Electron-gain and Electron-loss Centres derived from Chloro Amines

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Exposure of dilute solutions of various dialkyl and cyclic *N*-chloro amines in trichlorofluoromethane to ^{60}Co γ-rays at 77 K gave the corresponding cations, $R_2\dot{N}Cl^+$, characterised by ^{14}N, ^{35}Cl, and ^{1}H hyperfine coupling. The results suggest that these radicals are essentially planar at nitrogen, the SOMO being the N–Cl π* orbital. Similar treatment of dilute solutions in methanol or methyltetrahydrofuran gave the corresponding amino radicals, $R_2N^{\bullet}$, also characterised by their e.s.r. spectra. There was no evidence for the formation of the parent radical anions. These results are contrasted with those for *N*-halogeno imides and with the formation of σ* radicals from the cations $R_3N^{\bullet+}$ and halide ions.

One of us (J. R. M.) and his co-workers have made extensive studies of the structure and reactivity of bicyclic *N*-chloro amines.[1–4] It seemed of interest to use radiolysis, coupled with e.s.r. spectroscopy, to study the basic redox reactions of these compounds, since they do not seem to have been studied previously by this method. We report here our results for some acyclic and cyclic *N*-chloro amines. This technique[5,6] involves cooling solutions of the substrate (R_2NCl in this case) in suitable solvents and exposure to ionising radiation. For dilute solutions, only solvent molecules suffer electron ejection, and in suitable solvents the substrate interacts either with electrons or with 'positive holes'. For electron-capture reactions, CD_3OD is an ideal solvent since the electron loss centre, $(CD_3OD)^{\bullet+}$, is rapidly deprotonated and is trapped, whilst the ejected electrons are relatively mobile and will react with electron-affinic solutes. In contrast, solvents such as $CFCl_3$ scavenge ejected electrons with high efficiency, but the radical cations $(CFCl_3)^{\bullet+}$ are mobile, *via* electron transfer, and react with any solute molecules having ionisation potentials less than *ca.* 11.8 eV.[6]

Experimental

The *N*-chloro amines were prepared from the appropriate secondary amines by treatment with *N*-chlorosuccinimide in $CFCl_3$.[7] Commercial samples of diethylamine, di-isopropylamine, pyrrolidine, and piperidine were distilled from sodium hydroxide pellets. *N*-Chlorosuccinimide was recrystallised from benzene; $CFCl_3$ was passed down an alumina column prior to use.

In a typical experiment, *N*-chlorosuccinimide (1.11 g, 8.31 mmol) was added to a solution of piperidine (0.62 g, 7.28 mmol) in $CFCl_3$ (20 ml). The mixture was stirred for 2 h and the resulting solution washed twice with M-HCl. After drying (Na_2SO_4), the solution was filtered and concentrated by evaporation under dry nitrogen. Product purity was checked by ^{1}H n.m.r. spectrometry.

The substrates were dissolved in degassed solvents [$CFCl_3$, CD_3OD, or methyltetrahydrofuran (MTHF)] and the solutions were exposed to ^{60}Co γ-rays in a Vickrad cell at 77 K with doses up to *ca.* 1 Mrad.

E.s.r. spectra were measured with a Varian E-109 *X*-band spectrometer at 77 K. Samples were annealed by decanting the coolant from the insert Dewar and monitoring the spectrum continuously. They were recooled to 77 K whenever significant changes occurred. In the present experiments, this method showed small reductions in $A_{\parallel}$ values and linewidth changes, but no new radical species were detected.

Results and Discussion

Electron-loss Centres.—From very dilute solutions in $CFCl_3$, good but highly complex e.s.r. spectra were obtained (Figure 1).

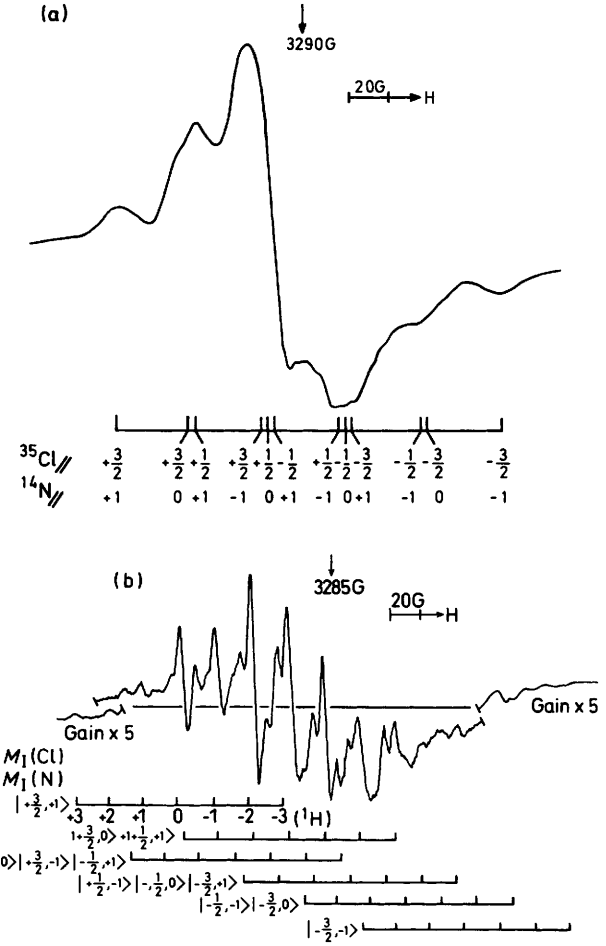

Figure 1. First-derivative *X*-band e.s.r. spectra for (a) $(Me_2CH)_2NCl$ and (b) $[CH_2]_4NCl$ in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the corresponding radical cations. (Features for ^{35}Cl are indicated: in general, the lines were too broad to allow good definition of those for ^{37}Cl)

From extensive experience with such systems, we can assign these with confidence to the radical cations, $R_2\dot{N}Cl^+$, or some unimolecular breakdown product therof. Of the two illustrated spectra, that derived from $(Me_2CH)_2NCl$ can be analysed in terms of hyperfine coupling to chlorine and nitrogen only, any proton coupling being unresolved [Figure 1(a)]. Absence of proton coupling is reasonable on steric grounds, the predicted structure having the two β-protons close to the radical plane. Hence we conclude that the product is, indeed, the parent cation.

Table 1. E.s.r. parameters and derived orbital populations for radical cations derived from *N*-chlorodialkylamines (solvent $CFCl_3$)

			Hyperfine coupling (G)[a]			Orbital populations (%)[b]	
Source/Solvent	Radical	Nucleus	$A_\parallel$	$A_\perp$	A_{iso}	a_s^2	a_p^2
Et_2NCl	$Et_2\dot{N}Cl^+$	$^1H(4)$			30		
		^{14}N			c		
$(Me_2CH)_2NCl$	$(Me_2N)_2\dot{N}Cl^+$	^{14}N	35	*ca.* 0	*ca.* 11.7	*ca.* 2.1	*ca.* 71
		$^{35}Cl^d$	40	*ca.* 0	*ca.* 13.3	*ca.* 0.8	*ca.* 26
$[CH_2]_4NCl$	$[CH_2]_4\dot{N}Cl^+$	$^1H(2)$			24		
		$^1H(2)$			48		
		^{14}N	37	*ca.* 0	*ca.* 12.3	*ca.* 2.2	*ca.* 75
		$^{35}Cl^d$	40	*ca.* 0	*ca.* 13.3	*ca.* 0.8	*ca.* 26
$[CH_2]_5NCl$	$[CH_2]_5\dot{N}Cl$	$^1H(2)$			*ca.* 11.5		
		$^1H(2)$			*ca.* 23		
		^{14}N			c		

[a] 1G = 10^{-4} T. [b] Approximate orbital populations derived from A_{iso} and 2*B* in the usual manner.[11] [c] Only the $|0, +\frac{1}{2}\rangle$ features were well defined. [d] ^{37}Cl Features were not sufficiently defined for estimation of the ^{35}Cl coupling.

Table 2. E.s.r. parameters and orbital populations for various amide radicals

			Hyperfine coupling (G)[a]			Orbital populations (%)[b]	
Source/Solvent	Radical	Nucleus	$A_\parallel$	$A_\perp$	A_{iso}	a_s^2	a_p^2
Et_2NCl/CD_3OD (77 K)	$Et_2\dot{N}$	^{14}N	42	0	14	2.5	85
		$^1H(4)$			40		
Et_2N-N_2-NEt_2[b]	$Et_2\dot{N}$	^{14}N			14.27		
		$^1H(4)$			36.9		
Et_2NH[c] (77 K)	$Et_2\dot{N}$	^{14}N	35	0 ± 5			
		$^1H(4)$			38 ± 2		
$[CH_2]_4NCl/CD_3OD$ (77 K)	$[CH_2]_4\dot{N}$	^{14}N	43	0	14.3	2.6	87
		$^1H(2)$			56		
		$^1H(2)$			28		
MTHF (77 K)	$[CH_2]_4\dot{N}$	^{14}N	42	0	14	2.5	85
		$^1H(2)$			55		
		$^1H(2)$			27.5		
$[CH_2]_4NH$/adamantane[d]	$[CH_2]_4\dot{N}$	^{14}N			14.4		
		$^1H(4)$			39.1		

[a] $g_\parallel = 2.002, g_\perp = 2.006$. [b] W. C. Danen and C. T. West, *J. Am. Chem. Soc.*, 1971, **93**, 5582. [c] Ref. 23. [d] D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, 1971, **75**, 3486.

Analysis of the spectrum in Figure 1(b), for *N*-chloropyrrolidine cations, is based upon the Me_2CH– derivative with the inclusion of extensive proton coupling. There is a clear set of seven lines which we assign to two equivalent protons, one having *ca.* twice the hyperfine coupling (*ca.* 48 G) of the other (*ca.* 24 G). These major features are centred on the position of the intense, almost isotropic line for radicals with $M_I(^{14}N) = 0$ and $M_I(^{35}Cl) = +\frac{1}{2}$ seen in Figure 1(a). It is common experience that this feature is the most intense and symmetrical in the solid-state powder spectra for many chlorine derivatives, so these lines serve to characterise the proton coupling. Weak outer features agree reasonably well with expectation for the 'parallel' features based on the ^{14}N and ^{35}Cl data derived from the Me_2CH derivative, as indicated in the stick diagram. The fact that these coupling constants (Table 1) are so similar suggests that hyperconjugative delocalisation involving the C–C bonds is not greatly different from that for C–H bonds despite the normal preference for the latter.[8]

Spectra for the cation $Et_2\dot{N}Cl^+$ were less well defined except for the $|+\frac{1}{2}, 0\rangle$ features, which showed the presence of four nearly equivalent protons [equal in pairs since there was marked broadening of the $M_I(^1H) = \pm 1$ features] with coupling of *ca.* 35 G. This large coupling suggests a reversal of conformation relative to the Me_2CH– derivative, with the two methyl groups lying close to the radical plane. This supports the concept that C–H hyperconjugation in radical cations dominates when steric requirements are not overriding. The result can be compared with those for the cation $Et_3N^{\bullet +}$.[9] In this case at 77 K only three of the six β-protons gave rise to hyperfine coupling (38 G), the other three being, presumably, close to the radical plane. We have previously shown that for ethyl substituents in benzene cations the competition between steric and C–H hyperconjugative control is subtle,[8] and is not well reproduced by theory at the INDO level.[10] Unfortunately, the other features were poorly resolved but those that do appear in the spectra agree with expectation for the ^{14}N and ^{35}Cl data derived from the spectra in Figure 1.

These comments also apply to the outer features for the

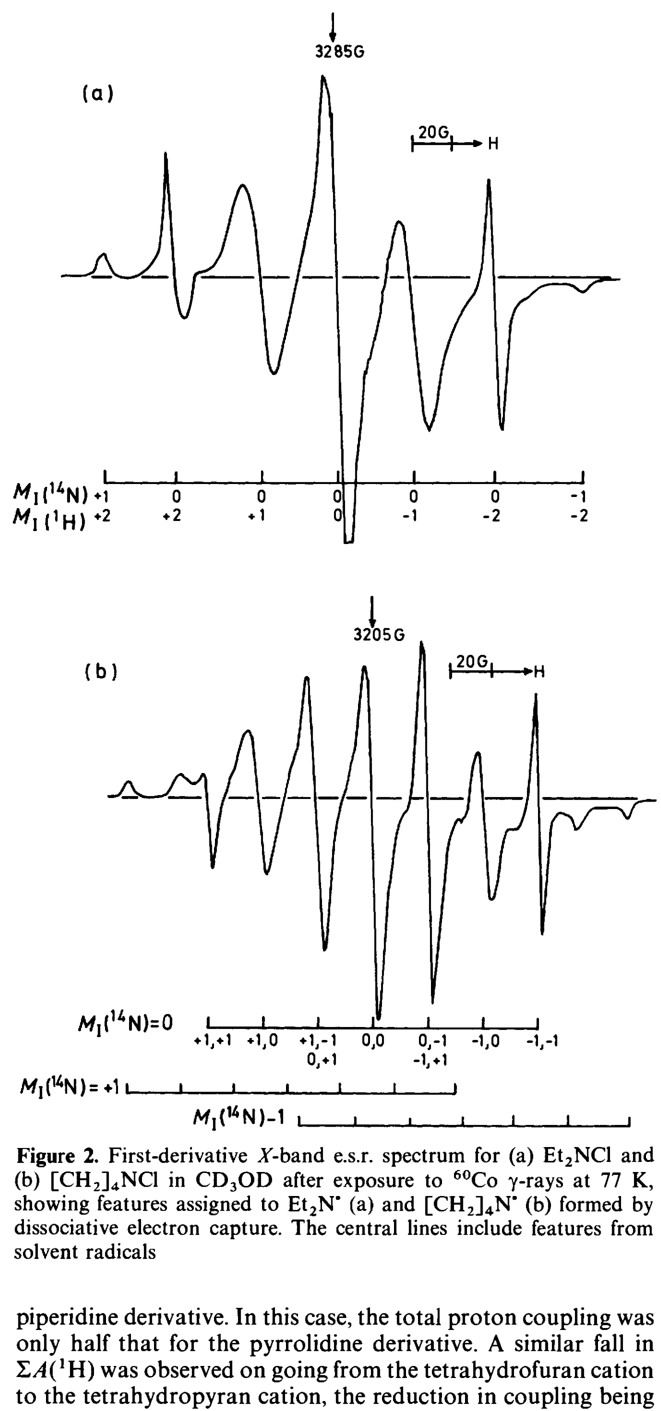

Figure 2. First-derivative *X*-band e.s.r. spectrum for (a) Et_2NCl and (b) $[CH_2]_4NCl$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $Et_2N^•$ (a) and $[CH_2]_4N^•$ (b) formed by dissociative electron capture. The central lines include features from solvent radicals

piperidine derivative. In this case, the total proton coupling was only half that for the pyrrolidine derivative. A similar fall in $\Sigma A(^1H)$ was observed on going from the tetrahydrofuran cation to the tetrahydropyran cation, the reduction in coupling being explained in terms of different ring conformers.[11]

The results for the cations $R_2\dot{N}Cl^+$ establish that these are planar at the nitrogen centre despite the marked pyramidality of the parent compounds. That this is the case is shown by the estimates of orbital populations (Table 1) obtained from the ^{14}N and ^{35}Cl coupling constants in the usual way.[12] For these calculations we set $A_\perp(^{14}N)$ and $A_\perp(^{35}Cl)$ to zero, since there were no defined features assignable to *x* or *y* splitting. Setting $A_\perp(Cl) = 0$ is undoubtedly a poor approximation but since the true value is likely to be negative,[13] we obtain an underestimate of the spin density using this approximation. As can be seen from the data, the sum of the spin densities on nitrogen and chlorine is close to unity. This must be an underestimate for the reason already given, and because of the considerable hyperconjugative delocalisation established by the large ^1H coupling.

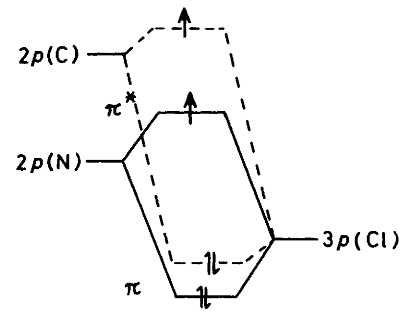

Figure 3. Qualitative bonding scheme for the C–Cl and N–Cl π-bonds in $R_2\dot{C}Cl$ and $R_2\dot{N}Cl^+$

Had the radical been non-planar, the observed results would have been less than the maximum values since $A_z(^{14}N)$ would not be co-linear with $A_z(^{35}Cl)$. The high spin densities obtained, therefore, strongly imply planarity. That the total spin-density is >1 arises, in part, from the positive charge, and the fact that atomic rather than cationic orbital parameters were used in the calculations.[11] Spin polarisation giving rise to some negative contributions will also be a factor.

These results are important because of the recent suggestion that certain more complex chloro amine cations may be pyramidal.[14] This tentative conclusion was based on the anomalous oxidation potentials obtained for these compounds in relation to their inversion barriers. It is certainly to be expected that these '3π-electron' cations, like the isostructural nitroxide radicals, will be either slightly pyramidal or planar with a very flat bending potential. Thus, although our results imply planarity, it may well be that ring strain, which dramatically changes the inversion barriers of the neutral, strongly pyramidal molecules, also causes some pyramidality in the more complex compounds studied by Nelsen *et al.*[14]

Comparison of the maximum hyperfine coupling for ^{35}Cl in the isoelectronic radicals $R_2\dot{C}Cl$ and $R_2\dot{N}Cl^+$ shows a marked increase from *ca.* 20 G,[15] to *ca.* 40 G. Taking $A_{max.}$ as proportional to the spin-density, this means an increase in spin-density on chlorine from *ca.* 0.13 to *ca.* 0.26. This result clearly illustrates the antibonding character of the π-orbital SOMO as indicated in Figure 3.

Electron Capture.—That R_2NCl molecules capture electrons efficiently is established by the intense e.s.r. spectra obtained at 77 K after irradiating solutions in CD_3OD. These are readily assigned to $R_2N^•$. For example, the spectrum shown in Figure 2 yields data close to those previously assigned to $EtN^•$, there being no sign of splitting from chlorine (Table 2).[16] The marked reduction in the violet colour associated with trapped electrons is also clear evidence for electron capture by the solute. Thus reaction (1) must be efficient at 77 K (both in CD_3OD and in MTHF).

$$R_2NCl + e^- \longrightarrow R_2N^• + Cl^- \qquad (1)$$

This results contrasts with work on the interaction between R_3N^+ and halide ions.[17–19] Here there is clear coupling to chlorine and an increase in the 2*s*-character on nitrogen, relative to simple radicals $R_3N^{•+}$, indicates that the R_3N units deviate from the planarity of the normal cations $R_3N^{•+}$. One factor is the reduced effective electron-affinity of $R_2N^•$ relative to $R_3N^{•+}$. This will make R_2N–Cl reactivity resemble that of R_3C–Cl in which dissociation is always effectively complete, even though very weak residual interaction with the halogen is sometimes detectable.[20]

The results are in sharp contrast with those for *N*-halogeno succinimides and related compounds.[21,22] These readily form σ^* anions, the unpaired electron being accommodated in the N$\overset{\cdot}{-}$Hal σ^* orbital with high spin densities on both nitrogen and halogen. Again this is partly due to the enhanced effective electronegativity on nitrogen caused by the C=O units. It is also probably a result of the inability of the nitrogen to relax in order to reduce the *s*-character of the SOMO to a major extent. For $R_2N\overset{\cdot}{-}Cl^-$ (and $R_3C\overset{\cdot}{-}Cl^-$) as the N–Cl (or C–Cl) bond stretches to accommodate the excess electron, so the N (or C) contribution to the SOMO moves from sp^2 (sp^3 for C) towards pure *p* as found in the resulting radicals. This cannot occur for the succinimide derivatives. A similar argument was used to explain the relative stabilities of the σ^* radicals $C_6F_5\overset{\cdot}{-}I^-$[23] and $RC{\equiv}C\overset{\cdot}{-}I^-$.[5,24]

Finally, there is a remarkable consistency in the ^{14}N and ^{1}H data reported in Tables 1 and 2 for the radicals $R_2N^{\bullet}$ and $R_2\dot{N}Cl^+$. For example, let us compare the data for $[CH_2]_4N^{\bullet}$ and $[CH_2]_4\dot{N}{-}Cl^+$. There is a reduction of *ca.* 85% for the strongly and weakly coupled β-protons, and also for the calculated 2*s* and 2*p* character for ^{14}N. These results suggest that the spin density on chlorine should be *ca.* 15%, as compared with the value of 26% estimated from the ^{35}Cl data. As already stressed, the latter is an approximate result, but spin polarisation, giving rise to some negative spin density, must help to explain the difference.

The most surprising result is that the β-proton hyperfine coupling constants correspond so accurately. This implies the absence of a major positive charge effect for $R_2\dot{N}Cl^+$, such as is found, for example, when $R_2N^{\bullet}$ and $R_2\dot{N}H^+$ are compared, the latter giving considerably enhanced β-proton coupling constants. The contrast cannot simply arise because of delocalisation onto chlorine, since this is not large. It also implies that the ring conformations are very similar in the two cases.

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