$\sigma^*\text{-Radicals R}_3\text{N} \doteq \text{hal}$: Electron Paramagnetic Resonance Studies of the Radiolysis of Alkylammonium Halides

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Exposure of various ammonium and alkylammonium salts to ⁶⁰Co γ -rays at 77 K gives a range of paramagnetic products including several R₃N - hal radicals (R = H, alkyl; hal = Cl, Br, I) characterised by their EPR spectra. These showed large hyperfine couplings to ¹⁴N and to halogen nuclei, indicating that they are genuine neutral radicals whose SOMO comprises, primarily, σ -orbitals from N and hal. Hence these species can be classified as σ^* radicals. The stability of these R₃N - hal radicals is contrasted with the instability of the isoelectronic R₃C - hal⁻ radical-anions, which normally have no significant lifetime, but dissociate directly to give R₃C' radicals sometimes weakly associated with the ejected halide ions. Proton and ¹⁴N hyperfine coupling constants show that the R₃N- moleties in these σ^* radicals are pyramidal, in contrast with the parent amminium cations, R₃N'+ which are planar. The extent of deviation from planarity increased on going from -Cl to -I, as does the extent of delocalisation onto halogen. For the iodide complexes, the spin density on iodine decreases from *ca*. 70% to *ca*. 40% on going from the NH₃ derivative to the Et₃N derivative. A range of other radicals, also detected in the irradiated salts, are briefly described.

There has been a great deal of interest in the possibility of detecting alkyl halide radical anions using EPR spectroscopy at low temperatures. The reaction

 $e^- + R - hal \rightleftharpoons R - hal^- \rightarrow R' + hal^-$ (1)

appears to be purely dissociative in the gas-phase and in fluid solution.^{1,2} In the gas phase there may be weak electron binding to the molecular dipole in an expanded Rydberg-type orbital, but the σ^* intermediate (I) is not detected. We stress that many σ^* (three-electron) systems are known (Table 1),³



perhaps the best known being the hal-hal⁻ species (V_{K} centres) formed in irradiated alkali-metal halide crystals,⁴ or by electron addition to halogen molecules. Theoretical studies have helped to reveal details of the bonding involved in these intermediates, for which a simple three-electron bonding scheme is indicated in Fig. 1. This figure shows that there are at least two factors that facilitate dissociation; (a) a large orbital energy difference between the $A\sigma$ and $B\sigma$ orbitals (in $A \div B^-$), and (b) a tendency for rehybridisation of the A- or B-orbitals from an sp hybrid to a p orbital. (b) Has the effect of increasing the energy difference, and increasing the bond length. This concept led to the discovery that for C-hal systems in which such rehybridisation cannot occur extensively, σ^* anions are, in fact, stable. For example, C₆H₅I and PhC=CI readily form localised anions, $C_6H_5 - I^-$ and $PhC \equiv C \div I^{-.5,6}$



Fig. 1 Atomic orbital energies for carbon, nitrogen and chlorine, with an indication of possible bonding interactions; α represents the change in energy for CH₃ on moving from pyramidal (sp³) to planar (p). Hybridization for Cl of sp⁹ is used to indicate the small admixture of s-character detected by EPR

Table 1 EPR parameters for a selection of nitrogen-halogen σ^* radicals

	14	'n	h	al		¹⁴ N				
species	$A_{\parallel}/{ m G}$	A_{\perp}/G	A_{\parallel}/G	A_{\perp}/G	a ² s	a²p	λ^2	$\rho(^{14}N)$	p(hal)	ref.
NH;+	44.6	6.9	_		0.030	0.756	25.1	0.79		12
NH ₂ Cl.	46.5	9.0	43.3	13.5	0.033	0.752	22.6	0.79	0.21	12
NH ₃ Br	51.5	36.0	459.6	114.0	0.064	0.311	4.9	0.38	0.49	12
R ₂ NCl	68.0	49.6	117.7	26.3	0.086	0.369	4.3	0.46	0.57	31
R ₂ NBr [•]	61	41.5	603	125.5	0.074	0.391	5.3	0.47	0.67	31
R ₂ NI	45	27	560	145	0.051	0.361	7.1	0.41	0.63	32
MeCONHBr ^{•–}	69	45	560	150	0.082	0.481	5.9	0.56	0.58	31

hal = 35 Cl, 81 Br or 127 I. R₂Nhal = halogenosuccinimide.

An important result which supports the idea that σ^* radical anions do not represent stable intermediates in the dissociation pathway (1) is that in certain solid-state situations the alkyl radicals show weak hyperfine coupling to halogen nuclei, and have slightly reduced ¹H and ¹³C coupling constants.⁷⁻⁹ These species readily give normal alkyl radicals on annealing. It can be argued that this interaction indicates the limit of an extremely weak σ^* bond, or that it is due to slight charge transfer which occurs only because of cage trapping. The difference is somewhat esoteric. The point is that it is most unlikely that two such species can have stability since this would correspond to double minima in the dissociation energy profile.¹⁰ Hence there can be no true σ^* anions in these cases.

If carbon is replaced by nitrogen, the orbital energies are much more closely matched (Fig. 1), and hence electron addition would be expected to give a σ^* species. Similarly, formation of R_3N^{*+} close to hal⁻ or of hal⁻ close to R_3N could give the required species if bonding is significant:

$$\mathbf{R}_{3}\mathbf{N}^{+} + \mathbf{hal}^{-} \to \mathbf{R}_{3}\mathbf{N} - \mathbf{hal}$$
 (2)

A similar reaction to reaction (2), involving R_3P^{*+} radical cations, was reported some time ago.¹¹ In fact, Patten showed that when $NH_4^+Cl^-$ or $NH_4^+Br^-$ are irradiated, $\cdot NH_3^+$ -halide ion adducts are formed,¹² but the significance of these results to chemistry was perhaps not fully appreciated.¹³

The aim of the present work was to confirm and extend the work of Patten on ammonium salts, and to attempt to prepare various alkyl-substituted $R_3N \div$.hal species. We hope that the results shed more light on the factors which govern the stability of these important σ^* intermediates. In view of the success with ammonium salts, the obvious sources of these radicals are alkylammonium salts. The effect of ionizing radiation on such salts has already been extensively studied. Generally, for ammonium salts, (hal)₂⁻ (V_K) centres have been detected,¹⁴⁻¹⁶ together with a 'hydrazine-like' defect.^{17,18} For pure compounds, F-centres are not detected.¹⁹ For a range of alkylammonium halides, V_K centres and uncomplexed alkylamminium cations, R_3N^{*+} , have been reported, but not amminium halide adducts.²⁰⁻²⁶ Various carboncentred radicals were also detected. Alkylamminium cations have also been prepared and studied by EPR spectroscopy in a range of other systems.²⁷⁻³⁰

Nitrogen-halogen σ^* radicals have been ootained by electron addition to certain R₂N-hal systems, especially *N*-halogenosuccinimide and related species.³¹⁻³⁴ We have recently shown that certain *N*-chloroamines (R₂NCl) in methanol glasses undergo dissociative electron capture, giving R₂N^{*} radicals, with no evidence for σ^* -radical formation.³⁵

Experimental

Preparation of Alkylammonium Halides

Methyl, dimethyl and trimethylammonium chlorides and dimethylammonium bromide (Aldrich) were recrystallised from methanol and dried over phosphorus pentaoxide. Other mono-, di- and tri-alkylammonium halides were prepared by neutralisation of the corresponding alkylamine with the appropriate hydrohalogenic acid. The substituted ammonium iodides were prepared by bubbling hydrogen iodide vaoour through alcoholic solutions of the appropriate amine. Deuteration of methylammonium iodide and the other alkylhalides was performed via ammonium repeated recrystallisation from D₂O-CD₃OD. Samples were then placed into a Vickrad 60 Co γ -ray source and irradiated at a nominal dose rate of 0.5 Mrad h⁻¹ for up to 5 h.

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EPR spectra were recorded using a Bruker ER200D spectrometer equipped with a dedicated ASPECT 2000 computer for spectral accumulation and manipulation. Spectra were taken at temperatures between 77 K and room temperature using a quartz finger Dewar insert or a commercial variable-temperature accessory.

Thermal cycling experiments were performed either using the variable-temperature accessory or removing the sample and placing it into a dry ice-solvent slush bath for an appropriate length of time. Pulse annealing experiments were carried out by decanting the liquid nitrogen from the quartz insert Dewar and continuously monitoring the signal using the spectrometer's rapid-sweep facility. The liquid nitrogen was replaced when significant spectral changes were detected.

Results and Spectral Analysis

Ammonium Halides

Exposure of polycrystalline samples of ammonium chloride and bromide to ⁶⁰Co γ -rays at 77 K gave outer EPR features characteristic of Ct₂⁻ and Br₂⁻. However, after annealing to *ca.* 180 K and re-cooling to 77 K, the spectra shown in Fig. 2 and 3 were obtained. These are assigned to H₃N $\dot{-}$ Cl and H₃N $\dot{-}$ Br, respectively. Parameters derived from these



Fig. 2 First-derivative X-band powder EPR spectrum of γ -irradiated ammonium chloride warmed to *ca*. 180 K and recooled to 77 K, showing features assigned to H₃N \div Cl radicals



Fig. 3 First-derivative X-band powder EPR spectrum of γ -irradiated ammonium bromide warmed to *ca*. 180 K and recooled to 77 K, showing features assigned to H₃N \div Br radicals

Table 2 Experimental EPR parameters of amminium halide σ^* radicals

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	$A_{\parallel}/{ m G}$	A_{\perp}/G	g_{\parallel}	g_{\perp}
		H ₃ N÷Cl		
³⁵ Cl	43.6	22	2.0020	2.0085
¹⁴ N	47.8	$(ca. 9.0)^{a}$		
'Η	$A_{ins} = (-)24$	(,		
	180 ()	H ₃ N – Br		
⁸¹ Br	458	106	2.00	2.06
^{14}N	50	а		
1H	$A_{\rm iso} = 14$			
	130	H ₂ N÷I		
¹²⁷ I	530.0	180	1.98	2.25
^{14}N	55	а		

" Not well defined.

spectra (Tables 2 and 3) agree well with the single-crystal data,¹² and give us confidence in the use of powder samples. Irradiation of pure ammonium iodide gave I_2^{-} and $H_3N - I$ radicals, but only the parallel features for the latter were well defined. When NH_4^+ ions were doped into various alkalimetal iodide lattices, better defined features for $H_3N - I$ radicals were obtained (Fig. 4). Coupling to ¹⁴N is resolved on the parallel features but not on the perpendicular features. There proved to be a small variation in the ¹²⁷I hyperfine coupling constants with the nature of the lattice, the results suggesting that the tigher the lattice, the larger the spin density on iodine.

Table 3 Approximate spin densities on nitrogen and halogen in $R_3N - hal$ complexes

	spin density			
	on nitrogen	on halogen	total	
$H_3N \div Cl$	0.8	0.2	1.0	
$H_{3}N - Br$	0.4	0.5	0.9	
$H_{3}N - I$	0.3	0.7	1.0	

Derived by comparing A_{\parallel} (hal) with A_{\parallel} data (averages over a range of experimental values) for Cl_2^{-} , Br_2^{-} and I_2^{-} assuming spin densities of 0.5 in each case. For ¹⁴N, $A_{\rm iso}$ values were converted into 2s character and 2*B* values into $2p_z$ character using A^0 and $2B^0$ values for the atom.



Fig. 4 First-derivative X-band powder EPR spectrum assigned to $H_3N \div I$ radicals isolated in an ammonium-doped potassium iodide host matrix at 77 K after exposure to ⁶⁰Co γ -rays

Alkylammonium Iodides

After removing features for I_2^{-} by annealing, well defined features for MeH₂N \div I radicals were obtained from methylammonium iodide, showing hyperfine coupling to ¹⁴N, ¹²⁷I and ¹H nuclei (Fig. 5). The results suggest that the MeH₂N \div I features gained in intensity at the expense of those for I_2^{-} on annealing. The two extra ¹H splittings shown in Fig. 5(*b*) [which shows only the $M_I(^{127}I) = +5/2$ parallel line], changed to the single doublet splitting (17 G) shown in Fig. 5(*c*), when CH₃ND₃⁺I⁻ crystals were used. This leads to the conclusion that only one of the methyl protons is strongly coupled to the electron (see below).

Well defined spectra for $RH_2N \doteq I$ radicals were also obtained for n-propyl-, n-butyl- and isobutyl-ammonium iodides on irradiation at 77 K. However, these adducts were not observed for R = tert-butyl or phenyl. $(CH_3)_2NH_2^+I^-$



Fig. 5 First-derivative X-band EPR spectra for methylammonium iodide after exposure to ⁶⁰Co γ -rays at 77 K and annealing to *ca.* 200 K to remove features for I_2^- radicals, showing features assigned to MeH₂N \div I adducts: (a) the complete spectrum, (b) the $M_I = +5/2^{127}I$ parallel feature and (c) the same feature for irradiated CH₃ND₃⁺I⁻

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(a)





Fig. 6 First-derivative X-band EPR spectra for ethylammonium iodide after exposure to ⁶⁰Co γ -rays at 77 K and annealing to remove I_2^- signals, showing features assigned to EtNH₂-I radicals (α is due to trapped organic radicals) (a) and simulated spectrum (b)

and $(Et)_2NH_2^+I^-$ also gave well defined adducts, especially after thermal cycling. We were unable to detect the σ^* adduct for Me₃NH⁺I⁻, but broad features for Et₃N \div I were found for the triethyl derivative. Spectra for EtH₂N \div I, $(Et)_2HN \div$ I and $(Et)_3NXI$ are compared in Fig. 6. This shows a marked decrease in the ¹²⁷I coupling with increased alkyl substitution. Unfortunately, the lines are too broad for the di- and tri-ethyl derivative to give accurate ¹⁴N parameters. EPR parameters for these iodide adducts are given in Table 4.

EPR parameters have been derived from simulated spectra, examples of which are given in Fig. 6(b) and 7(b). However,

 Table 4
 EPR parameters for a variety of alkylamminium iodide radicals

species	A /MHz	A⊥/MHz	A _{iso} ^a /MHz	В	g_{\parallel}	g_{\perp}
H ₁ N – I	1490.9	600.8	897.5	296.7	1.96	2.18
$MeH_{2}N - I$	1332.9	479.2	763.8	284.6	1.97	2.15
$EtH_{2}N - I$	1295.9	464.2	741.4	277.3	1.97	2.14
Me ₂ ^H N – I	1047.7	387.5	607.6	220.1	1.98	2.13
Et ₂ HN – I	1089.1	447.2	661.1	214.0	1.98	2.13
$Et_{2}N \rightarrow I$	767.6	310.1	462.6	152.5	1.99	2.11
Quin $\doteq I^b$	1083.6	425.2	644.7	219.5	1.98	2.15

^{*a*} Isotropic and anisotropic data corrected for orbital magnetic contributions. ^{*b*} Quin = (quinuclidine, 1-aza[2.2.2]bicyclooctane).



Fig. 7 First-derivative X-band EPR spectra for quinuclidine iodide after exposure to ⁶⁰Co γ -rays at 77 K and annealing to remove $I_2^$ features, showing (a) features assigned to the quinuclidine radical cation-iodide adduct and (b) a computer simulation using the data given in Table 2

these spectra are difficult to simulate accurately, and there is considerable error, especially in g_{\perp} and A_{\perp} . In the particular case of the quinuclidine-iodide adduct the features were relatively well resolved (Fig. 7) and the data are more reliable.

Alkylammonium Bromides

Of a wide range of alkylammonium bromides studied, all gave Br_2^- centres, but only the MeNH₃⁺ and EtNH₃⁺ salts gave clear features for amminium bromide radicals, the spectrum for EtH₂N \div Br being relatively well defined (Fig. 8). Features for hydrogen atom-bromide ion adducts, H \div Br⁻ were also detected in the irradiated ethyl derivative.³⁶

Alkylammonium Chlorides

We were unable to detect any clear features for $R_3N \div Cl$ radicals in any of the wide range of salts studied. In most cases, features for Cl_2^{--} were detected, as well as those for carboncentred radicals such as $H_2\dot{C}NH_3^+$ from MeNH₃⁺Cl⁻ crystals. However, features for R_3N^{++} ions were detected, which suggests that alkyl substitution stabilises the amminium ions sufficiently to prevent the formation of weak bonds to chloride ions. A list of the major species detected in these studies is given in Table 5.



 $A_{\perp}(^{127}I)$

Fig. 8 First-derivative X-band EPR spectrum for ethylammonium bromide after exposure to ⁶⁰Co γ -rays at 77 K and warming to *ca*. 180 K to remove most of the Br₂⁻ features, showing features assigned to EtNH – Br radical adducts. [α is due to trapped organic radicals and the cluster of lines, β , to residual Br₂⁻ radicals]

Table 5 Major species detected in alkylammonium halides following irradiation at 77 K

	chloride	bromide	iodide
$MeNH_3^+$ $EtNH_3^+$ $MeNH_2^+$ $Et_2NH_2^+$ Me_3NH^+ Et_3NH^+	Cl_{2}^{*-a} Cl_{2}^{*-a} Cl_{2}^{*-a} Cl_{2}^{*-a} $Cl_{2}^{*-a,b}$ $Cl_{2}^{*-a,b}$ $Cl_{2}^{*-a,b}$	Br ^{2-a} Br ^{2-a} Br ^{2-a} Br ^{2-a} Br ^{2-a} Br ^{2-a} Br ^{2-a}	I_{2}^{-} , MeH ₂ N-I I_{2}^{-} , EtH ₂ N-I I_{2}^{-} , MeH ₂ N-I I_{2}^{-} , Et ₂ HN-I I_{2}^{-a} I_{2}^{-a} , Et ₃ N-I

^a Species $CH_2(CH_2)_n NR_3^+$ (n = 0 or 1). ^b Poorly defined.

Discussion

Structure

There can be little doubt that the centres discussed herein have the σ^* structure indicated in Fig. 1. The large coupling to halogen together with the relatively large isotropic component for the ¹⁴N coupling would be hard to explain in any other way. Furthermore, the single-crystal results for $H_3N - Cl$ and $H_3N - Br^{12}$ showed that the principle components of the ¹⁴N and halogen hyperfine coupling constants are collinear and lie along the nitrogen-halogen directions of the crystals.

As is usual with powder spectra for halogen-containing radicals, A_{\parallel} and g_{\parallel} can be measured accurately, but A_{\perp} and g_{\perp} are far more difficult to obtain. When these features were reasonably well defined, computer simulations were used to give improved data. In other cases, these have been gauged from the positions of the first and last perpendicular lines which were usually better defined. A plot of A_{\parallel} vs. A_{\perp} [Fig. 9(a)] shows that the estimated results are reasonably selfconsistent for the iodides, as expected for a set of structurally similar species. It is noteworthy that data for I_2^- fall close to those for the $R_2HN \rightarrow I$ centres, suggesting that the SOMO is fairly equally distributed between nitrogen and iodine in these species. This in turn suggests that for $H_3N - I$, the spin density on iodine is greater than that on nitrogen. An approximate estimate of the spin density on iodine, normalised to the I_2^{-} data, gives ca. 70% spin density on iodine for $H_3N \rightarrow I$. Similar calculations for $H_3N \rightarrow Cl$ and $H_3N \rightarrow Br$ gave ca. 20 and 43% on Cl and Br, respectively.

Unfortunately, we were unable to obtain an accurate value for $A_{\perp}(^{14}N)$ for $H_3N - I$. However, interpolating a value from



Fig. 9 A correlation between $A_{\parallel}(^{127}I)$ and A_{\perp} for various $R_3N \div I$ radical adducts, $R_3N \div I$. (a) $Et_3N \div I$, (b) $Me_2NH \div I$, (c) $Et_2NH \div I$, (d) (I_2^{-}) , (e) $EtNH_2 \div I$, (f) $MeNH_2 \div I$, (g) $H_3N \div I$, (h) quinuclidine–I. B, Correlation between the ionization potentials for R_3N and $A_{\parallel}(^{127}I)$ (taken as being proportional to the spin density). [These were taken from M. Takahashi, I. Watanabe and S. Ikeda, J. Electron Spectrosc., 1985, **37**, 275; R. H. Stanley and J. L. Beuchamp, J. Am. Chem. Soc., 1974, **96**, 1604 or from standard compilations

the data for the chloro and bromo derivatives and the linewidths, gave a calculated spin density of *ca.* 30% on nitrogen from $H_3N \pm I$. The values for the chloro and bromo derivatives are *ca.* 80% and *ca.* 40% (Table 3). The p/s ratio for ¹⁴N changes from *ca.* 28 for (NH₃⁺), *ca.* 19 for (H₃N \pm Cl), *ca.* 4.1 for (H₃N \pm Br), and *ca.* 2.5 for H₃N \pm I. (The last value is very approximate.) The (N \pm H) proton coupling was fully resolved only for the chloro derivative and hence it is impossible to infer structural information therefrom. Nevertheless, the structural picture is remarkably complete. On going from \cdot NH₃⁺ through to H₃N \pm I, there is a steady loss of spin density from nitrogen, and a concomitant fall in the p/s ratio from the value for \cdot NH₃⁺, indicating a steady increase in pyramidality at nitrogen.

On replacing H by alkyl this trend is reversed. This is, in part, due to the increasing stability of the planar imminium ions, R_3N^{*+} , as R changes from H to alkyl. The alkyl derivatives are strongly stabilised by hyperconjugation, as evidenced by the large β ¹H coupling (28.2 G for Me₃N^{*+}). For the quinuclidine adduct (II), there is strong resistance to flattening at nitrogen. Hence, the data are comparable with those for Et₂HN \div I rather than for Et₃N \div I [Table 4 and Fig. 9(b)].

The presence of a unique β -proton coupling for MeH₂N \div I also suggests marked deviation from planarity, since, for MeNH₂⁺ radicals the methyl group is freely rotating at 77 K. We suggest a structure such as (III) which minimises β -H \cdots I interaction and maximises overlap for the unique proton (x). A similar restriction of rotation giving rise to a single large

proton coupling is found, for example, H_3C' O radicals at low temperature.



Aspects of Mechanism

Probably the simplest sequence of reactions leading to the required products is the following, using $NH_4^+Cl^-$ as an example:

$$Cl^- \rightarrow Cl^+ + e^-$$
 (3)

$$\mathrm{Cl}^{\bullet} + \mathrm{Cl}^{-} \to \mathrm{Cl}_{2}^{\bullet-} \tag{4}$$

$$NH_4^+ + e^- \rightarrow NH_3 + H^{\bullet}$$
(5)

$$NH_4^+ + H^\bullet \rightarrow NH_3^+ + H_2 \tag{6}$$

$$\cdot \mathbf{N}\mathbf{H}_{3}^{+} + \mathbf{C}\mathbf{I}^{-} \to \mathbf{H}_{3}\mathbf{N} \doteq \mathbf{C}\mathbf{I}$$
(7)

It is our normal experience that electron-transfer reactions dominate under these circumstances. Primary ejection will be effectively from chloride ions, which react promptly to give relatively stable Cl_2^{-} units. Such units were almost invariably detected in the systems studied. Electron capture by NH_4^+ gives $NH_3 + H^*$ [reaction (5)] and the latter is expected to react to give $NH_3^+ + H_2$ [reaction (6)] probably as a hot reaction. Generally, H_1^* centres were not detected. Finally, NH_3^+ will move laterally to give $H_3N - Cl$ radicals [reaction (7)].

A similar sequence can explain the formation of hal_2^- and R_3N-hal radicals in the other systems studied. Other reactions such as

$$CH_3NH_3^+ + H^- \rightarrow H_2\dot{C} - NH_3^+ + H_2$$
(8)

$$CH_3NH_3^+ + e^- \rightarrow CH_3 + NH_3$$
(9)

will compete, and certainly α -amino carbon-centred radicals are important products. However, if reaction (9) occurs, in

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addition to H^{\cdot} formation [cf. reaction (5)], the resulting methyl radicals must react further via reactions equivalent to reactions (6) or (9) since they were never detected as significant trapped species.

In some cases, there was a growth in the $[R_3N - hal]$ as the V_K centres decayed. For Cl_2^{-} , hydrogen abstraction reactions are expected, but for Br_2^{-} and especially I_2^{-} they would be surprising at these low temperatures. It therefore seems possible that these reactions are not directly related. One possibility is that as a result of thermal mobility (halide-ion transfer), the Br_2^{-} or I_2^{-} units migrate and encounter radiolytically produced amine molecules and react by a nucleophilic displacement as in reaction (10).

$$RNH + hal_2^- \rightarrow RNHhal + hal^-$$
 (10)

Another result of such mobility would be various radicalradical reactions resulting in an overall decrease in signal strength. This indeed occurred, together with growth in $[R_3N - hal]$ radicals when the V_K centres decayed. These reactions are based on the species detected by EPR spectroscopy and on expectation. Hence there remains an element of speculation.

Correlations

Since the most complete set of data is for the iodides, we have used these results to illustrate two correlations (Fig. 9). In Fig. 9(a) the parallel and perpendicular values are compared. The errors are relatively large for A_{\perp} but, nevertheless, there is a reasonably linear increase in A_{\perp} as A_{\parallel} increases. Thus A_{\parallel} can be used as a fair measure of the relative spin densities on iodine $[\rho(I)]$, using $A_{\parallel} \approx 10\rho(I)\%$. These data correlate well with the ionization potentials for the parent amines [Fig. 9(b)]. The simplest explanation for this trend to high spin density on iodine as the ionization potential increases is in terms of the contributions to the overall structures from the valence-bond ionic limit, $\mathbf{R}_3 \mathbf{N} \cdot {}^+\mathbf{I}^-$. The lower E_i , the more this structure is favoured and hence the lower the spin density on iodine. One notable exception to the correlation in Fig. 9(b) is the quinuclidine derivative. This, being a tertiary amine derivative might be expected to resemble the Et₃N complex, as indeed is the case for its vertical E_i . However, the spin density on iodine is clearly greater than expected. This amine was chosen because the amine cation is unable to move far towards planarity at nitrogen. This reduces the tendency towards the limiting structure $R_3N\cdot\,^+I^-$ in which the R_3N^{*+} group is planar. This argument is correct only provided there is considerable flattening of the Et_3N^{+} group as is implied by the low spin density on iodine. It may be significant that the data, except that for $H_3N - I$, correlate linearly with the ionization potentials. The deviation for $H_3N - I$ is large and cannot be due to experimental errors.

In most examples, the ¹⁴N hyperfine coupling constants were too poorly defined to warrant analysis of this type. However, for the H_3N^{*+} derivatives (Tables 1 and 2) and the quinuclidine derivative the ¹⁴N data are more reliable. The former show a clear decrease in spin density and p/s ratio on going from the Cl⁻ to the I⁻ derivative, in good accord with expectation. A similar analysis of the iodoquinuclidine radical data shows that the spin density on nitrogen (ca. 40%) is similar to that for $H_3N - Br$. The p/s ratio is ca. 3.6, showing that the extent of flattening at nitrogen is small.

All g_{\parallel} values were only slightly less than the free-spin value (2.0023) as found for other halogen σ^* -radicals. The shifts in g_{\perp} , although difficult to estimate accurately, correlate well with the estimated halogen spin densities for $R_3N - I$ complexes, the shifts increasing with increasing spin densities. It is

interesting that if Δg_{\perp} for I_2^- (ca. 0.28) is halved, the result fits exactly on the Δg_{\perp} vs. spin density correlation. This confirms that the shift is solely associated with the iodine atom in the $R_3N \doteq I$ adducts.

Conclusions

These results confirm the formation of $R_3N - hal$ radicals and support the suggestion that these are three-electron σ^* radicals. Factors contributing to their stabilities have been described. The fact of their stability and the tendency for the R_3N- unit to flatten as the bond gets weaker is nicely in accord with explanations given for the inability to prepare the isoelectronic $R_3C - hal^-$ radical anions.¹³

References

- 1 E. Canadell, P. Karafiloglou and L. Salem, J. Am. Chem. Soc., 1980, 102, 855.
- 2 See, e.g. A. J. Swallow, Radiation Chemistry, Longman, London, 1973.
- 3 M. C. R. Symons, Pure Appl. Chem., 1981, 53, 223
- 4 T. G. Castner and W. Känzig, Phys. Chem. Solids, 1957, 3, 178.
- 5 S. P. Mishra and M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1981, 185.
- 6 D. J. Nelson, and M. C. R. Symons, Chem. Phys. Lett., 1977, 47, 436.
- 7 E. D. Sprague and F. Williams, J. Chem. Phys., 1971, 54, 5425.
- 8 S. P. Mishra and M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1973, 391.
- 9 M. C. R. Symons and I. G. Smith, J. Chem. Soc., Perkin Trans. 2, 1979, 1362; 1981, 1180.
- 10 M. C. R. Symons, Chem. Phys. Lett., 1980, 72, 559.
- 11 M. C. R. Symons and R. L. Petersen, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 210.
- 12 F. W. Patten. Phys. Rev., 1968, 175, 1216.
- 13 M. C. R. Symons, J. Chem. Res. (S), 1981, 160.
- 14 A. G. Kotov and S. Ya. Pshezhetskii, Russ. J. Phys. Chem., 1964, 38, 1046.

- 15 H. R. Zeller, L. Vannotti and W. Kanzig, Phys. Kondens. Mater., 1964, 2, 133.
- 16 F. W. Patten and M. J. Marrone, Phys. Rev., 1966, 142, 513.
 - 17 C. L. Marquardt and F. W. Patten, Solid State Commun., 1969, 7, 393.
 - 18 C. L. Marquardt, J. Chem. Phys., 1970, 53, 3248.
 - 19 F. W. Patten, Solid State Commun., 1968, 6, 65.
 - 10 V. N. Belevskii and L. T. Bugaenko, J. Radioanal. Nucl. Chem., 1986, 107. 67.
 - 21 M. Mardanov, A. P. Mamedov, M. R. Nadzhafova, V. R. Mardukhaev and E. Yu. Salaev, Dokl. Akad. Nauk. Az.S.S.R., 1977, 33, 38.
 - 22 J. P. Michaut and J. Roncin, Can. J. Chem., 1977, 55, 3554.
 - 23 A. P. Mamedov, L. Ya. Panova, R. A. Dzhafarov and V. R. Mardukhaev, Sov. Phys. Solid State, 1979, 21, 2152.
 - M. B. Khusidman, V. P. Vyatkin, N. V. Grigoreva and S. L. Dobychin, Zh. Prikl. Khim., 1981, 54, 132.
 - 25 M. B. Khusidman, V. P. Vyatkin, N. V. Grigoreva, S. L. Dobychin and I. A. Posadov, Zh. Prikl. Khim., 1982, 55, 2490.
 - 26 M. B. Khusidman, V. P. Vyatkin, N. V. Grigoreva and S. L. Dobychin, Zh. Prikl. Khim., 1983, 56, 222.
 - 27 M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1973, 797.
 - 28 P. Neta and R. W. Fessenden, J. Phys. Chem., 1971, 75, 738.
 - 29 Y. L. Chow, W. C. Danen, S. F. Nelsen and D. H. Rosenblatt, *Chem. Rev.*, 1978, 78, 243.
 - 30 G. W. Eastland, D. N. R. Rao and M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1984, 1551.
 - 31 G. W. Neilson and M. C. R. Symons, J. Chem. Soc., Faraday Trans. 2, 1972, 69, 1582.
 - 32 G. W. Neilson and M. C. R. Symons, Mol. Phys., 1974, 27, 1613.
 - 33 D. Pace, K. Ezell and L. D. Kispert, J. Chem. Phys., 1979, 71, 3971.
 - 34 H. Muto and L. D. Kispert, J. Chem. Phys., 1980, 72, 2300.
 - 35 H. Chandra, A. Bathgate, J. R. Malpass and M. C. R. Symons, J. Chem. Soc., Perkin Trans. 2, 1988, 1329.
 - 36 J. B. Raynor, I. J. Rowland and M. C. R. Symons, J. Chem. Soc., Dalton Trans., 1987, 421.

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