

The Heterobihalide Ions. Nuclear Magnetic Resonance Spectroscopy of Strong Hydrogen Bonds

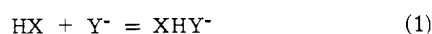
Fred Y. Fujiwara and John S. Martin*

Contribution from the Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received February 14, 1974

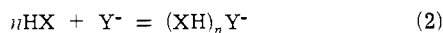
Abstract: The hydrogen and fluorine nmr spectra of the fluorine bihalide ions FHX^- ($X = \text{F, Cl, Br, and I}$) complete our study of the ten bihalide ions in aprotic solvents. The H-F coupling constant has been resolved in all four fluorine bihalides. Exchange of fluorine is slow; exchange of the other halogens is fast on the nmr time scale. The formation and interconversion equilibria may be adequately interpreted by assuming quantitative hydrogen transfer to the most basic (the smallest) halide ion in the system. Consistent with this, we find that the predominant complex in a solution of HCl and excess Br⁻ is ClHBr⁻ not BrHBr⁻ as previously reported (Fujiwara and Martin, *J. Chem. Phys.*, **56**, 4091 (1972)); the proton shieldings in these ions are coincidentally the same. A heterobihalide ion XHY^- behaves as an anion-molecule H-bonded complex $\text{XH} \cdots \text{Y}^-$, where Z_X is less than Z_Y . A simple electrostatic interpretation of the charge shifts on H bonding appears adequate to account for the observed formation constants and hydrogen shieldings. It is possible to make predictions of the bond lengths and charge distributions in the heterobihalide ions.

The bihalide ions, XHY^- ($X, Y = \text{F, Cl, Br, and I}$), whose structure and spectra are the subject of current interest and controversy¹ are the simplest entities exhibiting hydrogen bonding (H bonding). Consequently, they are important as model systems for this biologically significant interaction, as well as being significant in the acid-base chemistry of nonaqueous solvent systems. They span the entire range of H-bond energies; the strongest one is that of the bifluoride ion.² It is also one of the few H-bonded systems which is at present accessible to accurate *a priori* calculation³ of its electronic structure.

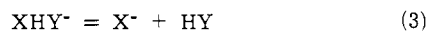
The nuclear shielding and couplings of the hydrogen are critical probes of the electronic rearrangements which accompany H bonding. In favorable cases, nuclear magnetic resonance (nmr) may also elucidate the energetics and dynamics of formation and interconversion reactions. We have recently presented a study⁴ of the formation and interconversion in aprotic solvents of the homobihalides ($X = Y$) and heterobihalides ($X \neq Y$) containing Cl, Br, and I. In these systems the reaction of interest was the formation of the bihalide *via* anion-molecule association.



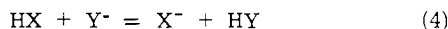
There was evidence, when the hydrogen halide was in excess, of multiple association.



If the ion X^- was larger (of greater atomic number) than Y^- , there was evidence that the alternative ion-molecule association was significant and that the heterobihalide might dissociate as follows.



Reactions 1 and 3 taken together result in simple transfer of hydrogen.



Studies of these reactions in the solid^{5,6} and gas phase⁷ indicate that hydrogen always transfers to the smaller halogen.

We also obtained a high resolution spectrum of the bifluoride ion in which the one-bond H-F coupling was sharply resolved.⁸ We have now found that this coupling can be observed in the heterobihalide ions containing fluorine and that it appears to be very sensitive to the strength of the H bond.

We present here the ¹H and ¹⁹F nmr spectroscopy of the

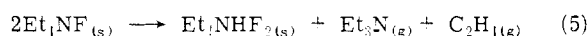
fluorine bihalides and thus complete our study of the high resolution nmr of all ten bihalide ions. We also reassess the interconversion equilibria of the heterobihalide systems studied previously⁴ and evaluate the information which nmr provides about the structure of the bihalide ions.

Procedures

Materials. Fisher reagent grade acetonitrile was stirred with calcium hydride for 2 days then decanted and fractionally distilled from phosphorus pentoxide. The distillate was refluxed over calcium hydride for 2 hr before a final fractional distillation. Eastman spectro grade nitromethane was distilled from CaSO₄ under reduced pressure. *N,N*-Dimethylformamide was stirred with P₂O₅ for 3 days, with KOH for 1 hr, and then fractionally distilled under reduced pressure at temperatures below 70°.

Tetraethylammonium halides were purified as previously described.⁴ They were analyzed for halide by potentiometric titration with AgNO₃. Bu₄NCl: chloride found 12.77%, calcd 12.76%. Bu₄NBr: bromide found 24.76%, calcd 24.79%. Bu₄NI: iodide found 34.42%, calcd 34.36%. We were unable to prepare tetraalkylammonium fluorides pure and dry enough for the study of the systems $\text{HX} + \text{F}^-$. Attempts to dry fluorides led us inadvertently to a synthesis of tetraethylammonium bifluoride.

Tetraethylammonium fluoride, Eastman, contained water which could not be removed by vacuum at room temperature. After 1 week's pumping the salt was analyzed gravimetrically⁹ for fluoride ion and by the Karl Fischer method for water. The analysis was consistent with a hydrate Et₄NF(H₂O)_{1.5}. Aqueous solution of the salt had a pH of about 8, indicating that it contained no acid. When slowly heated to 100° under vacuum the salt decomposed yielding an involatile material and gases which were collected in a liquid nitrogen trap. They were identified by nmr as ethylene, triethylamine, and water. These are products of dehydration accompanied by a known reaction¹⁰ analogous



to the Hoffman elimination of quaternary ammonium hydroxides.¹¹ The residue was precipitated twice from acetonitrile by adding diethyl ether and dried for several days under vacuum at 100°. Analysis was consistent with Et₄NHF₂: fluoride gravimetrically found 22.31%, calcd 22.45%; hydrogen ion titrated in aqueous solution found 0.5895%, calcd 0.5955%. The water content, by the Karl Fischer method, was less than 0.2% by weight. In a sealed

melting point capillary the salt decomposed with evolution of gas in the range 158.5 to 160.0°. The nmr spectrum was identical with that of tetrabutylammonium bifluoride prepared as described previously,⁸ in the anion region.

A partially deuterated form of tetraethylammonium bifluoride was prepared by dissolving Et₄NHF₂ in D₂O and evaporating off the excess water. The remaining salt was then prepared and purified as described above.

Hydrogen fluoride, Matheson, was stored in a polytrifluoroethylene tube attached to a monel and copper vacuum system. It was purified by three trap to trap distillations.

Sample Preparation. All materials were stored and handled either under dry nitrogen in a glove box or in the vacuum system. Solutions of bifluoride salts were prepared by weighing in the glove box. They were found to be stable indefinitely in glass sample tubes and caused no etching. They were degassed and sealed by the usual procedures.⁴

Solutions of heterobifluoride ions FHX⁻ were prepared in the nmr sample tube by condensing HF into a solution containing the tetrabutylammonium halide Bu₄NX. The sample tubes were made from polypropylene tubing, 0.125 in. o.d. and 0.016 in. wall, and attached to the vacuum line by a Cajon Ultra-Torr O-ring compression fitting. If a thin glass sleeve was fitted around the tube it could be sealed off by warming with a hot air gun. The polypropylene sample tube fits inside a 5-mm medium wall glass nmr sample tube and thus can be spun in the spectrometer.

The amount of hydrogen fluoride gas delivered was calibrated by measuring its pressure in a known volume with a Helicoid bourdon gauge, type 460K, monel, 0–1 atm. Since HF gas is quite nonideal, the actual amount was ultimately determined by condensing HF into water in a sample tube and then titrating with standard base. The amount of HF delivered was found thus to be reproducible to within 1%.

Nmr Spectra. Hydrogen and fluorine spectra were obtained using Varian HA-60 and HA-100 spectrometers. Tetramethylsilane (TMS) was used as internal lock and reference for ¹H spectra. Internal CF₄ was the reference for ¹⁹F spectra. A 50% v:v solution of trifluoroacetic acid in acetonitrile was used for the lock. It was put in a glass capillary for use with glass sample tubes; when polypropylene tubes were used, it was in the space between the inner and outer tubes.

Shieldings are reported as such, in parts per million (ppm). Note that shielding increases in the sense opposite to the conventional "δ" scales.

Observations

Line Shapes and Exchange Rates. Previous studies of hydrogen fluoride and its complexes have failed to resolve the H–F coupling.¹² Rapid exchange of nuclei leads to a single averaged line. When the inverse of the spin lifetime, τ^{-1} , is comparable to the coupling, J , the line shape may in principle be analyzed to determine τ .¹³ In our spectra the total signal was so weak, and the coupling so large, that this was not possible. All reported spectra are either in the slow exchange limit ($\tau^{-1} \ll J$, coupling resolved) or the fast exchange limit ($\tau^{-1} \gg J$, a single sharp line, coupling not measurable).

Purification of materials was usually carried out until coupling could be reproducibly measured at accessible temperatures. The success of this procedure confirms that intrinsic H–F exchange processes are quite slow and suggests that they are catalyzed by impurities, presumably hydrogen acids. Shieldings and couplings were reproducible but line shapes were not. We could not determine the rates of the various exchange reactions, but we can set limits on some of

them. In the descriptions of the spectra we shall report the minimum line widths we observed, which presumably represent the cleanest systems. Where it is relevant we shall give the values of exchange lifetimes corresponding to the limiting line widths.

Hydrogen Fluoride in Acetonitrile. Although the other hydrogen halides react with acetonitrile to form nitrilium or imino salts,¹⁴ there is evidence that hydrogen fluoride is molecular in this solvent.¹⁵ The nmr spectra are consistent with this: a doublet in both the ¹H and ¹⁹F spectra. The splitting is 479 ± 4 Hz at +34° and 476 ± 1 Hz at –40°; this is comparable to that in the liquid¹⁶ and gas.¹⁷

The line widths, measured as total width at half-height, were as small as 10 ± 5 Hz at –40° and 50 ± 10 Hz at +34°. This sets limits on exchange processes such as ionization or protonation reactions. The minimum exchange lifetimes are deduced¹³ as $(\pi\Delta\nu)^{-1}$ and are thus about 30 msec at –40° and 6 msec at +34°. These appear to be significantly longer than those observed in liquid HF¹⁶ and presumably represent the effect of dilution in lowering the concentration of HF polymers and reducing the frequency of encounters between HF molecules.

The Bifluoride Ion. In adequately pure solvents, this ion gives a doublet ¹⁹F spectrum and a triplet ¹H spectrum, intensity ratio 1:2:1, consistent with the symmetric structure FHF⁻. Well resolved spectra were obtained in three solvents. In the concentration range 0.05 to 0.5 *M*, there was little change with concentration. Table I gives the observed

Table I. Nuclear Shieldings and Coupling in Tetraethylammonium Bifluoride Extrapolated to Infinite Dilution

Solvent	<i>T</i> , °C	Hydrogen shielding, ppm vs. int TMS	Fluorine shielding, ppm vs. int CF ₄	Coupling, ¹ J _{HF} , Hz
Acetonitrile	+34	–16.29 ± 0.01	86.09 ± 0.03	120.5 ± 1.0
	–30	–16.37 ± 0.01	83.35 ± 0.03	120.5 ± 0.1
<i>N,N</i> -Dimethylformamide	+34	–16.63 ± 0.01	86.30 ± 0.05	120 ± 2
	–40	–16.77 ± 0.01	82.70 ± 0.05	118.8 ± 0.1
Nitromethane	+34	–15.87 ± 0.03	90.9 ± 0.1	
	–30	–16.27 ± 0.03	87.4 ± 0.1	120.5 ± 0.2

shieldings and HF coupling of the anion of tetraethylammonium bifluoride extrapolated to infinite dilution in three solvents at two temperatures. Solutions of tetra-*n*-butylammonium bifluoride gave anion spectra identical with those of tetraethylammonium bifluoride. Thus the nmr properties of the bifluoride ion appear to be substantially independent of solvent, cation, concentration, and temperature. The only significant variation appears to be in the fluorine shielding. This is consistent with the exposed location of the fluorines compared to the hydrogen and with the known sensitivity of fluorine shielding to solvent interactions.¹⁸

The ¹⁹F shielding of bifluoride ion in aqueous solution, inferred from the concentration dependence of the averaged shieldings in fluoride solutions, is equivalent to 89 ppm vs. internal CF₄;¹⁹ this is close to the values we find in aprotic solvents.

The bifluoride line widths in acetonitrile were as small as 1 or 2 Hz at –30° and 5 to 10 Hz at +34°. These correspond to minimum exchange lifetimes of about 200 msec at –30° and 40 msec at +34°. Such slow exchange reflects a very large formation constant for FHF⁻ from HF and F⁻ and sets upper limits on the rates of dissociation of bifluoride. Slightly broader lines were observed in *N,N*-dimethylformamide and nitromethane. There is no reason to believe that the difference does not reflect differences in purity of the solvents. In a chlorinated solvent such as carbon tetrachloride or *s*-tetrachloroethane only a single broad anion signal was observed, whose position changed with time. Pre-

sumably bifluoride ion reacts with such solvents to produce chloride ion, which then promotes halide ion exchange with bifluoride. Further evidence for such processes will be presented in the section on the heterobihalide ions.

Deuterium Bifluoride. Figure 1 is the ^{19}F nmr spectrum of a roughly equimolar solution of Et_4NHF_2 and Et_4NDF_2 in acetonitrile at -10° . The isotope effect on the fluorine shielding is 0.40 ± 0.02 ppm, the fluorine in the deuterium ion being the more shielded. The isotope effect is independent of concentration and temperature in the range studied, to the limit of experimental precision. The fluorine shielding isotope effect is much larger in hydrogen fluoride: it is 1.6 ppm in the liquid¹⁶ and 2.5 ppm in the gas.²⁰

The measured DF splitting of 18.1 ± 0.3 Hz is somewhat reduced by spin exchange. If the spin lifetime is estimated from the line width, the D-F coupling is computed²¹ to be 18.5 ± 0.3 Hz. Since $18.5(\gamma_{\text{H}}/\gamma_{\text{D}}) = 120.5$ Hz, there appears to be no measurable isotope effect on the coupling.

Heterobihalide Ions. FHCl^- , $\text{FHB}r^-$, and FHI^- . These ions were prepared in solution by condensing HF into a solution of the appropriate tetrabutylammonium halide. If solutions containing a constant amount of HF are compared, it appears that addition of even a small amount of a different halide ion causes collapse of the spin-spin splitting and a downfield shift of the hydrogen signal. In the presence of excess halide ion the splitting reappears; in the chloride and bromide systems the ^1H and ^{19}F shieldings become invariant in the presence of excess halide. This is consistent with formation of the bihalide ion, with a large association constant. The association constant of FHI^- is relatively small. After the coupling doublet reappears, the coupling and both shieldings continue to change as the concentration of iodide ion continues to increase. They do not become constant within the limit of salt solubility. Their limiting values, and the association constant, were determined by the Benesi-Hildebrand-Scott method.²² This method was also used to produce estimates of the association constants for FHCl^- and $\text{FHB}r^-$. The accuracy of such determinations was reduced by the collapse of the spin coupling multiplet in the critical equimolar region. The association constant of FHI^- was verified to be independent of the HF concentration.

Although the line shapes in the equimolar region, which are determined by spin exchange, were not reproducible, the spin coupling doublet lines became sharp enough at high halide concentrations to allow accurate determination of the coupling constant. A typical spectrum is that of FHCl^- in acetonitrile, shown in Figure 2. The minimum line widths obtained, and the corresponding spin lifetimes, were: FHCl^- 3 to 4 Hz at -40° (ca. 100 msec) and 30 ± 10 Hz at $+34^\circ$ (ca. 10 msec); $\text{FHB}r^-$ 5 ± 2 Hz at -40° (ca. 60 msec) and greater than 20 Hz at $+34^\circ$ (less than 15 msec); FHI^- 60 ± 20 Hz at -40° (ca. 8 msec), spectrum not observable at higher temperatures.

The shieldings and couplings of the fluorine heterobihalide ions are summarized in Table II (the formation con-

Table II. Nuclear Shieldings and Couplings of Hydrogen Fluoride and Related Tetrabutylammonium Heterobihalides in Acetonitrile

	$T, ^\circ\text{C}$	Hydrogen shielding, ppm vs. int TMS	Fluorine shielding, ppm vs. int CF_4	Coupling, J_{HF} , Hz
HF	+34	-7.20 ± 0.05	121.4 ± 0.1	479 ± 4
	-40	-7.64 ± 0.02	118.7 ± 0.1	476 ± 1
FHCl^-	+34	-10.34 ± 0.06	84.6 ± 0.4	404 ± 2
	-40	-10.43 ± 0.03	83.3 ± 0.3	403.4 ± 0.2
$\text{FHB}r^-$	+34	-8.76 ± 0.05	84.4 ± 0.5	428 ± 2
	-40	-8.88 ± 0.03	83.2 ± 0.3	427.1 ± 0.2
FHI^-	-40	-7.4 ± 0.2	82 ± 4	437 ± 5

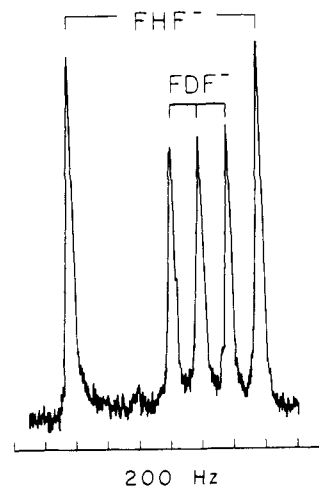


Figure 1. The fluorine nmr spectra of FHF^- and FDF^- in acetonitrile at -10° .

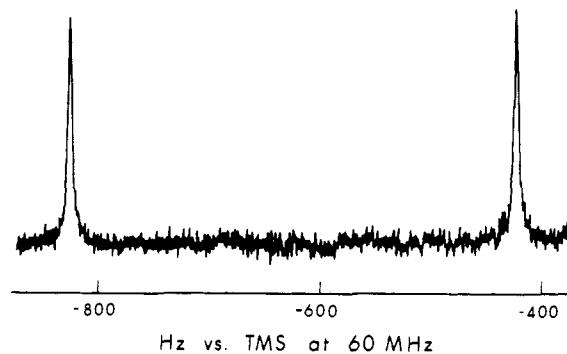


Figure 2. The ^1H nmr spectrum of FHCl^- in acetonitrile at -40° .

stants can be found in Table V). The dependence of the shieldings and coupling in FHCl^- and $\text{FHB}r^-$ on the bihalide ion concentration was investigated by examining solutions containing a large amount of halide salt (ca. 0.7 M) and varying the hydrogen fluoride concentration from 0.05 to 0.22 M. Using our deduced formation constants, it can be shown that bihalide formation is quantitative to within 1% in these solutions. The spectra were invariant to concentration, except that the fluorine shielding in both ions increased by 0.5 ppm on dilution from 0.22 to 0.05 M. The values in Table II may thus be regarded as characteristic of the isolated ions.

A Reexamination of ClHBr^-

In our initial publication⁴ we observed that the population averaged ^1H shielding in solutions of hydrogen chloride and tetrabutylammonium bromide approached that of bromide ion when the salt was in excess. We took this to be evidence that the heterobihalide ion ClHBr^- is relatively unstable, so that BrHBr^- is formed in the presence of large amounts of bromide ion.

We have now obtained infrared spectra of our solutions which allow us to distinguish among the possible ions ClHCl^- , ClHBr^- , and BrHBr^- . We find that HCl plus excess bromide gives a solution in which the predominant complex ion is in fact the heterobihalide ion ClHBr^- , whose hydrogen shielding must therefore be identical with that of BrHBr^- .

Infrared spectra of the solutions were observed in the region from 4000 to 500 cm^{-1} using a Perkin-Elmer Model 337 spectrometer, with 0.1 to 0.5 mm path lengths. Samples using NaCl and KBr windows gave identical spectra, so halide exchange with the windows does not influence the observations. Solutions in both dichloromethane and acetonitrile were studied, to circumvent the solvent absorptions.

Figure 3 shows the infrared spectra of three critical systems in dichloromethane. Portions of the corresponding spectra in acetonitrile are shown by dashed lines. Figure 3a is the spectrum of equimolar $\text{HCl} + \text{Br}^-$. The peak near 1100 cm^{-1} is that assigned to the bend, ν_2 , by Evans and Lo.²³ The broad absorption above 1600 cm^{-1} is the stretch, ν_3 . These absorptions, characteristic of the heterobihalide, are indicated by arrows. They become more prominent as the bromide ion is added to excess, as in Figure 3b. In no case were any features of the dibromide spectrum visible, such as the strong absorption in the region 700 to 1050 cm^{-1} , which is readily observable in Figure 3c, the spectrum of the system $\text{HBr} + \text{Br}^-$.²⁴

Similarly, the infrared spectra of solutions containing $\text{HCl} + \text{I}^-$ showed features characteristic of ClHI^- ⁵ but not of IHI^- .²⁵ No distinguishable anion peaks were visible in infrared spectra of solutions containing HBr and I^- . No spectra of the ion BrHI^- have been reported yet.

Table III gives the deduced association constant of

Table III. Formation Constants, Complex Shifts, and Shieldings of Heterobihalide Ions in *sym*-Tetrachloroethane at $+34^\circ$ ^a

System	Formation constant, K , l. mol ⁻¹	Complex shift, ppm	Bihalide shielding, ppm vs. int TMS
$\text{HCl} + \text{Br}^-$	107 ± 28	-9.25 ± 0.06	-10.15
$\text{HCl} + \text{I}^-$	21 ± 3	-6.23 ± 0.06	-7.13
$\text{HBr} + \text{I}^-$	27 ± 4	-7.80 ± 0.06	-5.07

^a All salts were tetra-*n*-butylammonium halides.

ClHBr^- in *s*-tetrachloroethane, its complex shift (difference in shielding between ClHBr^- and HCl), and its hydrogen shielding. They are deduced from the bromide concentration dependence of the observed shielding on the assumption that the only equilibrium of significance is the ion-molecule association $\text{HCl} + \text{Br}^- = \text{ClHBr}^-$. The table also gives more refined data for the systems involving iodide ion, which supersede those published previously.⁴

Analysis of the $\text{HCl} + \text{Br}^-$ system in terms of a single heterobihalide equilibrium implies that the hydrogen is always associated with chlorine. Therefore in the complementary system $\text{HBr} + \text{Cl}^-$ hydrogen transfer from Br to Cl should occur, as described in eq 1, 3, and 4. To test this we used our measured values of shieldings and equilibrium constants to predict the population averaged proton shieldings in the system $\text{HBr} + \text{Cl}^-$, as chloride ion is added to a constant concentration of HBr .

Figure 4a presents the results of this calculation as the solid line; it is within experimental error of the observed points everywhere except in the region where the HBr concentration exceeded that of Cl^- . It was previously shown⁴ that in this region there is multiple association of the form $\text{Cl}(\text{HBr})_n^-$, which would produce deviations in the direction of those observed. Figure 4b shows the concentrations of the various species at equilibrium predicted by our model. The cusps arise because hydrogen transfer is assumed to be quantitative.

Similar agreement was obtained for the systems $\text{HI} + \text{Cl}^-$ and $\text{HI} + \text{Br}^-$. Note that in all cases the calculations were performed using shieldings and equilibrium constants previously evaluated; no parameters were adjusted.

Summary of Bihalide Spectra

In Table IV we present a summary of the observed shieldings and couplings in all ten bihalide ions. The absolute shieldings appropriate to spherical samples ("abs sph" in Table IV) are computed for ^1H using Raynes' recent

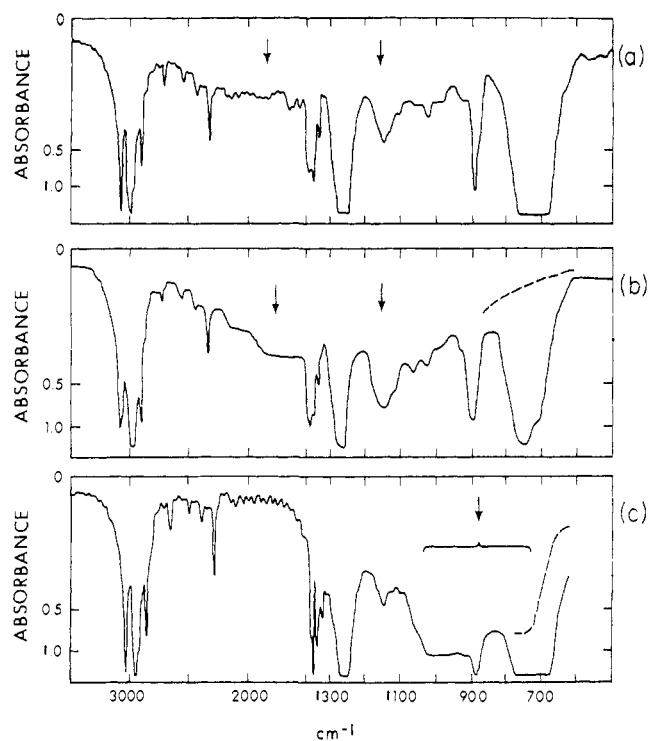


Figure 3. Infrared spectra of solutions in dichloromethane. Dashed lines give absorbances of corresponding solutions in acetonitrile. The arrows indicate characteristic bihalide ion absorptions: (a) hydrogen chloride and equimolar bromide ions (the ClHBr^- absorptions near 1100 cm^{-1} and 1600 cm^{-1} are marked); (b) hydrogen chloride and excess bromide ion (ClHBr^- lines marked); (c) hydrogen bromide and equimolar bromide ion (the BrHBr^- absorption in the range 700 to 1050 cm^{-1} is marked).

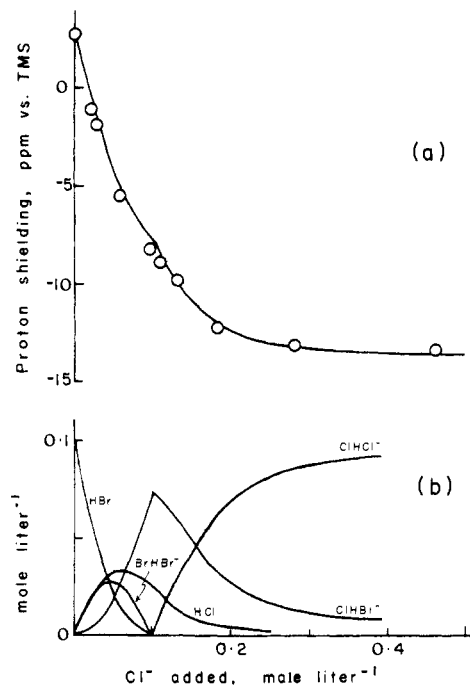


Figure 4. (a) Comparison of the observed shieldings of hydrogen in solutions containing 0.1 M HBr and added Bu_4NCl with the calculated values (solid line). (b) Concentration of hydrogenated species calculated using measured equilibrium constants, to give the predicted shieldings above.

redetermination of the absolute shielding of methane gas,²⁶ $30.52 \pm 0.17 \text{ ppm}$. From this and the relative shieldings of methane and TMS in the gas phase²⁷ we estimate the absolute shielding of TMS to be $30.65 \pm 0.2 \text{ ppm}$. The relative solvent effects on ^1H shieldings in the bihalide ions have

Table IV. Summary of Observed Shieldings and Couplings in the Bihalide Ions, etc.

Species	Hydrogen shielding, ppm			Fluorine shielding, ppm			Coupling, $^1J_{\text{HF}}$, Hz
	vs. int TMS	Abs sph	Shift	vs. int CF ₄	Abs sph	Shift	
HF (g)		28.42 ^a			410 ^a		529 ± 23 ^b
FHF ⁻	-16.30	14.35	-14.07	86	345	-65	120.5
FHCl ⁻	-10.34	20.31	-8.11	84	343	-67	403
FHBr ⁻	-8.76	21.89	-6.53	84	343	-67	427
FHI ⁻	-7.2	23.4	-5.0	82	341	-69	437
HCl (g)		31.13 ^c					
ClHCl ⁻	-13.92	16.73	-14.40				
ClHBr ⁻	-10.15	20.50	-10.63				
ClHI ⁻	-7.14	23.51	-7.62				
HBr (g)		35.08 ^d					
BrHBr ⁻	-10.15	20.50	-14.58				
BrHI ⁻	-5.06	25.59	-9.49				
HI (g)		43.77 ^e					
IHI ⁻	-0.90	29.75	-14.02				

^a Reference 28. ^b Reference 17. ^c W. T. Raynes and B. P. Chadburn, *Mol. Phys.* **24**, 853 (1972). ^d W. T. Raynes and B. P. Chadburn, *J. Magn. Resonance*, **10**, 218 (1973). ^e W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

been shown to be small. There is reason to believe that the absolute solvent effects are also small, since the hydrogen is isolated from solvent interactions and near a center of symmetry. If this is so, the "abs sph" ¹H shieldings may be regarded as representative of the free ions, and it is legitimate to compare them to the shieldings in the gas phase hydrogen halides. We believe that the entries may be regarded as reliable to 0.5 ppm, and that their relative values are probably reliable to 0.1 ppm.

The fluorine "abs sph" shieldings have been deduced using absolute shieldings of the gas phase reference compounds determined by Hindermann and Cornwell.²⁸ The absolute values are estimated to be reliable to about 6 ppm; relative shieldings among similar species are somewhat more accurately known.

Discussion

Thermodynamics of Bihalide Formation in Solution. We have now estimated formation constants of all ten bihalide ions, although we have not been able to obtain them all at the same temperature in the same solvent. Heterobihalide formation constants have been obtained subject to the assumption that there is no hydrogen transfer from the smaller to the larger halogen; this is supported by our success in reproducing the observed concentration dependence of the shieldings and by the infrared spectra described above.

Table V is a summary of all the bihalide formation con-

Table V. Bihalide Formation Constants and Computed Electrostatic Energies^a

System	Formation constant, K, l. mol ⁻¹	Computed energy, kJ mol ⁻¹
HF + F ⁻	Very large	-219
HF + Cl ⁻	250 ± 100 ^b	-123
HF + Br ⁻	100 ± 50 ^b	-105
HF + I ⁻	2.8 ± 0.5 ^b	-84
HCl + Cl ⁻	ca. 600 ^c	-104
HCl + Br ⁻	107 ± 28	-94
HCl + I ⁻	21 ± 3	-73
HBr + Br ⁻	ca. 200 ^c	-93
HBr + I ⁻	27 ± 4	-68
HI + I ⁻	7.3 ± 0.4 ^c	-69

^a The formation constants are in *s*-tetrachloroethane at +34° unless otherwise stated. ^b In acetonitrile at -40°. ^c Reference 4.

stants measured so far. Some values have been refined since our first publication; the changes are not significant.⁴ Note that the fluorine bihalides were not studied in the same solvents or at the same temperature as the others. Nevertheless, it is evident that for a given hydrogen halide the formation constants increase as the complexed halide ion becomes

smaller. This order agrees with the ordering of enthalpies of the reactions measured in solid²⁵ and liquid²⁹ phases.

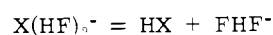
Correlations of enthalpy changes with formation constants are always subject to the uncertainty arising from the fact that the ion-molecule reaction in solution is really a process of competitive solvation, in which displacement effects and entropy contributions may occur which cannot be evaluated. In addition, no self-consistent set of enthalpy measurements has been made for the bihalide ions in a single phase.

We have estimated bihalide ion-molecule interaction energies as the sum of the energies of the permanent and induced dipoles of the hydrogen halide in the field of the halide ion at the equilibrium distance, as described before.³⁰ In the absence of measured bond distances, the interhalogen distance in the bihalide XHY⁻ was taken to be the sum of the HX bond length and the Y⁻ ionic radius, where Z_X < Z_Y.

The calculated ion-molecule interaction energies, shown in the last column of Table V, are significantly larger than those measured in condensed phases, as one would expect.² The electrostatic energies reproduce the ordering of measured formation enthalpies^{25,29} and correlate about as well as one would expect with the ordering of formation constants.

Kinetics of Bihalide Exchange Reactions. The information we have deduced concerning exchange lifetimes may be summarized as follows. In aprotic solvents, exchange of hydrogen among species involving Cl, Br, and I is rapid on the nmr time scale: the various entities have lifetimes of no more than a few microseconds, since the observed signals are sharp. On the other hand, processes which destroy H-F spin correlation are slow; lifetimes of fluorinated species are of the order of many milliseconds at least and appear to be determined by exchange catalyzed by impurities. One systematic exception to these generalizations is that in solutions containing HF and relatively small concentrations of other halide ions rapid H-F exchange is observed.

A reasonable interpretation of these phenomena is that exchange takes place *via* the dissociation of halide ions Cl⁻, Br⁻, and I⁻ which are thermodynamically stable in aprotic solvents, but that such solvents are incapable of solvating such a small ion as F⁻. Consequently no pathway for H-F spin exchange normally exists, and this process is inherently slow. However, if HF is present in excess over a reasonable amount of a halide ion X⁻, the following process may occur.



Multiple complexes of this type have been observed.^{4,25}

They provide a pathway for H-F spin exchange which does not involve free fluoride ion in aprotic solvents.

Hydrogen Shielding. It is clear from Table IV that formation of a bihalide ion from a given hydrogen halide produces increasingly negative change in the hydrogen shielding as the complexing ion becomes smaller, in accord with the order of H-bond strength. In the absence of reliable H-bond energies, the shieldings must be related to other relevant observables. We have chosen the base strength of the ions, since basicity of the H-bond acceptor appears to be most important in determining the bond energy.³¹

Figure 5 shows the relationship between the hydrogen shielding shifts on formation of a hydrogen bonded complex to a halide and the halide basicities measured as proton affinities.³² The relationship is linear and in the sense expected for the hydrogen halides and for hydrogen donors involving OH³³ and CH²² bonds.

Other important points are evident. Strong departures from linear correlation, indicated by the dashed lines, occur only where the bihalide complex would be of the form HY + X⁻, where X is a smaller halogen than Y, for example, HCl + F⁻. The shielding changes thus support a view of a heterobihalide ion as an anion-molecule complex to the weaker anionic base.

The susceptibility of hydrogen donors to perturbation is in the order CH < OH < FH < ClH < BrH < IH; this is the order of bond polarizabilities. One could attempt to make this quantitative by using the Buckingham linear polarization model.³⁴ The shielding change induced by electrostatic field E is

$$\Delta\sigma_E = -AE_z - BE^2 \quad (6)$$

If B is assumed to have the hydrogen atom value³⁵ 7.4×10^{-19} esu⁻², and the field in a linear complex is er^{-2} , then A may be evaluated from the derivative of a linear regression²² of $\Delta\sigma + BE^2$ with r^{-2} .

For reasonable assumed geometry, complexes of HF with Cl⁻, Br⁻, and I⁻ define a reasonable straight line and give $A = 4.5 \times 10^{-12}$ esu⁻¹. This is comparable to the value for OH³³ and somewhat greater than that for CH.^{34,22} The FHF⁻ point deviates from the HF regression line. Complexes of HCl, HBr, and HI do not define reasonable regression lines through the origin. The apparent A values are in the range 7 to 17×10^{-12} esu⁻¹; these are all much smaller than the value deduced for HCl from studies of weak interactions in the gas phase.³⁶ The discrepancy is in the direction to be expected if polarization of these molecules is saturated in the high fields in the bihalide complexes. Charge shifts estimated using bond polarizabilities³⁷ are immense and make it obvious that a linear polarization model cannot account for the shielding changes in the bihalides. It is necessary to resort to a calculation in which the charge distribution is not implicitly evaluated but is treated as a variable.

In an earlier publication³⁰ we demonstrated that the hydrogen shielding in a homobihalide ion is simply related to the electronic charge distribution. A straightforward application of eq 16b and 18 of that paper yields the following equation governing the shielding in a heterobihalide ion XHY⁻

$$\rho_H = 21.4\rho_H + K_X(R_{HX})(2 - \rho_X) + K_Y(R_{HY})(2 - \rho_Y) \quad (7)$$

ρ_H is the hydrogen 1s charge density. ρ_X and ρ_Y are the charge densities in the appropriate valence shell halogen orbitals of σ symmetry. A constraint is that $\rho_H + \rho_X + \rho_Y = 4$. $K(R_{HX})$ and $K(R_{HY})$ are functions of hydrogen-halo-

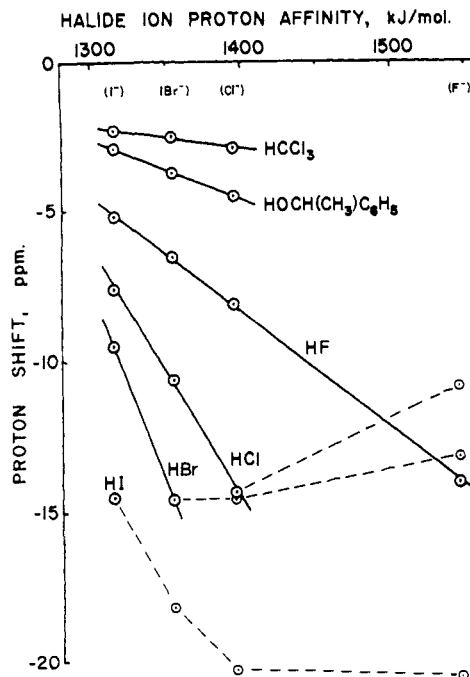


Figure 5. Hydrogen shielding shift as a function of halide ion proton affinity, for anion complexes in solution.

gen distances, each characteristic of a halogen. A reasonable form is $K_X(R_{HX}) = k_X R_{HX}^{-3}$, etc., where k_X is characteristic of the halogen X.

In the absence of experimental heterobihalide bond distances, eq 7 contains four adjustable parameters: the distances R_{HX} and R_{HY} , and two electron density values from the set ρ_H , ρ_X , and ρ_Y . The halogen constants k_X and k_Y may be deduced from the hydrogen halide shieldings.³⁰ Until some of the undetermined quantities have been measured it will not be possible to obtain a realistic test of the ability of eq 7 to fit the heterobihalide shieldings. We can report that such a fit is possible. If the bond distances are estimated by the method used in the energy calculation, the observed shieldings may be reproduced using hydrogen charge densities similar to those found in the homobihalide ions³⁰ and halogen charge densities appropriate to anion-molecule complexes of the form XH...Y⁻, in which the greater part of the excess negative charge is on the larger halogen Y. Thus, while we cannot prove the validity of the shielding function, it can be shown to be consistent with our other conclusions about the structure of the bihalide ions.

It may be possible to measure the hydrogen-halogen distances in heterobihalide ions by diffraction or by liquid crystal nmr; nuclear quadrupole resonance could provide estimates of the halogen charge densities. As these measurements become available, the number of adjustable constants in eq 7 will be reduced and a meaningful test will be possible. Alternatively, eq 7 would allow a measurement of an ion's geometry to be used to estimate the charge distribution, or vice versa.

Coupling Constants and Fluorine Shieldings. The one bond H-F couplings in Table IV show a considerable decrease as the H-bond strength increases. The fluorine shielding is smaller in the H-bonded entities relative to gas phase hydrogen fluoride, but no clear trend is apparent. Similar effects on the coupling and the fluorine shielding were found when hydrogen fluoride was dissolved in aprotic basic solvents. They are presented in the report immediately following.³⁸ A discussion of the H-F coupling and the fluorine shielding will be found there, in the context of hydrogen bonding to HF.

Conclusions

It is appropriate to summarize here our findings which are relevant to the structure and dynamics of the bihalide ions. There are uniform trends in the formation constants, exchange rates, and hydrogen shielding shifts which can be accounted for in terms of simple H-bonding effects. These trends all appear to be governed by the gross distribution of electronic charge, which is perturbed in accord with a simple electrostatic mechanism: the stronger the base, the stronger the H bond, and the greater the polarization of electronic charge away from the hydrogen. In anticipation of the conclusions of the following paper³⁸ we wish to point out that a similar mechanism accounts for the changes in the H-F coupling.

We conclude with a summary.

1. Experimental evidence of several kinds suggests that the equilibria of hydrogen halides and halide ions in aprotic solvents may be accounted for in terms of two types of reaction: (a) quantitative hydrogen transfer to the smaller, more basic halogen; and (b) ion-molecule association of the resulting species to form bihalides.

2. Consistent with this, supported by infrared evidence, we reassign the complex observed⁴ when excess bromide ion is added to a solution of HCl; it is ClHBr⁻ rather than BrHBr⁻. These two ions happen to have identical hydrogen shieldings.

3. On the nmr time scale, exchange processes involving H-F bonds are slow and those involving H-Cl, H-Br, and H-I bonds are fast. The implication of this is that fluoride ion is not stable in aprotic solvents.

4. A heterobihalide ion XHY⁻ may reasonably be regarded as an anion-molecule complex of the form X-H ··· Y⁻, where the halogen X has the smaller atomic number. We predict that the bond lengths will show that the hydrogen is more strongly bound to X, and the greater part of the excess negative charge will be on Y.

5. The decrease of hydrogen shielding when a hydrogen halide is complexed by a halide ion is greater the smaller the halide ion and the more polarizable the molecule.

6. The hydrogen shieldings in the bihalide ions may be accounted for in terms of a local diamagnetic term and a halogen paramagnetic term.³⁰ The shielding can be related to bond lengths and atomic charge densities and thus may be used to estimate one set of these quantities when some of the others become available from experiment.

Acknowledgment. We wish to thank Dr. R. M. Lynden-Bell for valuable advice. Dr. Fujiwara thanks the National Research Council of Canada for a scholarship. This research was supported in part by N.R.C. Grant No. A-2051.

References and Notes

- (1) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **53**, 2034 (1970); **55**, 2550 (1971); G. C. Pimentel and A. L. McClellan, *Ann. Rev. Phys. Chem.*, **22**, 347 (1971).
- (2) H. P. Dixon, H. D. B. Jenkins, and T. C. Waddington, *J. Chem. Phys.*, **57**, 4388 (1972).
- (3) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970).
- (4) F. Y. Fujiwara and J. S. Martin, *J. Chem. Phys.*, **56**, 4091 (1972).
- (5) J. A. Salthouse and T. C. Waddington, *J. Chem. Soc. A*, 4664 (1964).
- (6) R. St. C. Smart and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **320**, 417 (1971).
- (7) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).
- (8) J. S. Martin and F. Y. Fujiwara, *Can. J. Chem.*, **49**, 3071 (1971).
- (9) N. H. Furman, "Standard Methods of Chemical Analysis," 6th ed, Van Nostrand, New York, N.Y., 1962, p 441.
- (10) W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).
- (11) R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1959, p 553.
- (12) J. Soriano, J. Shamir, A. Netzer, and Y. Marcus, *Inorg. Nucl. Chem. Lett.*, **5**, 209 (1969).
- (13) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N.Y., 1967, Chapter 12.
- (14) G. J. Janz and S. S. Danyluk, *J. Amer. Chem. Soc.*, **81**, 3850 (1959).
- (15) P. van Huong and M. Couzi, *J. Chim. Phys. Physiochim. Biol.*, **67**, 1994 (1970).
- (16) E. L. Mackor, C. MacLean, and C. W. Hilbers, *Recl. Trav. Chim. Pays-Bas*, **87**, 655 (1968).
- (17) J. S. Meunter and W. Klemperer, *J. Chem. Phys.*, **52**, 6033 (1970).
- (18) W. T. Raynes and M. A. Raza, *Mol. Phys.*, **20**, 555 (1971).
- (19) K. Schaumberg and C. Deverell, *J. Amer. Chem. Soc.*, **90**, 2495 (1968).
- (20) D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.*, **48**, 2017 (1968).
- (21) R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).
- (22) R. D. Green and J. S. Martin, *J. Amer. Chem. Soc.*, **90**, 3659 (1968).
- (23) J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **70**, 20 (1966).
- (24) J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **71**, 3942 (1967).
- (25) D. H. McDaniel and R. E. Vallee, *Inorg. Chem.*, **2**, 996 (1963).
- (26) W. T. Raynes, "Specialist Periodical Reports—NMR," Vol. 2, R. K. Harris, Ed., The Chemical Society, London, 1972.
- (27) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
- (28) D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.*, **48**, 4148 (1968).
- (29) R. L. Benoit, M. Rinfret, and R. Domain, *Inorg. Chem.*, **11**, 2603 (1972).
- (30) J. S. Martin and F. Y. Fujiwara, *J. Chem. Phys.*, **56**, 4098 (1972).
- (31) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).
- (32) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).
- (33) R. D. Green, J. S. Martin, W. B. McG. Cassie, and J. B. Hyne, *Can. J. Chem.*, **47**, 1639 (1969).
- (34) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
- (35) T. W. Marshall and J. A. Pople, *Mol. Phys.*, **1**, 199 (1958).
- (36) W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.*, **36**, 3481 (1962).
- (37) Landolt and Bornstein, "Zahlenwerten und Funktionen," Vol. I, Springer-Verlag, Berlin, 1951, Part 3.
- (38) J. S. Martin and F. Y. Fujiwara, *J. Amer. Chem. Soc.*, **96**, 7632 (1974).