Radicals produced during y-Irradiation of 1-Substituted 5-Aminotetrazoles

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The 1-methyl site of alkyl substituted 5-aminotetrazoles was found to be the most susceptible to γ -irradiation. The main paramagnetic radicals formed were identified as CH₃, and R-CH₂. (R = substituted 5-aminotetrazole). With a 5-nitraminotetrazole cleavage of the nitramino N-N bond, yielding an NO₂, radical, was the major interaction.

ALTHOUGH photochemical reactions of tetrazoles in solution at ambient temperatures have been much studied,1-3 no solid-state low-temperature irradiation study, where detection of radicals might be expected, has been carried out on these materials. Tetrazole-type radicals, however, are known and e.s.r. spectra have been measured on tetrazolinyl radicals produced chemically by oxidation of formazans,⁴ by reduction of tetrazolium salts,^{5,6} and by disproportionation of a mixture of the two.⁵ We now report an e.s.r. study of the radicals formed by γ -irradiation of some substituted 5-aminotetrazoles.

EXPERIMENTAL

Compound (I) was prepared by direct methylation of 5-aminotetrazole by the method of Henry and Finnegan.⁷ Acetylation of compound (I) yielded the 5-acetamido-1-methyltetrazole (VII).⁸ Each of the other tetrazoles was prepared as previously described.⁹

The samples were sealed in quartz tubes and irradiated for 0.25-8 hr. at 298 and 77°K with a 1000 c 60Co source (dose, 0.17 megarads per hr.). No difference was observed in the spectra of samples irradiated for periods between 0.25 and 8 hr. The spectra were measured at temperatures between 298 and 77° k on a Varian E3 and V4502-03 spectrometer with variable-temperature accessories.

RESULTS

The series of compounds (I)—(VII) were irradiated both at ambient temperatures and $77^{\circ}\kappa$. At $77^{\circ}\kappa$ quite complex spectra were obtained. These changed markedly on warming (Figure 1), and when the samples were warmed to room temperature the signals which remained were identical with those obtained when the irradiation was carried out at room temperature. The main radicals identified at 77° k were NO₂, CH₃, and R-CH₂ and at room temperature R-CH₂.

R-CH₂· Radical.—Typical e.s.r. spectra of the radicals obtained after irradiation at room temperature and also after warming a sample irradiated at 77°K to room temperature, from compounds (I), (II), (III), and (VII) are shown in Figure 1. The spectrum [Figure 1 (B)] is dominated by a triplet composed of essentially three equally spaced lines

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with intensity ratio of ca. 1: 2: 1. This spectrum may arise from (a) a radical having three g-values, (b) a nitrogen radical, or (c) an R-CH2 radical. Using S-, Q-, and X-band spectrometers we established that the components were not the result of g-anisotropy. The intensity distribution of the spectrum suggests that it does not arise from a ¹⁴N interaction and points to an R-CH₂, type radical. The



FIGURE 1 Typical first derivative X-band e.s.r. spectra of y-irradiated 1-methyl-5-substituted aminotetrazoles

A, Compound (I) irradiated at 77°K; B, compound (I) irradiated at 77°K, warmed to 298°K, and then measured at 77°K; and C, compound (III) irradiated at 77°K

g and A values of radical (VIII) (Table 1) are in agreement with those quoted for other $R-CH_2$ type radicals. When the samples were cooled from room temperature to $77^\circ\kappa$ the central $(M_{I} = 0)$ line remained a singlet and the outer $(M_{\rm I}=\pm 1)$ lines exhibited || and \perp features, characteristic of an R-CH₂ radical with two equivalent protons, which are rapidly exchanging sites.^{10,11} Using the hyperfine tensor, measured in the usual way,12 we were able to obtain

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 A_{iso} and hence calculate the spin density on the CH_2 carbon atom using the McConnell relationship.13 Under high amplification additional lines were detected flanking the main triplet. The relative intensity of these suggested

TABLE 1

Comparison of magnetic parameters of some RCH2.

	radicals	,	
Radical	α -H Coupling $ A_{100} $ (G)	gav.	Ref.
(VIII)	$18\cdot4\pm0\cdot2$	2.0020 ± 0.0004	а
·CH,COOH	21.6	2.0032	ь
•CH,Me	$22 \cdot 2$	2.0025	С
·CH,C,H,	16.4		d
•CH,OH	18	2.001	е
·CH,-CH=CH,	13.7 - 14.7	2.0026	С
•CH ₂ NH ₃ +	25.0		f

^a This work. ^b A. Horsfield, J. R. Morton, and D. H. Whiffen, Mol. Phys., 1961, **4**, 475; Nature, 1961, **189**, 481. ^e A. L. J. Beckwith and R. O. C. Norman, J. Chem. Soc. (B), 1969, 400. ^d Ref. 14. ^e M. Fijimoto and D. J. E. Ingram, Trans. Faraday Soc., 1958, **54**, 1304. ^f R. P. Kohin and P. G. Nadeau, J. Chem. Phys., 1966, **44**, 691.

that they arise from a ¹³C splitting in agreement with the $R-CH_2$ assignment. Unfortunately, the resolution did not permit a complete analysis of the ¹³C hyperfine tensor.

The results show that, as in the benzyl radical,¹⁴ the unpaired electron of radical (VIII) is concentrated mainly in the $2p\pi$ atomic orbital of the CH₂ group with about 20% delocalisation into the ring. The narrowest (central) linewidth was about 12 g and we were not able to ascertain whether the expected 4-5 G splitting due to the nitrogen nuclei was present. The delocalisation into the tetrazole ring should restrict the rotation about the N(1)-C bond. However, the observed equivalence of the methylene hydrogens can still be explained in terms of internal rotations.¹¹

radical ¹⁵ and was centred on g = 2.0026. It was very unstable and disappeared rapidly on warming above 77°K. The methyl radical was also observed at 77°K in compounds (I), (II), and (VII) [Figure 1 (A)].

NO2. Radical.-The spectrum obtained with compound (VI) was markedly different from those of the other compounds. The spectrum (Figure 2) was dominated by a



FIGURE 2 X-Band e.s.r. spectrum of the NO₂ radical found in γ -irradiated 1-methyl-5-methylnitraminotetrazole (VI) at 77° κ ($\nu = 9.2184$ Gc./sec.)

triplet which largely obscured any other features. The triplet is characteristic of a species containing a single interacting magnetic nucleus (I = 1) and possessing completely anisotropic g- and A-tensors. The results obtained from this spectrum by the usual procedure 16, 17 are in Table

TABLE 2

E.s.r. data for the NO2 radical in various media

	g-Tensor				Hyperfine tensor (G)				
Medium	gra	Buu	g _{zz}	gav.	\tilde{B}_{xx}	Byy	Bzz	Also	Ref.
Compound (VI)	2.0055	1.9916	2.0021	1.9994	4.3	-6.4	+10.8	56.2	a
н,0	2.0066	1.9920	$2 \cdot 0022$	2.0003	-6.3	-7.0	+13.3	56.9	Ь
Pb(NO ₃),	2.004	1.995	1.995	1.998	-4.7	+2.3	+2.3	54.7	С
NaNO,	2.0057	1.9910	2.0015	1.9994	-5.3	-7.9	+13.2	54.7	d
-	2.0036	1.9910	2.0036	1.9994	+3.97	-7.95	+3.97	54.7	Ь
CaSO ₄	2.0059	1.9921	2.0011	1.9997	-4.1	-8.0	+12.1	59 ·8	е
a This must b Daf 10	D.f. 10	d TT 7.14	D has a	T in in materia	I Cham	DL 1061	95 509	D C E	1

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CH₃· Radical.—The e.s.r. spectrum of the CH₃· radical obtained from compound (III) after irradiation at $77^{\circ}\kappa$ is shown in Figure 1 (C). The main spectrum consists of a quartet of sharp symmetrical lines in the ratio 1:3:3:1which indicates that the methyl radical has almost complete rotational freedom within the matrix. The quartet had a coupling constant (22.7 G) as expected for the methyl

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2, together with those obtained for NO₂ radicals in various media. The e.s.r. data show that the NO₂ radical is fixed rigidly in the lattice unlike that in argon,^{11, 18} Pb(NO₃)₂,¹⁹ and NaNO₂¹⁸ where rotation of the radical results in g- and nitrogen hyperfine tensors which are axially symmetric about the axis of rotation. When the sample was heated from 77 to 200° κ the NO₂· radicals were lost.

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DISCUSSION

We postulate that the methyl radicals are formed by cleavage of the N(1)-Me bond in the compounds (I), (II), (III), and (VII). Each of the compounds for which the methyl radical was observed contained an N(1)-methyl group. Compounds (II) also contains an N(5)-methyl group but since no methyl radical was observed with compounds (IV) and (V) both of which contain N(5)methyl groups but no N(1)-methyl group it seems unlikely that the methyl radical from compound (II) comes from the 5-amino-site. The spectra observed with compounds (IV) and (V) consisted of a broad asymmetrical line in which there was no evidence of the CH₃. or R-CH₂· radicals. The R-CH₂· radical observed with the compounds (I), (II), and (VII) also arises from an interaction at the 1-methyl group. The formation of these radicals may be rationalised in terms of the Scheme.



Removal of an electron from the parent molecule yields a positively charged species which is stabilised by proton loss resulting in the formation of the R-CH₂· radical. Simultaneously, electron capture by an undamaged parent molecule gives an anion which loses a CH₃· radical to form the stable tetrazole anion by a process often described as dissociative electron capture. (The acidity of 5-substituted tetrazoles is well documented ²⁰ and the species R-CN₄H has been described as the nitrogen analogue of the carboxylic acids R-CO₂H.) When compound (I) was bombarded with hydrogen atoms the radical (VIII; $R^1 = R^2 = H$) was again obtained, confirming the high reactivity of the N(1)-Me site.

It was not possible to identify clearly a triplet signal assignable to the $R-CH_2$ radical in compounds (III)

and (VI) but such a signal may be present beneath the broad envelope observed with compound (III) and is



probably present, to some extent, with compound (VI). The dominating interaction which occurred with the latter compound was the cleavage of the exocyclic N-N bond yielding the NO₂• radical. An easy cleavage of this bond is also observed in the chemical reactions of 5-nitraminotetrazoles.⁹ If, as we expect, the NO₂• radical is formed as a result of electron capture, then it is of interest that process (1) rather than process (2) was

$$RNO_{2}^{-} \longrightarrow R^{-} + NO_{2} \cdot (1)$$

$$RNO_{2}^{-} \longrightarrow R \cdot + NO_{2}^{-} (2)$$

$$R = N - N$$

$$R = N - N$$

$$Me$$

$$N - N$$

$$Me$$

favoured, since they appear to be almost equally probable. Normally it is the inorganic fragment that forms the anion in dissociative electron-capture reactions, and presumably it is the high stability of the NO₂• radical which tips the balance in this case. In comparable studies of nitrobenzene and its derivatives ²¹ there was no evidence for NO₂• formation.

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