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SPIN-TRAPPING OF α-AZIDOALKYL RADICALS

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Spin-trapping with 2-methyl-2-nitrosopropane of the α-azidoalkyl radicals derived from isopropyl and benzyl azides competes effectively with loss of nitrogen from these radicals at 313 K.

We have shown previously that e.s.r. spectra of iminyl radicals may be observed during continuous generation of t-butoxyl radicals in the presence of primary or secondary alkyl azides.[1,2] For example, when a t-butylbenzene solution containing isopropyl azide and di-t-butyl hyponitrite (TBHN) was heated at 343 K in the cavity of an e.s.r. spectrometer, the spectrum of the propan-2-iminyl radical (2) was observed [eqns. (1)-(3)]. No spectrum attributable to the intermediate 2-azidoprop-2-yl radical (1) was detected. Iminyl radicals were

$$\mathrm{Bu^tON{=}NOBu^t \xrightarrow{heat} 2Bu^tO\cdot + N_2} \qquad (1)$$

$$\mathrm{Bu^tO\cdot + Me_2C(H)N_3 \longrightarrow Bu^tOH + Me_2\dot{C}N_3} \qquad (2)$$

$$\mathrm{Me_2\dot{C}N_3} \xrightarrow{k_1} \underset{(2)}{\mathrm{Me_2C{=}N^{\cdot}}} + \mathrm{N_2} \quad \overset{(1)}{} \qquad (3)$$

also detected over a wide range of temperatures during photolysis of cyclopropane solutions containing di-t-butyl peroxide (DTBP) and the azide. Since no intermediate α-azidoalkyl radicals could be detected even at very low temperatures (133 K in experiments with $\mathrm{MeN_3}$), it was concluded that such species are very unstable with respect to loss of nitrogen, although it was pointed out[1,2] that a mechanistic ambiguity exists since photolysis of alkyl azides is known to yield imines, which could provide an alternative source of the iminyl radical [eqns. (4) and (5)]. Furthermore, the e.s.r. spectra of α-azidoalkyl radicals could be very complex

$$\mathrm{R_2C(H)N_3 \xrightarrow{h\nu} R_2C{=}NH + N_2} \qquad (4)$$

$$\mathrm{Bu^tO^{\cdot} + R_2C{=}NH \longrightarrow Bu^tOH + R_2C{=}N^{\cdot}} \qquad (5)$$

(and therefore difficult to detect) and loss of nitrogen from these radicals might be induced photochemically.

Recently, Al-Khalil and Bowman[3] have reported that 2-azido-2-nitropropane reacts with azide ion in the presence of light to give 2,2-diazidopropane. The reaction does not proceed in the dark, is inhibited by *p*-dinitrobenzene or by di-t-butyl nitroxide, and is therefore thought to proceed by the $\mathrm{S_{RN}1}$ mechanism shown in equations (6)-(8). At room temperature the addition of (1) to $\mathrm{N_3^-}$ must be sufficiently rapid to compete effectively with loss of nitrogen from (1) to give (2)[eqn. (3)]. We were somewhat surprised by this conclusion and so set out to obtain

$$\underset{(1)}{\mathrm{Me_2\dot{C}N_3}} + \mathrm{N_3^-} \longrightarrow [\mathrm{Me_2C(N_3)_2}]^{\overline{\cdot}} \tag{6}$$

$$[\mathrm{Me_2C(N_3)_2}]^{\overline{\cdot}} + \mathrm{Me_2C(N_3)NO_2} \longrightarrow \mathrm{Me_2C(N_3)_2} + [\mathrm{Me_2C(N_3)NO_2}]^{\overline{\cdot}} \tag{7}$$

$$[\mathrm{Me_2C(N_3)NO_2}]^{\overline{\cdot}} \longrightarrow \mathrm{Me_2\dot{C}N_3} + \mathrm{NO_2^-} \tag{8}$$

independent evidence for the occurrence of bimolecular reactions of α-azidoalkyl radicals.

When a benzene solution containing isopropyl azide (1.7 M) and TBHN (0.2 M) was heated at 303-335 K in the cavity of a Varian E-4 or E-109 spectrometer, the spectrum of the iminyl radical (2) was observed, as reported previously.[1,2] If 2-methyl-2-nitrosopropane (NtB; 0.02-0.07 M) was also present as a 'spin-trap',[4] overlapping spectra of three nitroxide radicals were observed [see Figure 1] and (2) was not detectable, even when very low concentrations of NtB were employed.[5] The lines marked A are assigned to t-butoxy t-butyl nitroxide (4) [*a*(1N) 27.2 G, *g* 2.0055] formed by trapping of t-butoxyl radicals.[6] Those marked B, which grew in relative intensity with time, are assigned to di-t-butyl nitroxide (5) [*a*(1N) 15.4 G, *g* 2.0061], formed mainly by trapping of t-butyl radicals produced in the decomposition of (4).[6] The lines marked C are assigned to the nitroxide (3) [*a*(1N) 15.2, *a*(1N) 1.70 G, *g* 2.0059], formed by trapping of the 2-azidoprop-2-yl radical (1). The reactions leading to these three nitroxides are shown in equations (9)-(12). In a series of experiments with a fixed concentration of NtB, the initial relative concentration of (3) increased as the concentration of isopropyl azide increased. We found no conclusive evidence for trapping of the iminyl radical (2), to give the hydrazon-*N*-oxyl radical[7] (6), although a weak unidentified spectrum could be detected in addition to lines A-C, especially at higher temperatures (>320 K) and when [NtB] was small.

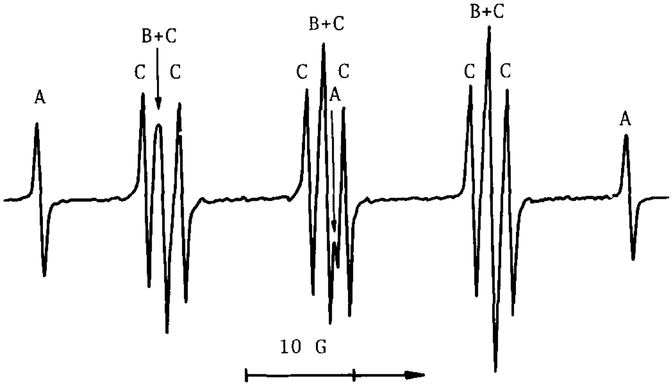


Figure 1: E.s.r. spectrum obtained during heating of isopropyl azide (5 M), TBHN (0.2 M), and NtB (0.05 M) in benzene at 306 K.

$$\mathrm{Me_2\dot{C}N_3} + \mathrm{Bu^tN{=}O} \xrightarrow{k_2} \underset{(3)}{\mathrm{Me_2C(N_3)N(\dot{O})Bu^t}} \tag{9}$$

$$\mathrm{Bu^tO^{\cdot}} + \mathrm{Bu^tN{=}O} \rightleftharpoons \underset{(4)}{\mathrm{Bu^tON(\dot{O})Bu^t}} \tag{10}$$

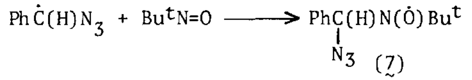
$$\mathrm{Bu^tON(\dot{O})Bu^t} \longrightarrow \mathrm{Bu^tON{=}O} + \mathrm{Bu^t\cdot} \tag{11}$$

$$\mathrm{Bu^t\cdot} + \mathrm{Bu^tN{=}O} \longrightarrow \underset{(5)}{\mathrm{Bu^t_2NO\cdot}} \tag{12}$$

$$\mathrm{Me_2C{=}N\cdot + Bu^tN{=}O \longrightarrow \underset{(6)}{Me_2C{=}N{-}N(\dot{O})Bu^t}} \tag{13}$$

Trapping of α-azidoalkyl radicals by NtB was confirmed by experiments with benzyl azide. The e.s.r. spectrum shown in Figure 2 was observed during thermolysis (306-320 K) of a benzene solution containing benzyl azide (5 M), TBHN (0.2 M), and NtB (0.03 M), and it is assigned to the nitroxide (7) [a(1N) 14.3, a(1N) 2.35, a(1H) 1.85 G, g 2.0061 at 313 K].

$$\mathrm{Bu^tO\cdot + PhCH_2N_3 \longrightarrow Ph\dot{C}(H)N_3 + Bu^tOH} \tag{14}$$



$$\mathrm{Ph\dot{C}(H)N_3 + Bu^tN{=}O \longrightarrow \underset{\displaystyle N_3\ (7)}{PhC(H)N(\dot{O})Bu^t}} \tag{15}$$

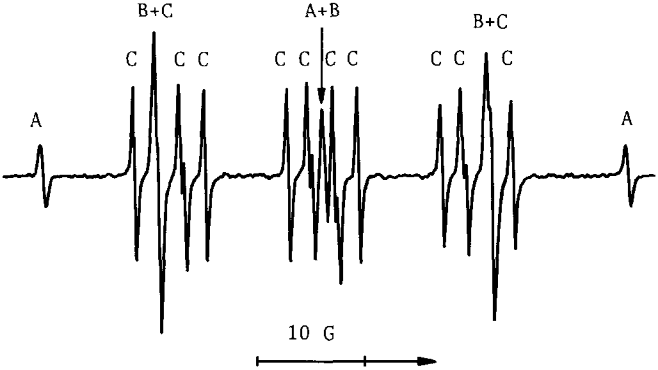
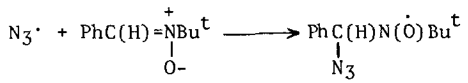


Figure 2: E.s.r. spectrum of the nitroxide (7) (lines marked C) in benzene at 313 K. The lines marked A and B are due to (4) and (5), respectively.

The nitroxide (7) has been generated previously[8-10] by addition of azido radicals to phenyl-*N*-t-butyl nitrone at room temperature. In aqueous solution the reported e.s.r. parameters were a(1N) 15.0, a(1N) 2.0, a(1H) 2.0 G[8] and it is noteworthy that the nitrogen splitting



$$\mathrm{N_3\cdot + PhC(H){=}\overset{+}{N}Bu^t \ (\text{with } O^- \text{ on N}) \longrightarrow \underset{\displaystyle N_3}{PhC(H)N(\dot{O})Bu^t}} \tag{16}$$

is larger than that reported here for benzene solvent. The difference may be ascribed to the shift of spin population from O to N in the nitroxide moiety as a result of hydrogen bonding to water, and such solvent effects are well-documented.[11] In aqueous solution, the proton and azide-nitrogen splittings are apparently equal, but in benzene these splittings are slightly different (see Figure 2) giving us further confidence in the assignment.

All attempts to detect the α-azidoalkyl radical (1) during photolysis of a cyclopropane solution containing DTBP and isopropyl azide at low temperature failed and only the spectrum of the iminyl radical (2) [a(1N) 9.90, a(6H) 1.38 G, g 2.0029] was detected down to 160 K.[12]

It is not easy to reconcile our ability to trap (1) with NtB at 313 K with our inability to detect (1) at 160 K in the absence of the nitroso compound. However, as pointed out above, α-azidoalkyl radicals might be difficult to detect and interpretation of the photochemical experiments could be complicated by photolysis of the azide and/or of the α-azidoalkyl radical itself. Setting aside these difficulties, it is instructive to consider the implications of the results in a semi-quantitative way.

Assuming that ⩾90% of the 2-azidoprop-2-yl radicals are trapped by 0.03 $\underline{\underline{M}}$ NtB at 313 K while ⩽10% lose nitrogen to give (2), then k_1 [eqn. (3)] must be $\leqslant 2 \times 10^4$ s^{-1}, if we take[14,15] k_2 [eqn. (9)] to be *ca.* 6×10^6 $\underline{\underline{M}}^{-1}$ s^{-1} at this temperature. Now, the inability to detect (1) at 160 K implies[2,16] that $k_1 \geqslant$ *ca.* 1×10^3 s^{-1} at this temperature and thus that $k_1(313\ K)/k_1(160\ K) \leqslant 20$. This would require that the activation energy for loss of nitrogen from (1) is ⩽ *ca.* 8.2 kJ mol^{-1} and that the corresponding *A*-factor is ⩽ *ca.* $10^{5.7}$ s^{-1}. Although such an *A*-factor is impossibly small for a straightforward unimolecular process, there is good reason to expect an *A*-factor which is substantially smaller than might, at first sight, be predicted (10^{12}-10^{13} s^{-1}) for this type of fragmentation.

The azidomethyl radical ($H_2\dot{C}N_3$) should be a planar π radical and, as has been noted previously,[17] this does not correlate with ground state nitrogen and ground state $H_2C{=}N\cdot$ (a σ radical). It does correlate with ground state nitrogen and an excited state (π) of the iminyl radical (*i.e.* $H_2\dot{C}\text{-}\ddot{N}:$) but, presumably, the activation energy for such a cleavage would be large. Replacement of the hydrogens by alkyl groups could (depending on their conformation) remove the symmetry plane and allow mixing of σ and π states but, even so, a 'memory' of the crossing would exist,[18] and the *A*-factors for unimolecular processes which involve electronic state cross-over are predicted to be anomalously low.[19] There is clearly a need for accurate measurements of the Arrhenius parameters for loss of nitrogen from α-azidoalkyl radicals.

References and Notes

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