

Unstable Intermediates

Part 111.—Electron Spin Resonance Studies of γ -Irradiated Frozen Aqueous Solutions of Alkali-metal Azides ¹

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Aqueous glasses containing potassium or sodium azide at 77 K after exposure to ^{60}Co γ -rays, had e.s.r. spectra containing features characteristic of NH_2 radicals. Exposure to 2537 Å light also gave NH_2 radicals together with an isotropic 5 G triplet characteristic of nitrogen atoms. The NH_2 radicals are probably formed from N_3^{2-} or HN_3 by loss of nitrogen molecules and protonation of NH^- . This occurs even in glasses containing 10 M alkali hydroxide.

The alkali-metal azides have been extensively studied by e.s.r. spectroscopy after exposure to ultraviolet light or high energy radiation,²⁻⁵ and barium azide has been included more recently.^{6, 7} Ultraviolet photolysis (generally with 2537 Å light) has been shown by e.s.r. to give N_2^- (Na, K and Ba salts), N_4^- (Na and K salts) and F-centres (Na salt), whilst X-rays gave nitrogen atoms in addition. The molecule N_3 has not been detected by e.s.r. spectroscopy (although it is well known in the gas phase) but it has been reported in an infra-red spectroscopic study of discharged nitrogen deposited at 4.2 K.⁸

When azide ions are added to water in pulse radiolysis experiments, they are found to be good scavengers of hydroxyl radicals,⁹ and of hydrogen atoms.¹⁰ Hydroxyl radicals are thought to react by electron-transfer to give N_3 ,⁹ but no specific reactions were postulated for their interaction with hydrogen atoms.

The aim of the present study was to extend our investigations of frozen aqueous salt solutions, in which the species Hal_2^- , HalOH^- , MH^+ , HCN^- and H_2CN have previously been detected,¹¹⁻¹³ to include the azides.

EXPERIMENTAL

Sodium azide (Fisons) was used as supplied. Potassium azide (Alfa Inorganics) was purified by recrystallization from water, the first batch only being used. Solutions ranging in concentration from 1 M to saturated, were prepared by dissolving the respective salts in water doubly distilled from alkaline potassium permanganate. Solutions were also prepared in D_2O supplied by Koch-Light (99.7 % D). Sodium and potassium hydroxide (B.D.H. Reagent Grade), and NaOD (40 % in D_2O , B.D.H.) were used as supplied. Concentrated aqueous sodium azide solutions gave good glasses on cooling to 77 K, but some phase separation was always detected for the potassium salt solutions. The latter were therefore studied in aqueous potassium hydroxide glasses. Tests for phase separation were as described previously.¹³ Samples in the form of small beads were irradiated with ^{60}Co γ -rays at 77 K in a Vickrad source (4 Mrad h^{-1}) to total doses between 2 and 4 Mrad. Samples were photolyzed with a medium pressure mercury lamp whilst immersed in liquid nitrogen in a quartz dewar for up to 2 h.

Spectra were recorded on a Varian E3 spectrometer at 77 K. The samples were annealed by allowing the beads to warm for fixed periods and recooling to 77 K.

RESULTS AND DISCUSSION

Glasses of sodium azide in pure water and either sodium or potassium azide in aqueous alkaline glasses on exposure to γ -rays at 77 K gave 5-line spectra such as that shown in fig. 1a. Replacement of H_2O by D_2O resulted in a 3-line pattern (fig. 1b). These spectra are characteristic of NH_2 or ND_2 radicals in aqueous solution,¹⁴ but as a check on the presence of two interacting protons, we studied solutions prepared from 50 % H_2O and 50 % D_2O (fig. 1c). These gave, as expected, clear evidence for the species NHD, thus supporting our identification. Data for these radicals are given in table 1.

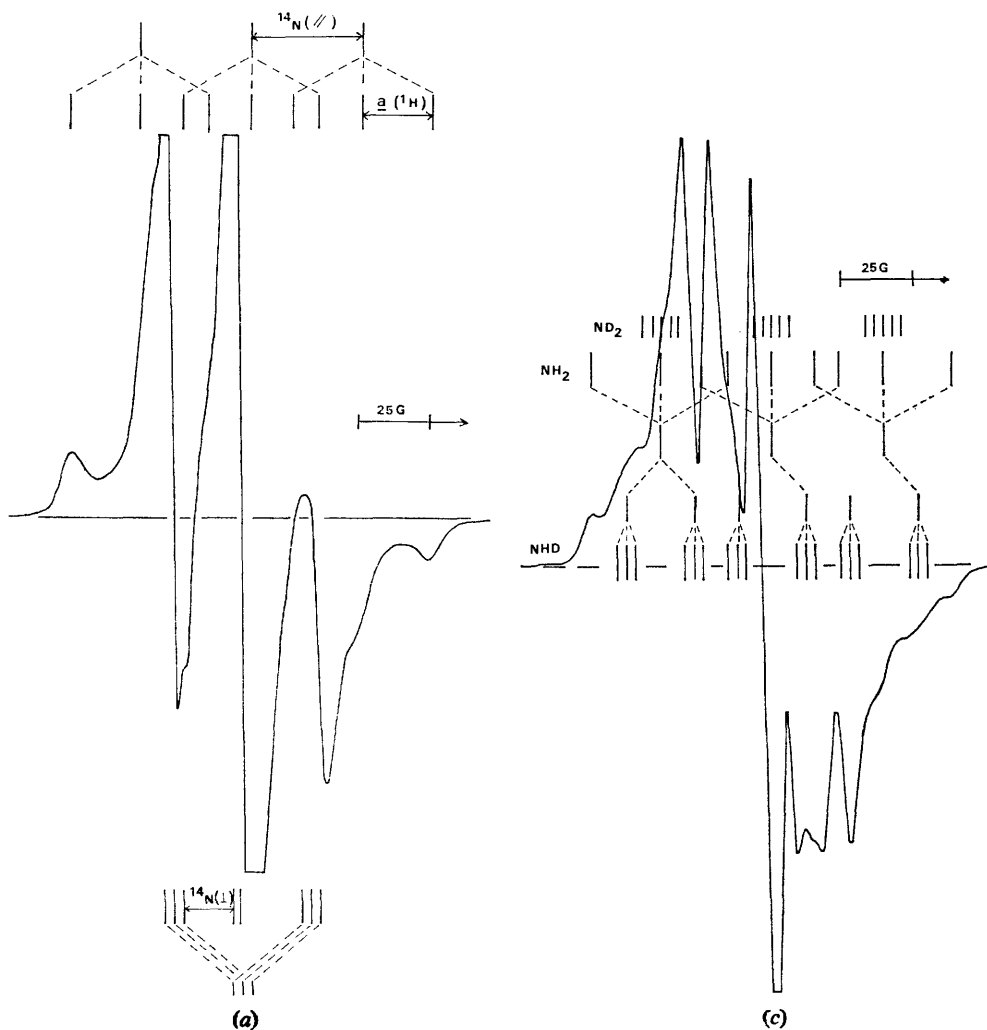


FIG. 1.—(a) E.s.r. spectrum of NH_2 obtained from the γ -radiolysis of an aqueous glass of sodium azide. Parallel and perpendicular features are indicated. (b) (*opposite*) Spectrum of ND_2 from sodium azide/ D_2O glass. Parallel features only are shown. (c) Spectrum of NHD from 50 % H_2O /50 % D_2O glass of sodium azide. Features due to NH_2 , ND_2 and NHD are outlined. Parallel features are shown.

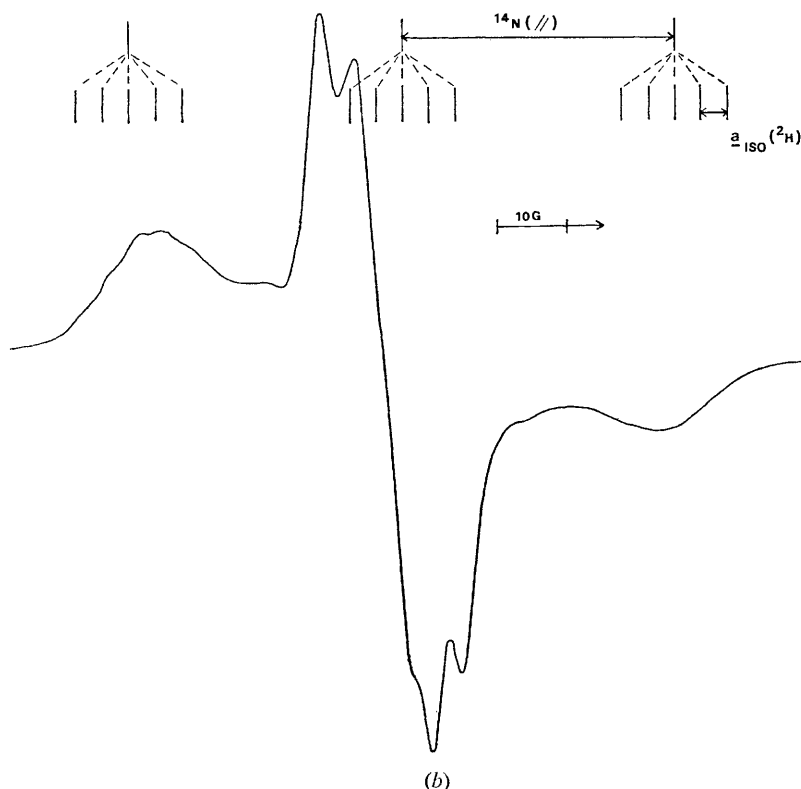
The amino radicals (NH_2) were also formed in high yield on exposure of these glasses to 2537 Å light at 77 K. In most cases central triplets having $a = 5.0$ G were obtained, superimposed on the broad NH_2 lines (fig. 2). (Weaker lines in the

TABLE 1.—E.S.R. PARAMETERS FOR NH_2 , NHD , ND_2 AND NITROGEN ATOMS FORMED IN AQUEOUS SOLUTIONS OF AZIDES

radical	g -value	$A_{\parallel}/\text{G}(^{14}\text{N})$	$A_{\perp}/\text{G}(^{14}\text{N})$	$A_{\text{iso}}/\text{G}(^{14}\text{N})$	$A_{\text{iso}}/\text{G}(^1\text{H})$
NH_2^a	2.003	39 ± 2	$(-) 3.0 \pm 1$	11 ± 1	(2) 24 ± 1
NH_2^b		41 ± 2	0 ± 3	13 ± 3	(2) 24 ± 1
NH_2^c				10.3	(2) 23.9
ND_2^a	2.003	39 ± 2	$(-) 3.0 \pm 1$	11 ± 1	(^2H)(2) 3.75 ± 0.5
NHD^a	2.003	39 ± 2	$(-) 3.0 \pm 1$	11 ± 1	(1) 24 ± 1
					(^2H)(1) 3.75 ± 0.5
N^a	2.001 ± 0.001			5.0 ± 0.5	
N^d	2.0021			6.2	
N^e	2.0020			4.3	

^a this work; ^b ref. (14); ^c S. N. Fouer, E. L. Cochran, V. A. Bowers and C. K. Jen, *Phys. Rev. Letters*, 1958, **1**, 91; ^d ref. (6); ^e V. A. Bowers, E. L. Cochran, S. N. Fouer, and C. K. Jen, *J. Chem. Phys.*, 1958, **28**, 351.

same region could sometimes be observed in the spectra for γ -irradiated samples, but they were never clearly resolved.) These are thought to be a property of trapped nitrogen atoms, but the expected shoulders resulting from zero-field splitting of the



(b)

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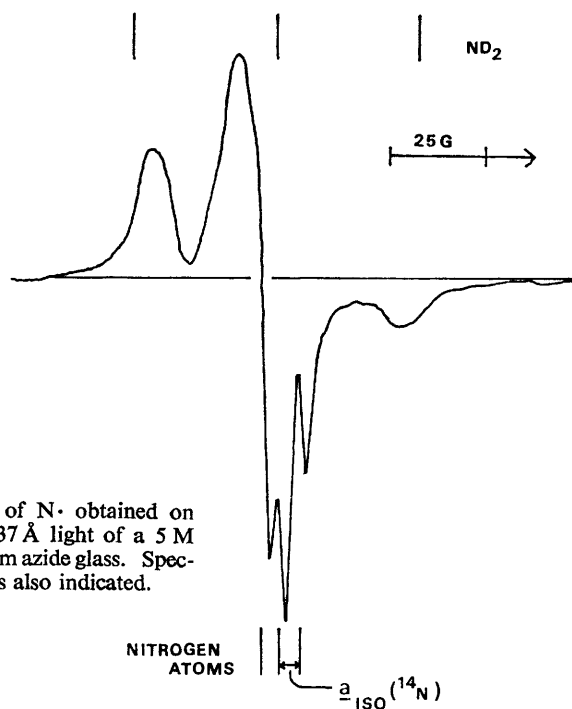


FIG. 2.—Spectrum of $\text{N}\cdot$ obtained on photolysis with 2537 Å light of a 5 M $\text{NaOD}+\text{D}_2\text{O}$ sodium azide glass. Spectrum of ND_2 is also indicated.

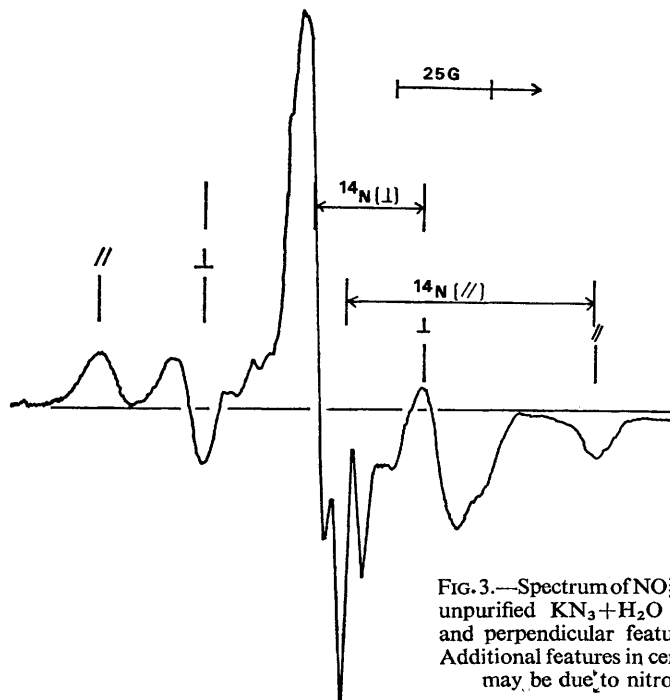


FIG. 3.—Spectrum of NO_3^{2-} obtained from unpurified $\text{KN}_3+\text{H}_2\text{O}$ glass. Parallel and perpendicular features are shown. Additional features in centre of spectrum may be due to nitrogen atoms.

⁴S-state of the atoms were not resolved. Such a splitting is expected but since it is very sensitive to the nature of the environment,⁶ and since the environment in these experiments is not likely to be very homogeneous, they were probably broadened beyond detection.

On annealing, the nitrogen atom features were lost, leaving only the NH₂ lines. Further annealing resulted in the loss of NH₂ radicals also, no other features being detected.

When unpurified potassium azide glasses were irradiated, e.s.r. spectra such as that in fig. 3 were obtained. These features are characteristic of NO₃²⁻ radicals in an aqueous environment,^{15, 16} our analysis being indicated in fig. 3. The same species was formed in the powdered salt, and it seems that the central features detected in our earlier studies of potassium azide⁶ were due to NO₃²⁻. This radical is almost certainly formed from nitrate impurities in the azide, which were removed by recrystallization from water. Its presence in other studies may account for failure to observe F-centres in the potassium salt.

MECHANISM OF RADIATION DAMAGE

The following stages are thought to be responsible for the species detected after exposure to ⁶⁰Co γ-rays:



together, possibly, with the reactions



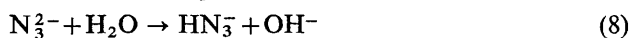
The formation of NH₂ radicals, even in concentrated alkaline solutions shows that NH⁻ is a very strong base, as expected by comparison with NH₂⁻. It is possible that NH⁻ radicals are also trapped, but not detected by e.s.r. spectroscopy because of an efficient spin-lattice relaxation. However, NH⁻ is isoelectronic with OH, and since hydroxyl radicals are readily detected in aqueous media,¹⁷ we would have expected to obtain evidence for NH⁻ also. Reaction (4) cannot be a major process since the yield of nitrogen atoms, when detectable, was always low. We also searched for the species HON⁻ which is an alternative product in (4). This is isoelectronic with HO₂, and so should have been detectable, but none of the expected features were observed.

PHOTOLYSIS

Since water does not absorb 2537 Å light, photolysis must have been by direct decomposition of the excited N₃⁻ ions, and our results strongly suggest a c.t.t.s.¹⁸ process:



The ejected electron must then be captured by another azide ion to give N₃²⁻ which protonates and decomposes:



followed by (2b) and (3), NH₂ being the final product. As in our previous studies,⁶

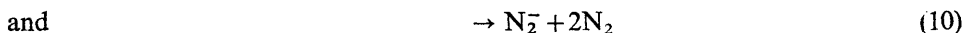
no evidence for N_3 radicals could be obtained, and we conclude that step (5) is efficient, even at 77 K. It seems that gas-phase studies also indicate that N_3 must have a very low binding energy,¹⁹ though the decomposition is probably slow because it is spin-forbidden if the nitrogen atoms are to be formed in their 4S ground state. Herzberg has concluded from the diffuse nature of the optical spectra that $D(N-N_2) < 4.55$ eV.²⁰

The anion N_3^{2-} has been characterized in ultra-violet irradiated barium azide,² but no evidence for its presence was obtained here. We conclude that it must be a strong base with respect to water, and that its conjugate acid is unstable.

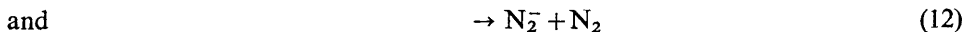
Our results make an interesting contrast with those obtained from the pure salts.¹⁻⁷ Had N_4^- been formed we should have detected its e.s.r. spectrum, but it is possible that N_2^- would have its e.s.r. features so broadened by spin-lattice relaxation as to be undetectable.

Since F-centres are formed in sodium azide, the first step in photolysis is probably (6), followed by the formation of N_3^{2-} (Ba salt), F-centres (Na salt) or NO_3^{2-} (K salt). It might have been supposed that, because of their relatively overwhelming concentration, azide ions would always trap electrons preferentially. However, N_3^{2-} ions are isoelectronic with NO_2 and CO_2^- ions which have bond angles in the region of 130° ,²¹ so efficient trapping will only occur at vibrationally excited azide ions. Hence trapping at F-centres or impurities can compete efficiently.

Since nitrogen atoms were not found in the ultra-violet photolyses, we suggest that N_3 radicals have life-times long enough for them to interact with neighbouring azide ions:



processes (9) and (10) having apparently fairly similar probabilities. The alternative, that nitrogen atoms react with azide,



is far less reasonable, since in radiolysis experiments they are trapped as such in these crystals.

CONCLUSIONS

These results confirm our previous conclusions that in protic media such as water or the alcohols, protonation of intermediates may be of vital importance, even at 77 K in rigid media. For example, the radical ion N_2O^- which is isoelectronic with N_3^{2-} may also be protonated by water to give N_2OH which subsequently gives $N_2 + OH$. This could account for the fact that all attempts to detect N_2O^- in e.s.r. experiments have so far failed.

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