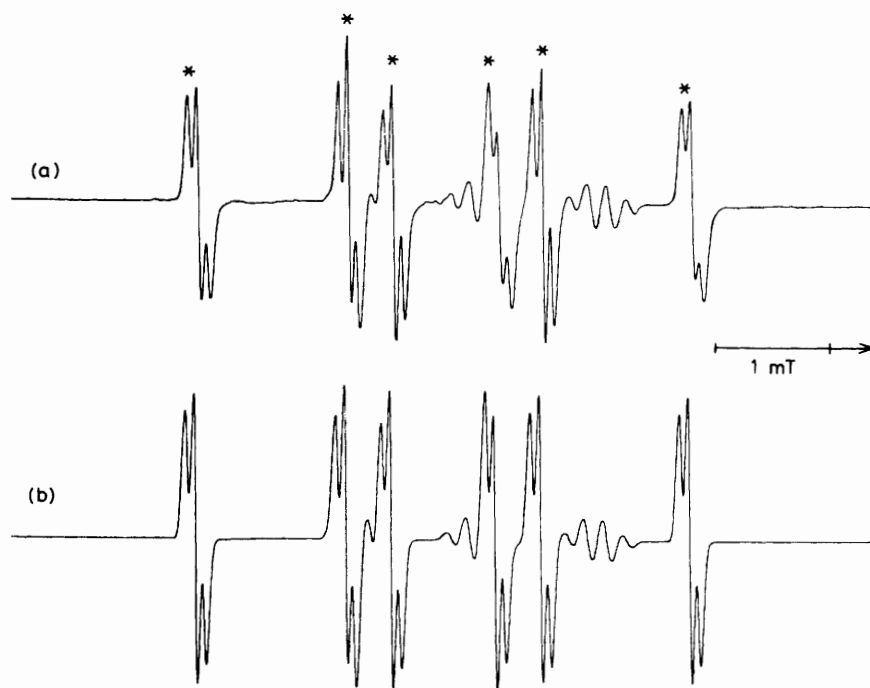


Figure 3. Experimental e.s.r. spectrum obtained during the decomposition of benzoyl peroxide in the presence of TNB and styrene in benzene at 333 K (a). The hyperfine lines arising from radical [1; X = H, Y = Ph], trapped by TNB, are indicated by *. The computer simulation (b), for a mixture of radical [1; X = H, Y = Ph], trapped by TNB, and radical [6; R = CH(Ph)CH₂ ~], is based on the splitting constants quoted in the text

There remains a further species present in the experiments with vinyl acetate [Figure 2(a)] which a computer reconstruction [see Figure 2(b)] reveals has $a(\text{N})$ 1 320, $a(2\text{H})$ 1 680, and $a(m\text{-H})$ 70 μT . This spectrum we assign to radical [2; X = H, Y = O(O)CMe], trapped by TNB, resulting from the head addition of the benzoyloxyl radical to vinyl acetate. It is interesting to note that the ratio of the trapped radicals resulting as a consequence of head addition to those resulting as a consequence of tail addition is *ca.* 3:10. This ratio is remarkably close to that reported by Moad *et al.* when studying the decomposition of benzoyl peroxide in the presence of vinyl acetate and various nitroxides.¹ It is quite possible, of course, that this agreement is a little fortuitous as there is no guarantee that radicals (1) and (2) are trapped with equal efficiency. However, these experiments do provide evidence which supports the view that there is significant head addition to vinyl acetate by benzoyloxyl radicals. This finding has important implications relating to the mechanism of the radical-initiated polymerisation of vinyl monomers, and to the properties of the resulting polymers.

Acknowledgements

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