Electron Spin Resonance Study of Radical Addition to Alkyl Isocyanides

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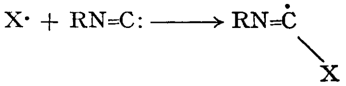
Summary The e.s.r. spectra of a number of imidoyl radicals, generated in solution by radical addition to alkyl isocyanides, have been detected and the fragmentation of these radicals has been studied.

A number of α-addition reactions of alkyl isocyanides are thought to proceed by free-radical chain mechanisms, involving the formation of intermediate imidoyl radicals (I) [reactions (1) and (2)].[1] It has also been proposed[2] that

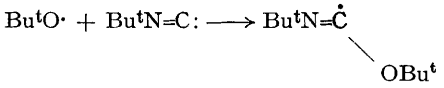


$$X\cdot + RN{=}C: \longrightarrow RN{=}\dot{C}{-}X \qquad (1)$$

(I)

$$\text{(I)} + X{-}Y \longrightarrow RN{=}C(X)Y + X\cdot \qquad (2)$$

the oxidation of t-butyl isocyanide to the isocyanate by t-butoxyl radicals involves β-scission of an intermediate imidoyl radical (II) [reactions (3) and (4)]. We have now



$$Bu^tO\cdot + Bu^tN{=}C: \longrightarrow Bu^tN{=}\dot{C}{-}OBu^t \qquad (3)$$

(II)

$$\text{(II)} \xrightarrow{k_4} Bu^tN{=}C{=}O + Bu^t\cdot \qquad (4)$$

confirmed that the imidoyl radical (II) is an intermediate in this oxidation, and further, established that a variety of free radicals add readily to alkyl isocyanides to produce imidoyl radicals, the structures and transformations of which may be studied using e.s.r. spectroscopy.

When a cyclopropane solution of t-butyl isocyanide and di-t-butyl peroxide (as a source of t-butoxyl radicals) was irradiated with high intensity u.v. light whilst the sample was in the cavity of the spectrometer, a strong spectrum [$a(^{13}C_\alpha)$ was determined without isotopic enrichment] of the imidoyl adduct (II) was detected at low temperatures (*ca.* 180 K). At higher temperatures the spectrum of (II) was less intense and, in addition, the spectrum of the t-butyl radical was apparent. The spectrum at 263 K is shown in the Figure.

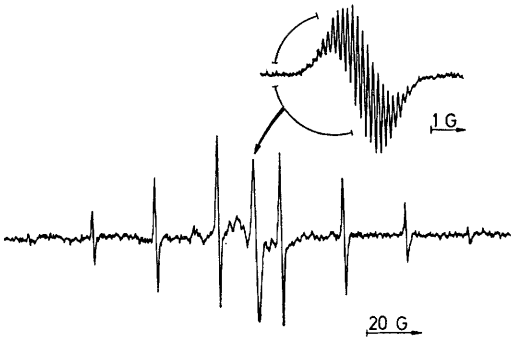


Figure. E.s.r. spectrum obtained during u.v. irradiation of a solution of t-butyl isocyanide and di-t-butyl peroxide in cyclopropane at 263 K. The signal from the imidoyl radical (II) is shown on an expanded scale; the remaining lines are due to the t-butyl radical.

When $C_4D_9{}^tOOC_4D_9{}^t$ was employed as a source of perdeuterio-t-butoxyl radicals, only perdeuterio-t-butyl radicals and no t-butyl radicals were detected as β-scission products of the labelled (II) at 270 K. In addition, t-butoxyl radicals add readily to methyl isocyanide and the resulting imidoyl radical undergoes β-scission to give t-butyl radicals at a similar rate to that for fragmentation of (II). The rate constant for reaction (4) was determined relative to that for self-reaction of t-butyl radicals, using the technique described previously.[3] In cyclopropane the

Table

E.s.r. parameters for imidoyl radicals (I) generated by addition of X· to alkyl isocyanides in cyclopropane solution

R in RNC	Addendum radical X·	T/K	g-Factor	Hyperfine splittings /G		
				$a(N_\beta)$	$a(^{13}C_\alpha)$	Others
Bu^t	$Bu^tO\cdot$	180	2·0016	a	108·0	b
Bu^t	$[^2H_9]$-$Bu^tO\cdot$	185	—	a	—	c
Me	$Bu^tO\cdot$	190	2·0013	$\leqslant 0{\cdot}2^d$	—	0·75(3H); 0·13(9H)
Bu^t	$Me_3SiO\cdot^e$	188	2·0013	f	116·0	g
Bu^t	$Bu^tS\cdot$	188	2·0014	5·0	—	—
Bu^t	$CF_3S\cdot$	187	—	5·8	—	—
Bu^t	$Et_3Si\cdot$	178	2·0014	8·6	32^h	—
Me	$Et_3Si\cdot$	171	2·0011	8·0	—	—
Bu^t	$(EtO)_2\dot{P}O$	175	2·0014	7·5	—	127·4 (1P)^g
Bu^t	$(\overline{OCMe_2CH_2O}{-})_2\dot{P}$	197	2·0016	8·6	41·5	147·9 (1P)^g

[a] Probably $a(N_\beta) \leqslant 0{\cdot}3$ G. [b] Spectrum appeared as a multiplet of at least 20 lines, approximately equally spaced by 0·15 G. It seems likely that $a(OC_4H_9{}^t) = 0{\cdot}15$ G and that the protons of the *N*-t-butyl group give rise to resolvable splitting which must be a multiple of the line spacing. [c] Spectrum appeared as a multiplet of at least 9 lines, approximately equally spaced by 0·3 G. [d] $MeN{=}\dot{C}OC_4D_9{}^t$ showed a 1:3:3:1 quartet with no further resolution and a peak–peak line-width of 0·4 G. [e] Fragmentation of $Bu^tN{=}\dot{C}OSiMe_3$ was undetected even at 273 K. [f] Unresolved; peak–peak line-width 1·6 G. [g] Some poorly resolved further splitting was apparent, probably arising from the *N*-t-butyl protons. [h] Only one line of the spectrum of $Bu^tN{=}^{13}\dot{C}SiEt_3$ could be clearly identified.

temperature-dependence of $(k_4/2k_t)$ between 216 and 253 K may be expressed by equation (5), where $\theta = 2{\cdot}303RT$ kJ mol^{-1}.

$$\log_{10}[(k_4/2k_t)/\mathrm{mol\,l^{-1}}] = 1{\cdot}1 - 34{\cdot}2/\theta \qquad (5)$$

Taking[4] the rate constant for self-reaction of t-butyl radicals $(2k_t)$ as $1{\cdot}1 \times 10^{10}$ l mol^{-1} s^{-1} at 250 K and assuming an activation energy of 8 kJ mol^{-1}, we obtain equation (6), whence $k_4 = 5 \times 10^3$ s^{-1} at 243 K.†

$$\log_{10}(k_4/\mathrm{s^{-1}}) = 12{\cdot}8 - 42{\cdot}2/\theta \qquad (6)$$

The radical (II) was also generated by abstraction of hydrogen from $\mathrm{Bu^tN{=}C(H)OBu^t}$ (prepared by the addition of t-butyl alcohol to t-butyl isocyanide catalysed by CuO[5]). Photolysis of bis(trimethylsilyl) peroxide‡ in the presence of $\mathrm{Bu^tN{=}C(H)OBu^t}$ gave rise to a strong e.s.r. spectrum of the radical (II), identical to that produced by addition of t-butoxyl radicals to the isocyanide.

The spectra of several other types of imidoyl adduct have been detected during the reactions of photochemically generated sulphur-, silicon-, and phosphorus-centred radicals with alkyl isocyanides, and representative examples are given in the Table.

There appears to be an increase in the deviation from linearity at $\mathrm{C_\alpha}$ [as judged by the magnitude of $a(^{13}\mathrm{C_\alpha})$] as the electronegativity of the substituent X in (I) increases, and the magnitude of $a(\mathrm{N_\beta})$ is also markedly dependent upon the nature of X.

The radical (I; R = $\mathrm{Bu^t}$, X = $\mathrm{SCMe_2Et}$) undergoes β-scission to give t-butyl isothiocyanate and the t-pentyl radical is detectable by e.s.r. spectroscopy at 170 K [equation (7)], whereas the radical (I; R = $\mathrm{Bu^t}$, X = $\mathrm{SiEt_3}$) undergoes rapid C–N cleavage [equation (8)] even at low temperatures (170 K) to give t-butyl radicals and, presumably, triethylcyanosilane.

$$\mathrm{Bu^tN{=}\dot{C}S{-}}\wr\mathrm{{-}CMe_2Et} \longrightarrow \mathrm{Bu^tN{=}C{=}S} + \mathrm{Me_2EtC^{\bullet}} \qquad (7)$$

$$\mathrm{Bu^t{-}}\wr\mathrm{{-}N{=}\dot{C}SiEt_3} \longrightarrow \mathrm{Bu^{t\bullet}} + \mathrm{N{\equiv}CSiEt_3} \qquad (8)$$

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† The spectrum of the radical $\mathrm{Bu^tN{=}\dot{C}Bu^t}$ was not detected in these experiments, and even methyl radicals do not add sufficiently rapidly to t-butyl isocyanide to give a detectable adduct spectrum. The spectra of such imidoyl radicals, generated by hydrogen abstraction from imines, have been reported previously (W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, 1973, **95**, 6872).

‡ The use of this peroxide removes any possible ambiguity which might arise if di-t-butyl peroxide were employed.

[1] For a review see T. Saegusa and Y. Ito in 'Isonitrile Chemistry,' ed. I. Ugi, Academic Press, New York, 1971, ch. 4.
[2] L. A. Singer and S. S. Kim, *Tetrahedron Letters*, 1974, 861.
[3] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.
[4] J. E. Bennett, J. A. Eyre, C. P. Rimmer, and R. Summers, *Chem. Phys. Letters*, 1974, **26**, 69.
[5] T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda, and K. Hirota, *Tetrahedron Letters*, 1967, 1273.