Electron Spin Resonance Study of Iminyl and Triazenyl Radicals Derived from Organic Azides

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Summary t-Butoxyl radicals react with primary or secondary alkyl azides to produce iminyl radicals, whilst triorganosilyl radicals add to organic azides to give triazenyl radicals.

The unimolecular decomposition (photochemical or thermal) of organic azides has been studied extensively,[1] but the bimolecular reactions of azides with free radicals have received much less attention. We report here a preliminary e.s.r. study of the reactions of a series of organic azides with t-butoxyl and triorganosilyl radicals.

When a solution containing 2-azidopropane (*ca.* 0·5 M) and di-t-butyl hyponitrite (*ca.* 0·5 M), as a thermal source of t-butoxyl radicals,[2] in t-butylbenzene was heated to 343 K whilst the sample was in the cavity of an e.s.r. spectrometer, a strong spectrum assigned to the dimethyliminyl radical[3] (I; $R^1 = R^2 = Me$) was detected. Other primary and secondary alkyl azides gave rise to the spectra of iminyl radicals under similar conditions and, since alkyl azides do not undergo thermal decomposition at significant rates at the temperatures employed,[1] we propose that hydrogen abstraction from the azide is accompanied or followed by loss of nitrogen to produce the iminyl radical [equations (1) and (2)].

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

$$\mathrm{Bu^tO}\cdot + \mathrm{HC(R^1)(R^2)}\overset{-}{\mathrm{N}}{-}\overset{+}{\mathrm{N}}{\equiv}\mathrm{N} \longrightarrow \mathrm{Bu^tOH} + \mathrm{N_2} + \underset{\text{(I)}}{\mathrm{R^1(R^2)C{=}N}\cdot} \qquad (2)$$

The same spectra were detected over a wide range of temperatures (143—303 K) when the t-butoxyl radicals were generated photochemically from di-t-butyl peroxide in cyclopropane solvent,† but even at very low temperatures (133 K for azidomethane in a mixture of cyclopropane and propane) we were unable to detect any other spectra which might be assigned to an intermediate α-azidoalkyl radical. The spectroscopic parameters of the iminyl radicals are given in Table 1.

Entirely different spectra were observed during the thermal or photochemical generation of t-butoxyl radicals in the presence of triethyl- or triphenyl-silane and a primary

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† A mechanistic ambiguity exists for the photochemical experiments since photolysis of alkyl azides is known (ref. 1) to produce imines of the type $R^1(R^2)C{=}NH$ which might undergo hydrogen abstraction to provide a second source of (I).

alkyl azide. Similar spectra were detected from 2-azidopropane, t-butoxycarbonyl azide, and phenyl azide when the t-butoxyl radicals were generated by thermolysis of di-t-butyl hyponitrite.‡ These spectra exhibit hyperfine coupling to three non-equivalent nitrogen nuclei, are characterised by relatively low isotropic *g*-factors (see Table 2), and probably result from triazenyl radicals produced by addition of triorganosilyl radicals to the azides [equations (3) and (4)].

TABLE 1

E.s.r. parameters for iminyl radicals $R^1(R^2)C{=}N\cdot$ derived from the reactions of photochemically generated t-butoxyl radicals with alkyl azides in cyclopropane at 223 K.

R^1	R^2	*g*-factor	Hyperfine splittings (G) a_N	a_H[a]
H	H	2·0028	9·8	85·2 (2)
Me	Me	2·0029	9·6	1·40 (6)
Et	Et	2·0029	9·6	1·48 (4); 0·43 (6)
Et	H	2·0028	9·6	79·5 (1); 2·76 (2); 0·45 (3)
Pr^n	H	2·0029	9·5	80·4 (1); 2·64 (2); 0·70 (2); 0·35 (3)

[a] The number of nuclei coupling is shown in parentheses.

TABLE 2

E.s.r. parameters for triazenyl radicals generated thermally at 343 K in t-butylbenzene.

R^1	R^2	*g*-factor	Hyperfine splittings (G) a_N	a_N'	a_N''
Et	Pr^n	2·0010	17·6	3·6	1·8
Ph	Pr^n	2·0011	18·0	3·6	1·4
Et	Bu^n	2·0010	17·6	3·6	1·7
Et	Pr^i	2·0011	17·0	3·5	1·5
Ph	Pr^i	2·0011	17·6	3·6	1·2
Ph	Bu^t	2·0012	17·8	3·4	1·3
Et	Ph	2·0010	18·1	4·0	1·5
Ph	Ph	2·0011	18·0	3·6	1·2
Et	$Bu^tO.CO$	2·0010	20·0	3·8	1·9

$$Bu^tO\cdot + R^1_3SiH \longrightarrow Bu^tOH + R^1_3Si\cdot \qquad (3)$$

$$R^1_3Si\cdot + R^2\text{–}\overset{-}{N}\text{–}\overset{+}{N}{\equiv}N \longrightarrow \underset{\text{(II)}}{R^2\text{–}N{=}N\text{–}\dot{N}SiR^1_3}$$

$$\text{or } \underset{\text{(III)}}{R^2(R^1_3Si)N\text{–}N{=}N\cdot} \qquad (4)$$

The e.s.r. parameters appear to be more in accord with those expected for the 3,3-disubstituted triazenyl radical (III). It seems reasonable to suppose that the 1,3-disubstituted triazenyl radical (II) would be a 'π-radical' like the isolectronic species $R_2C{=}N\text{–}NSiR_3$,[4] whereas the radicals detected have *g*-factors less than that of the free electron (2·0023) and their spectra do not exhibit resolvable splittings from protons of the groups R^2. The low *g*-factor is consistent with the unpaired electron occupying an orbital orthogonal to the π-orbital of the N=N bond in (III).§

The spectra ascribed to (III) were still strong at 353 K when such species might be expected to lose nitrogen rapidly; however conjugative effects of the type (A) may serve to strengthen the $N_3\text{–}N_2$ bond.

$$\underset{\text{(A)}}{R^2(R^1_3Si)\ddot{N}_3\text{–}\ddot{N}_2{=}\dot{N}_1{:} \longleftrightarrow R^2(R^1_3Si)\overset{+}{N}{=}\ddot{N}\text{–}\underset{\cdot\cdot}{\dot{N}}{:}^-}$$

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‡ Intense spectra of unidentified long-lived nitrogen-containing radicals were observed during photochemical generation of t-butoxyl radicals in the presence of triethylsilane and each of these three azides. Direct photolysis of the azides is presumably responsible for the differences between thermal and photochemical experiments.

§ Assignment to $R^2(R^1_3Si)N\text{–}N{=}N\text{–}O\cdot$ (IV) [*cf.* J. I. G. Cadogan, R. M. Paton, and C. Thompson, *J. Chem. Soc.* (*B*), 1971, 583] was also considered and rejected because the spectra were unaffected by careful deoxygenation of the samples. The possibility that the oxygen atom in (IV) could originate from the t-butoxyl radical seems unlikely, since photolysis of a mixture of acetone, 1-azidobutane, and triethylsilane in cyclopropane gave rise to the same spectrum as that obtained when di-t-butyl peroxide replaced the ketone.

[1] 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, Ch. 5.
[2] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.
[3] D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 4115.
[4] W. Ahrens and A. Berndt, *Tetrahedron Letters*, 1975, 2295.