# AN E.S.R. STUDY OF SPIN-TRAPPING BY AZODICARBOXYLATES TO GIVE HYDRAZYL RADICALS

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Addition of photochemically- or thermally-generated radicals (X·) to dialkyl azodicarboxylates gives hydrazyl radicals $[RCO_2(X)N\dot{N}CO_2R]$ which are readily detected by e.s.r. spectroscopy.

In 1972 Stilbs et al.[1] proposed that diazenyl radicals of the type (2) were responsible for e.s.r. spectra observed during photolysis of dialkyl azodicarboxylates (1) in hydrocarbon solution.

$$RO_2CN=NCO_2R \xrightarrow{h\nu} RO_2CN=N\cdot + \cdot CO_2R \qquad (i)$$
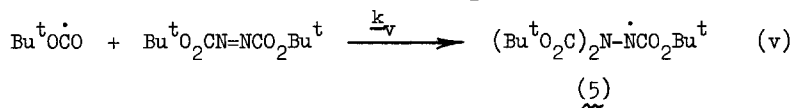$$(1) \qquad\qquad\qquad (2)$$
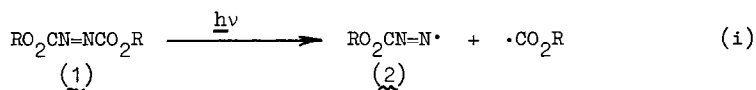
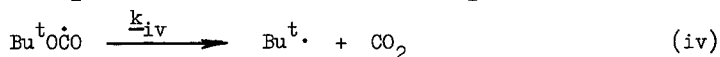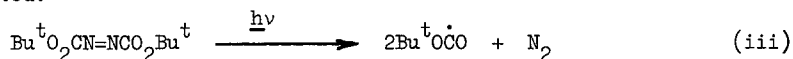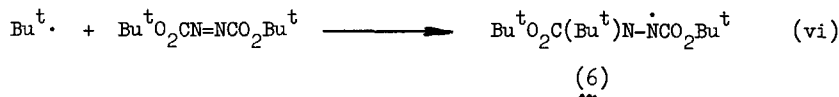In 1973 Marnett et al.[2] concluded that these spectra were due to hydrazyl radicals of the type (3), formed by addition of solvent-derived radicals to (1). Product studies certainly indicate that reaction (ii) must proceed readily.[3]

$$X\cdot + RO_2CN=NCO_2R \longrightarrow RO_2C(X)N^2-\dot{N}CO_2R \qquad (ii)$$
$$(3)$$
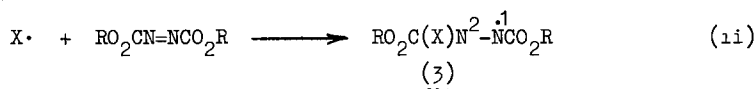
Later that year, Malatesta and Ingold[4] showed that the signals were in fact due to hydrazoxyl radicals $RO_2C(X)N-N(\dot{O})CO_2R$ (4), and e.s.r. spectra of authentic hydrazyl radicals resulting from homolytic addition to (1) have not been observed.

We now report that a variety of hydrazyl radicals can be generated by reaction (ii) and that the e.s.r. spectra of (3) may be readily detected. The azodicarboxylates were commercial materials, used without further purification, and the samples were degassed and sealed under vacuum in the normal way.[5] Photolysis[6] of a ca. 0.2 M solution of (1; R = Bu^t) in cyclopropane/t-butylbenzene (1:1) in the absence of oxygen at 220 K gave rise to overlapping e.s.r. signals which we ascribe to the hydrazyls (5) and (6), formed as shown in equations (iii) - (vi). If oxygen was not excluded, variable concentrations of hydrazoxyl radicals were also detected.

$$Bu^tO_2CN=NCO_2Bu^t \xrightarrow{h\nu} 2Bu^tO\dot{C}O + N_2 \qquad (iii)$$

$$Bu^tO\dot{C}O \xrightarrow{k_{iv}} Bu^t\cdot + CO_2 \qquad (iv)$$

$$Bu^tO\dot{C}O + Bu^tO_2CN=NCO_2Bu^t \xrightarrow{k_v} (Bu^tO_2C)_2N-\dot{N}CO_2Bu^t \qquad (v)$$
$$(5)$$

$$Bu^t\cdot \quad + \quad Bu^tO_2CN=NCO_2Bu^t \quad \longrightarrow \quad Bu^tO_2C(Bu^t)N-\overset{\cdot}{N}CO_2Bu^t \quad (vi)$$

$$(6)$$

Addition of $Bu^tN=NBu^t$ (a photochemical source of $Bu^t\cdot$.) brought about a very large increase in the relative intensity of the signal assigned to (6). Similar results were obtained from experiments in which $(1; \quad R = Bu^t)$ was photolysed in isobutane solvent with di-t-butyl peroxide as an indirect source of t-butyl radicals [equation (vii); $X = Bu^t$], and it appears that the quantum yield of radicals from direct photolysis of (1) is small.

$$Bu^tO\cdot \quad + \quad XH \quad \longrightarrow \quad Bu^tOH \quad + \quad X\cdot \quad (vii)$$
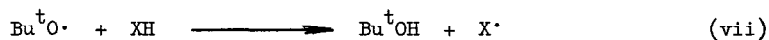
Strong spectra of (5) and (6) were observed during photolysis of a solution containing $(1; \quad R = Bu^t)$, Bu^tOCHO and Bu^tOOBu^t, the latter two reagents providing a better source of $Bu^t\overset{\cdot}{O}CO$ [equation (vii), $X = Bu^tOC(O)$] than the azodicarboxylate. Under otherwise identical conditions, the concentration ratio $[(5)]:[(6)]$ increased with decreasing temperature and with increasing concentration of $(1; \quad R = Bu^t)$, as expected on the basis of equations (iv) – (vi). We did not attempt to determine[7] $\underline{k}_v$ relative to $\underline{k}_{iv}$ because the hydrazyl (6) was much longer-lived (half-life ca. 5 s at 250 K) than (5), and because radical addition to cis- and trans-(1) probably takes place at different rates.[8]

A variety of other radical addenda were generated photochemically, from azoalkanes or from di-t-butyl peroxide via reaction (vii), in the presence of $(1; \quad R = Et$ or $Bu^t)$ and the spectroscopic parameters of the resulting hydrazyl radicals (3) are gathered in the Table. The spectrum of $(3; \quad R = Et, X = Bu^t)$ is shown in the Figure.[10]
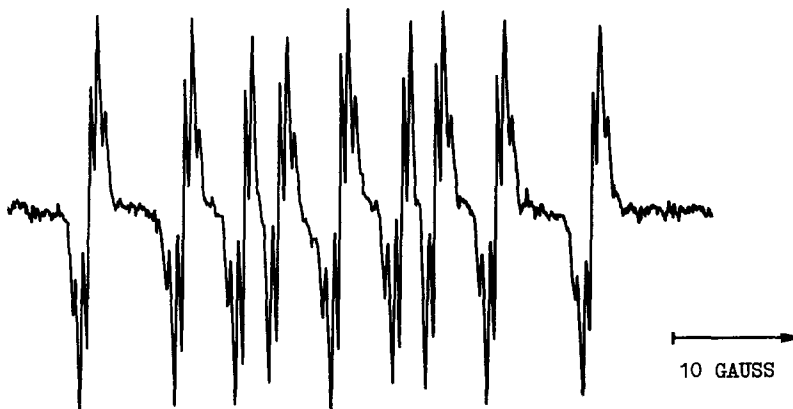
ESR Spectrum of $EtO_2C(Bu^t)N\overset{\cdot}{N}CO_2Et$ in Isobutane at 280 K

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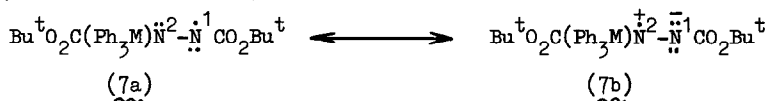E.s.r. Spectroscopic Parameters for Hydrazyl Radicals (3) and (8) in Hydrocarbon Solvents

(3)		Source of X. [a]	T/K	g	Hyperfine Splittings [b]/G		
R	X				a(N)	a(N')	Others
Bu^t	Me	A, B	209	2.0040	11.6	5.8	7.1 (3H)
Bu^t	Pr^i	C	283	2.0040	14.0	5.8	2.3 (1H)
Bu^t	cyclo-C_6H_{11}	C	340	2.0040	15.8	5.9	2.7 (1H)
Bu^t	cyclo-C_3H_5	C	260	2.0040	13.4	5.8	3.5 (1H), 0.3 (1H)
Bu^t	Bu^t	A, C	200	2.0040	12.6	7.8	3.0 ($^{13}C_\beta$)
Bu^t	Bu^tOC(O)	A, C	206	2.0041	11.8	5.0	
Bu^t	Ph_3Si	C	260	2.0041	14.5	3.4	
Bu^t	Et_3Si	C	263	2.0041	14.4	3.7	
Bu^t	Ph_3Ge	C	255	2.0042	11.6	5.2	
Bu^t	Ph_3Sn	C	254	2.0039	8.0	6.9	
Bu^t	Bu^n_3Sn	D	239	2.0044	8.5	6.2	17.2(^{117}Sn),18.0(^{119}Sn)
Et	Pr^i	C	274	2.0041	14.1	5.6	2.2 (1H), 0.5 (4H)
Et	Bu^t	A, C	273	2.0041	12.3	7.6	0.6 (4H)
Et	Bu^tOC(O)	C	262	2.0041	11.8	5.0	1.0 (2H), 0.4 (2H)
(8) X							
PhC(O)		A	215	2.0047	10.1	5.2	
Bu^t		A, C	235	2.0044	10.0	8.3	
Et_3Si		C	284	2.0040	14.4	3.7	

a A = photolysis of XN=NX; B = photolysis of MeC(O)OOC(O)Me; C = reaction (vii); D = Bu^tO· + $Bu^n_6Sn_2$· Radical chain addition of R_3MH to (1) was rapid for M = Ge or Sn; the hydrazine produced is a probable additional source of (3). b Splittings did not vary significantly with temperature.

The hydrazyl (3; R = Bu^t, X = cyclo-C_6H_{11}) was detected during photolytic (from Bu^tOOBu^t) or thermolytic (from Bu^tON=NOBu^t) generation of Bu^tO· in the presence of cyclohexane (solvent) and (1; R = Bu^t) at 340 K. No signals were detected when (1) alone was heated in cyclohexane

at 340 K.

^{15}N-Labelling studies would be required for the unequivocal assignment of the nitrogen splittings to N^1 and N^2 in (3), however some support for assignment of the larger splitting to N^1 may be adduced from the spectra of (7; M = Si, Ge, Sn). The relative importance of (7a), and hence the value of $\underline{a}(N^1)/\underline{a}(N^2)$, should increase with the π-acceptor character of M in the order Sn $<$ Ge $<$ Si (compare ref. 11).

$$Bu^tO_2C(Ph_3M)\ddot{N}^2\text{-}\dot{N}^1CO_2Bu^t \quad\longleftrightarrow\quad Bu^tO_2C(Ph_3M)\overset{+}{N}{}^2\text{-}\ddot{\bar{N}}{}^1CO_2Bu^t$$

$$(7a) \qquad\qquad\qquad\qquad\qquad (7b)$$

Addition of photochemically or thermally generated radicals to PhC(O)N=NC(O)Ph yields hydrazyls PhC(O)N(X)ṄC(O)Ph (8) which are, in general, longer lived than (3) under similar conditions. Examples are included in the Table.

References and notes

1. P. Stilbs, G. Ahlgren, and B. Åkermark, _Tetrahedron Letters_, 1972, 2387.

2. L.H. Marnett, P. Smith, and N.A. Porter, _Tetrahedron Letters_, 1973, 1081.

3. G. Koga, N. Koga, and J.-P. Anselme in "The Chemistry of the Hydrazo, Azo, and Azoxy Groups", ed. S. Patai, John Wiley, 1975, ch. 19.

4. V. Malatesta and K.U. Ingold, _Tetrahedron Letters_, 1973, 3311.

5. P.M. Blum and B.P. Roberts, _J.C.S. Perkin II_, 1978, 1313; samples were maintained under nitrogen, but not sealed, in experiments involving thermal generation of radicals from $Bu^tON=NOBu^t$.

6. With light from a Philips CS 500 mercury lamp, using silica optics, filtered through 8 cm of 0.04 $\underline{M}$ $NiSO_4$ in distilled water.

7. M.J. Perkins and B.P. Roberts, _J.C.S. Perkin II_, 1974, 297.

8. The azodicarboxylates normally exist in the _trans_-configuration about the N=N bond, although photolysis would bring about partial conversion to the less stable _cis_-isomer.[9]

9. E. Koerner von Gustorf, D.V. White, B. Kim, D. Hess, and J. Leitich, _J. Org. Chem._, 1970, _35_, 1155.

10. Restriction of rotation about the N-N or N-C bonds could give rise to conformational isomers, but only one spectrum was detected for each adduct. The hydrazyl $Me_2\dot{C}C(O)N(H)\dot{N}CO$ [$\underline{a}(N)$ 8.8, $\underline{a}(N')$ 4.9, $\underline{a}(1H)$ 7.4 G, $\underline{g}$ 2.0049 at 258 K], generated by H-abstraction from the parent hydrazine, must be non-linear at N' and have _cis_-carbonyl groups.

11. R. West and B. Bichlmeir, _J. Amer. Chem. Soc._, 1973, _95_, 7897.

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