

Hydrogen Halide Radical Anions †

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Exposure of Me_3NSO_3 doped with Me_3NHX ($X = \text{F}, \text{Cl}, \text{Br}, \text{or I}$) to ^{60}Co γ -rays at 77 K gives radicals whose e.s.r. spectra show hyperfine coupling to ^1H and X nuclei. These are identified as $\text{HX}^{\cdot-}$ radical anions. The species $\text{HF}^{\cdot-}$ has properties of normal trapped hydrogen atoms, but the remainder are thought to be genuine radical anions with a σ^* semi-occupied molecular orbital. The $\text{HCl}^{\cdot-}$ and $\text{HBr}^{\cdot-}$ radicals rotate about a specific axis normal to the σ bond at 77 K but the motion is quenched on further cooling. Possible mechanisms for the radiolytic processes are discussed. Other radicals detected during the course of the work include $\text{SO}_3^{\cdot-}$, $\text{Me}_3\text{N}^{\cdot+}$, and $\text{H}_2\dot{\text{C}}\text{NMe}_2\text{SO}_3$.

Although many diatomic radicals or radical ions have been studied by e.s.r. or laser magnetic resonance spectroscopic methods, we know of only one previous report of radical anions of hydrogen halides:¹ this was $\text{HCl}^{\cdot-}$ formed in argon gas matrices by electron transfer between K and HCl. The magnetic properties established that this centre cannot be thought of as a 'trapped hydrogen atom,' and that a molecular description was required, the s.o.m.o. (semi-occupied molecular orbital) being the $\text{H}-\text{Cl}$ σ^* orbital. Since the potassium cation is not expected to have migrated away from the anion, this centre is undoubtedly an ion pair, but the interaction is so weak that no hyperfine coupling to ^{39}K could be detected.

The aim of the present study was to prepare the whole range of $\text{HX}^{\cdot-}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{or I}$) radical anions in a constant matrix, and to estimate the character of their s.o.m.o.s using the e.s.r. parameters, thereby discovering the variation of the spin-density distribution with the nature of the halogen.

An important method for generating electron-gain and -loss centres in matrices is by the use of ionizing radiation.² In many cases, the best method for generating specific electron-gain or -loss centres is to use dilute solid solutions of the required diamagnetic precursor in suitable host lattices that either trap holes or electrons efficiently.² In the present case, it was found that dilute solutions of $\text{Me}_3\text{NH}^+\text{X}^-$ in Me_3NSO_3 were ideal for generating $\text{HX}^{\cdot-}$ centres.

We note that the corresponding radical cations, $\text{HX}^{\cdot+}$ (π^*) have never been studied by e.s.r. in condensed phases, although they have recently been extensively studied in the gas phase using laser magnetic resonance.³

Experimental

Trimethylammonium fluoride was prepared by condensing an excess of trimethylamine and anhydrous hydrogen fluoride into a cold trap and carefully warming.

Trimethylammonium chloride was used as supplied (Aldrich); the other trimethylammonium halides were prepared by neutralization of the alkylamine with the corresponding concentrated acid followed by recrystallization from methanol. Trimethylamine-sulphur trioxide (Aldrich) was recrystallized from purified water prior to use. Dilute solid solutions of the alkylammonium halide in trimethylamine-sulphur trioxide were prepared by dissolving both compounds in methanol and co-precipitating by the addition of dry diethyl ether. All samples were compressed as pellets (except where indicated) and γ -irradiated at 77 K for up to 2 h using a Vickrad ^{60}Co source at a

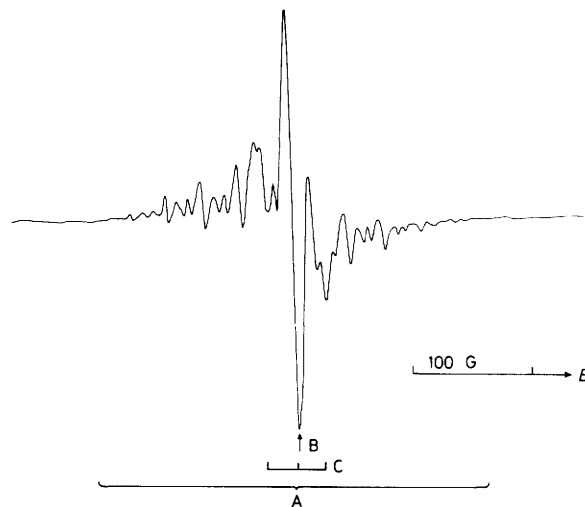


Figure 1. First-derivative X-band e.s.r. spectrum for Me_3NSO_3 after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to $\text{Me}_3\text{N}^{\cdot+}$ radicals (A), $\text{SO}_3^{\cdot-}$ radicals (B), and $\text{H}_2\dot{\text{C}}\text{NMe}_2\text{SO}_3$ radicals (C)

dose rate of ca. 0.8 Mrad h^{-1} . Spectra were recorded at 77 and at ca. 4 K on a Bruker ER200-D X-band spectrometer. Pulse-annealing experiments above 77 K were carried out by decanting the liquid nitrogen from the quartz insert dewar and replacing only when significant spectral changes were observed.

Results and Discussion

Before considering results assigned to $\text{HX}^{\cdot-}$ radical anions, the effects of ionizing radiation on the matrix, Me_3NSO_3 , are outlined here as, to our knowledge, there has been no previous studies of the radiolysis of this compound.

Me_3NSO_3 Matrix.—Irradiation at 77 K gave the spectrum shown in Figure 1. This can be largely interpreted in terms of features from $\text{Me}_3\text{N}^{\cdot+}$ and $\text{SO}_3^{\cdot-}$ radicals, both of which have been extensively studied by e.s.r. spectroscopy.⁴⁻⁶ A third species more readily observable at lower microwave power is identified as the $\text{H}_2\dot{\text{C}}\text{NMe}_2\text{SO}_3$ radical.

These results nicely illustrate the normal mode of interaction between ionizing radiation and polar solids. Electron loss gives the parent cation (not detected) which readily dissociates to give $\text{Me}_3\text{N}^{\cdot+}$ radicals and sulphur trioxide, equation (1). Electron

† Non-S.I. units employed: rad = $10^{-2} \text{ J kg}^{-1}$, G = 10^{-4} T .

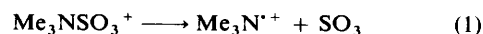


Table. E.s.r. parameters^a for hydrogen halide^b anions formed in Me₃NSO₃ matrices, and for HCl⁻ in argon

Radical Source	HF ⁻	HCl ⁻		HBr ⁻	HI ⁻
	Me ₃ NHF	Me ₃ NHCl	HCl + K in Ar ^c	Me ₃ NHBr	Me ₃ NHI
$A_{ }(\text{expt}) (\text{X})^d$	17.8	15.0 ^e		100.5 ^e	100.5 ^e
$A_{\perp}(\text{expt}) (\text{X})^d$	17.8	25.1 ^e		151.0 ^e	151.0 ^e
$A_z (\text{X})$	17.8	35.2 ^f	47.3	228.5 ^f	139.0 ^f
$A_{x,y} (\text{X})$	17.8	15.0 ^f	19.0	100.5 ^f	69.0 ^f
$A_{\text{iso}} (\text{X})$	17.8	21.7	28.4	143.1	92.3
$A_{\text{aniso}} (\text{X})$		13.5	18.9	85.3	46.7
$A (\text{H})$	509.1	467	429.3	447.5	481.0
% <i>s</i> (on H)	100.4	92.1	84.7	88.3	94.9
% <i>s</i> (on X) ^g	0.1	1.1	1.4	1.2	0.6
% <i>p</i> (on X) ^h		13.4	18.7	17.3	10.3
<i>p/s</i> ratio		12.6	13.5	14.9	16.5
Total spin	100.4	106.6	104.8	106.7	105.8
<i>g</i>	2.003	2.010		2.017	2.013

^a All hyperfine couplings in G. ^b X = ¹⁹F, ³⁵Cl, ⁸¹Br, or ¹²⁷I. ^c From ref. 1. ^d At 77 K. ^e Radical undergoing specific rotation at 77 K. ^f Non-rotating radical. ^g Using the atomic parameters given in ref. 11. ^h Using the atomic parameters given in refs. 9 and 10.

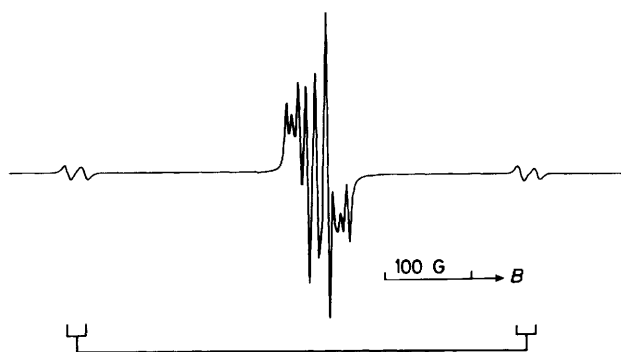


Figure 2. First-derivative X-band e.s.r. spectrum for Me₃NSO₃ doped with Me₃NHF after exposure to ⁶⁰Co γ-rays at 77 K, showing features assigned to HF⁻



capture must give the parent anion, which is also unstable at 77 K, decomposing to give Me₃N and SO₃^{·-} radicals (2).

The radical H₂CNMe₂SO₃ was probably formed by attack of 'hot' SO₃^{·-} or Me₃N^{·+} radicals on neighbouring matrix molecules.

HF⁻ Radical.—γ-Irradiation of Me₃NSO₃ doped with Me₃NHF yielded an isotropic doublet clearly due to ¹H, each split into a doublet by coupling to ¹⁹F (Figure 2). This radical is assigned to HF⁻, the hyperfine parameters being given in the Table. In view of the similarity of the large coupling to that normally found for hydrogen atoms (*ca.* 508 G), this identification seems to be unambiguous. The suitability of the radical anion description in this case is discussed below.

HCl⁻ Radical.—Irradiation of Me₃NSO₃ doped with Me₃NHCl gave the e.s.r. spectrum shown in Figure 3(a). In addition to the central features already assigned, there is a doublet of quartets. Clearly the large doublet splitting of *ca.* 467 G is due to hyperfine coupling to ¹H, whilst the appearance of quartet features characteristic of coupling to ³⁷Cl and ³⁵Cl clearly establishes the presence of chlorine. The data given in the Table for HCl⁻ were used to give the simulated spectrum shown in Figure 3(b), the fit being such that these results appear quite reliable.

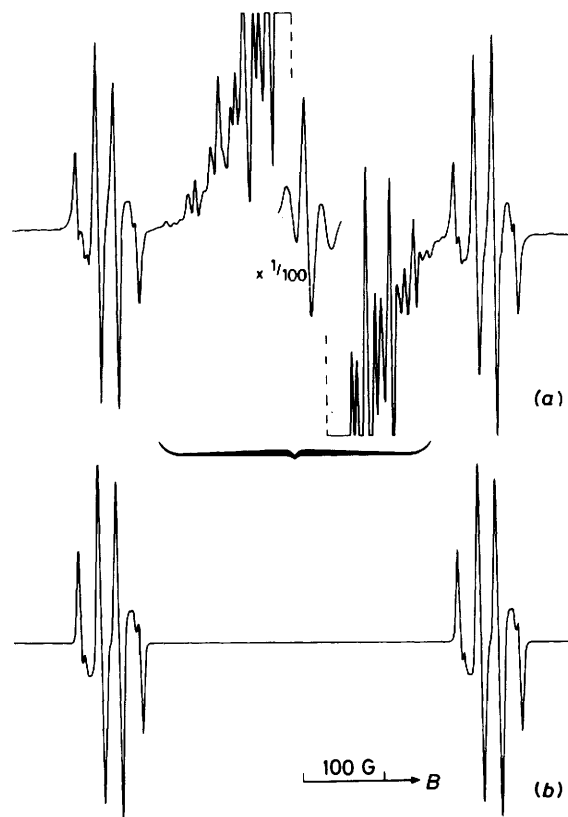


Figure 3. (a) As for Figure 2, with Me₃NHCl as dopant, showing outer features assigned to HCl⁻. (b) Computer simulation for HCl⁻, using the parameters given in the Table

An unexpected aspect of these results is that $|A_{\perp}| > |A_{||}|$ for ³⁵Cl. This suggests some form of restricted rotation. The species was therefore studied at *ca.* 4 K. As expected a normal spectrum was then obtained with $|A_{||}| > |A_{\perp}|$. The nature of this restricted rotation is discussed later. On annealing to room temperature, the features assigned to HCl⁻ radicals were lost irreversibly. There was no evidence for the formation of trapped hydrogen atoms from HCl⁻ (or from any other X⁻ centre) during pulse-annealing studies.

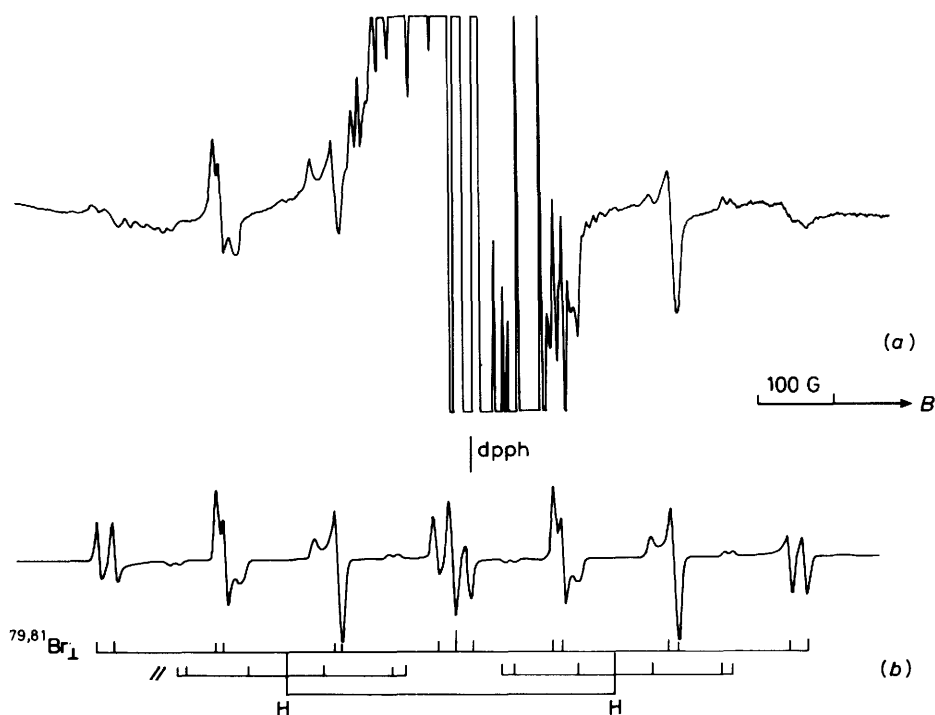


Figure 4. (a) As for Figure 2, with Me_3NHBr as dopant, showing outer features assigned to $\text{HBr}^{\bullet-}$. (b) Computer simulation for $\text{HBr}^{\bullet-}$ using the parameters given in the Table; dpph = diphenylpicrylhydrazyl

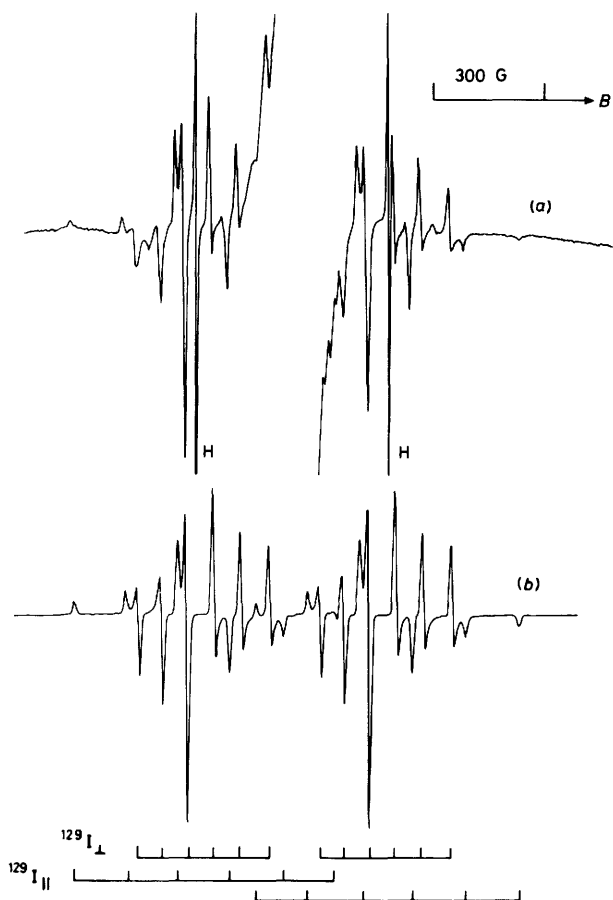


Figure 5. (a) As for Figure 2, with Me_3NHI as dopant, showing outer features assigned to $\text{HI}^{\bullet-}$; the H atoms arise from the quartz tube. (b) Computer simulation for $\text{HI}^{\bullet-}$, using the parameters given in the Table

$\text{HBr}^{\bullet-}$ Radical.—Exposure of Me_3NSO_3 doped with Me_3NHBr gave the spectrum shown in Figure 4. In addition to the large doublet splitting assigned to coupling to ^1H , there are anisotropic quartet splittings characteristic of ^{81}Br and ^{79}Br , so again, identification is unambiguous. As with $\text{HCl}^{\bullet-}$ at 77 K, $|A_{\perp}| > |A_{\parallel}|$ for the bromine coupling. This is presumably caused by the same restricted rotation as for $\text{HCl}^{\bullet-}$ and the true tensor components were estimated on this assumption (Table).

$\text{HI}^{\bullet-}$ Radical.—The spectrum obtained for Me_3NSO_3 doped with Me_3NHI is shown in Figure 5. In addition to a central feature associated with a methyl radical, a large doublet splitting was observed, each line being split into sextets assigned to hyperfine coupling to ^{127}I . Again, identification is unambiguous. In this case $|A_{\parallel}| > |A_{\perp}|$, so it seems that this species is not rotating at 77 K.

Matrix Effects.—The reason why Me_3NHX units are readily incorporated into the Me_3NSO_3 lattice can be appreciated by considering the unit cells for these species (Figure 6). The significant feature is the close similarity of the c -axis dimensions for these unit cells;^{7,8} the way in which Me_3NHCl can fit into a unit cell of Me_3NSO_3 ⁷ is indicated in Figure 6. Both molecular units are dipolar, the ionic charges for Me_3NH^+ and Cl^- being greatly reduced by strong hydrogen bonding so that each ion pair can be incorporated as a unit.

There are clear differences between the data for $\text{HCl}^{\bullet-}$ in Me_3NSO_3 and in argon (Table). These may be caused in part by the perturbing effect of K^+ in the latter and by hydrogen bonding in the former (see below).

Consideration of the unit cell and trapping site for Me_3NHCl gives no clear indication why there should be facile rotation about a single axis (x in Figure 7) with no rotation about the other (y axis). However, the $-\text{H}-\text{Cl}$ unit of the parent ion pair is clearly locked by the strong linear hydrogen bond. Effective hydrogen atom addition should occur in the plane (yz) perpendicular to this bond (x axis), provided the hydrogen in

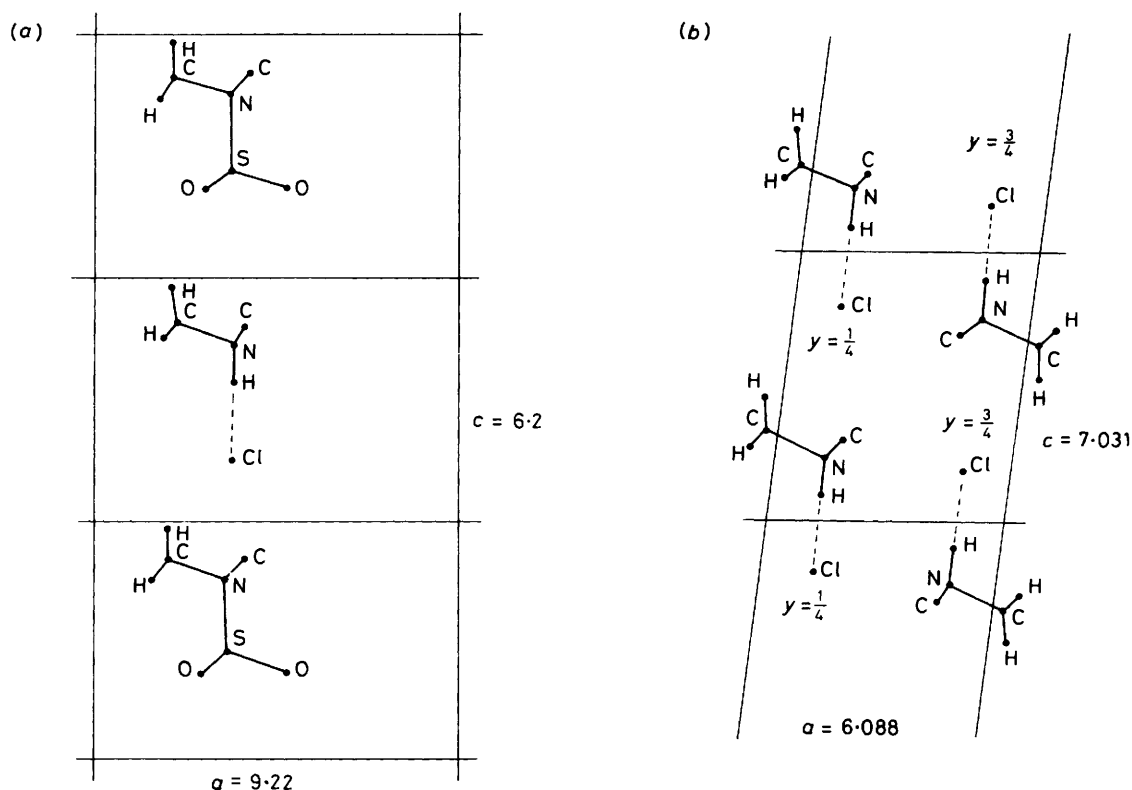


Figure 6. (a) The unit cell of Me_3NSO_3 viewed along the b axis with one molecule replaced by Me_3NHCl . The N-S and N-H...Cl atoms are in the plane of the paper. The SO_3 and Me_3N units have three-fold symmetry about the N-S and H...Cl axes. (b) A similar view of Me_3NHCl . The chain of Me_3NHCl molecules on the left is at $y = \frac{1}{4}$ and that on the right is at $y = \frac{3}{4}$. The repeating chain of atoms N-H...Cl is linear. Values are in Å

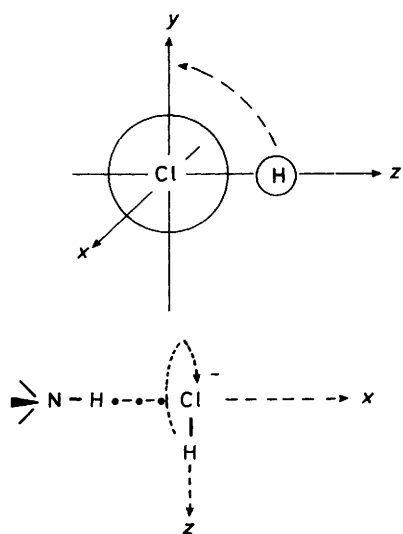


Figure 7. Suggested structure for trapped $\text{HCl}^{\cdot-}$, designed to explain the specific rotation detected at 77 K. The postulated motion is indicated by the arrows

the original hydrogen bond is not itself the source of the HCl unit. This gives the system depicted in the lower part of Figure 7. Clearly it must be the added hydrogen that moves rather than the bulky halide ion, and this motion is automatically restricted to the yz plane. This motion is frozen out at ca. 4 K for $\text{HCl}^{\cdot-}$, and is sterically inhibited even at 77 K for the bulky iodide derivative.

Aspects of Structure.—Approximate values for the atomic orbital populations of s.o.m.o.s for these species have been calculated for the isotropic and anisotropic parts of the hyperfine tensor components in the usual way,^{9,10} but using the corrected values for A^0 (calc. A_{iso} for 100% s character) given by Morton and Preston.¹¹ The results are included in the Table.

It is noteworthy that the estimated total spin densities exceed 100% by up to ca. 7.1%. These results are within the experimental errors involved in the calculations, but it may be significant that in all cases the error leads to an overestimate. This is a common result for small radicals and can have a variety of causes. In the present systems there is probably no single dominant factor. The effect of matrix 'compression' increasing the measured hyperfine coupling for trapped hydrogen atoms has been discussed by Weil.¹²

HF⁻ Radical.—The e.s.r. parameters for this centre show that it is essentially a normal trapped hydrogen atom, there being no need to invoke specific bonding to F^- . Furthermore the isotropic nature of the ^{19}F hyperfine coupling is not in accord with σ bonding, which must involve $2p$ rather than $2s$ orbitals on fluorine. Nevertheless it is notable that 'normal' trapped hydrogen atoms were not detected in this system, so that F^- ions must play a significant stabilising role.

For the other $\text{HX}^{\cdot-}$ radicals, a molecular description is required. The simple model adopted in Figure 8, in which the s.o.m.o. is an antibonding combination of the hydrogen $1s$ and halogen np_z orbitals, seems to be adequate. For the three species $\text{HX}^{\cdot-}$ ($X = \text{Cl}, \text{Br}, \text{or I}$), the extent of delocalization onto the halogen atom does not follow the ionization potentials of the halide ions, which fall steadily on going from Cl^- to I^- . This surprising result is, we suggest, the result of two opposing

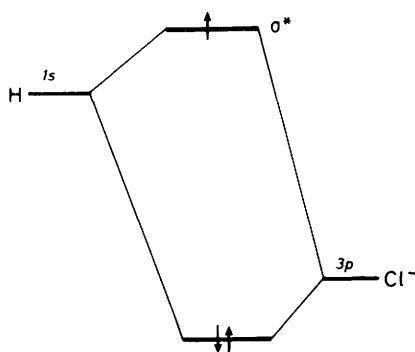


Figure 8. Qualitative energy-level diagram for HCl^-

factors. One is the increase in spin density expected to occur with decreasing ionization potential, and the other is the decrease in delocalization as the size of the p (σ) orbital on the halogen increases because of unfavourable overlap. This results in a fortuitous maximum delocalization for $\text{HBr}^{\cdot-}$.

Aspects of Mechanism.—Although the mechanism of radiation damage to the matrix appears to be well defined (see above), the formation of $\text{HX}^{\cdot-}$ radicals is more ambiguous. The obvious route, *via* electron capture, equation (3), would be



acceptable were it not for the apparent retention of the hydrogen bond indicated in Figure 7. We see no alternative to this model if we are to understand the selective and precise rotation detected at 77 K. On the other hand, two protons are

then essential: $\text{HCl}^{\cdot-}$ is unlikely to remain hydrogen-bonded to Me_3N and even if it were, the unit would presumably remain 'linear'. Indeed, the hydrogen bond would serve to lock the hydrogen in one site, thereby inhibiting any rotatory motion. We conclude that if the model indicated in Figure 7 is correct, then these units must be formed either by hydrogen atom generation followed by specific trapping at one of the $\text{Me}_3\text{N}^+\text{H}\cdots\text{Cl}$ units, or that electron capture [equation (3)] does occur, but that it is followed by protonation to give the required structure (Figure 7).

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