the K_{3s} peak, and another near the K_{3p} peak. It would be very desirable to have further runs on other salts of the nitrate ion.

In summary, there is a moderate correlation between the calculated MO levels and XPS peaks for the nitrate ion. This was also found to be true in the case of the cyanide ion. In both anions the CNDO(1) method gives the best overall agreement with the experimental XPS energies. However, this could very well be fortuitous. In the case of the cyanide MO calculations, the CNDO calculations come the closest to the *ab initio* calculation, with the INDO calculation seemingly having trouble with the lowest binding energy levels. Both of the cyanide extended Hückel treatments give poor agreement with the *ab initio* calculation. The same qualitative trends are also evident in the nitrate ion MO calculations.

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Calorimetric Studies in the Halide–Hydrogen Chloride Systems

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The free energy and enthalpy of the reactions $X^-(solv) + HCl(solv) = HClX^-(solv)$ were determined at 30° from calorimetric measurements in sulfolane, a very weakly basic dipolar aprotic solvent. $X^-(solv)$ denotes solvated chloride, bromide, and iodide ions. From the heat of solution of gaseous hydrogen chloride, the following enthalpy changes are obtained for the reactions $X^-(solv) + HCl(g) = HClX^-(solv)$: 13.9, 10.7, and 8 kcal mol^{-1}, respectively, for Cl^-, Br^-, and I^-. These enthalpies which are minimum values for hydrogen bond energies for $HClX^-$ are compared with values previously predicted from reported measurements on some solid halide salts–hydrogen chloride systems.

Introduction

Hydrogen dihalide HX_2^- anions[1] are well characterized in salts whose lattice is stabilized by large cations such as tetraalkylammonium. The mixed HXY^- anions have received less attention. Attempts have been made to evaluate the corresponding hydrogen bond energies. In aqueous solutions, HF_2^- is well-known but there is no evidence for the other ions which are apparently too unstable. However, in some nonaqueous solvents, the equilibria

$$X^-(solv) + HY(solv) = HYX^-(solv) \qquad (1)$$

have been studied for HCl_2^- and HBr_2^-.[2,3] Dipolar aprotic solvents, in particular, favor the formation of hydrogen dihalide ions because the differences in solvation energies for small (X^-) and large (HYX^-) anions[4] are considerably smaller in these solvents than in protic solvents.

Among the dipolar aprotic solvents, sulfolane was selected for a study of reactions 1 (X = Cl, Br, I; Y = Cl) as it behaves as a very weak base[5] so that HCl does not appreciably dissociate, its dissociation constant is estimated to be $\sim 10^{-13}$. Results of a preliminary nmr study were recently published.[6] The present calorimetric investigation was carried out to provide thermodynamic data for the reactions involving the formation of HCl_2^-, $HClBr^-$, and $HClI^-$ ions. Such data are combined with the heat of solution of HCl in sulfolane to lead to values which are related to hydrogen bond energies and can be compared with previous estimates.

Experimental Section

Materials.—Sulfolane was purified according to a procedure described previously.[4] Tetraethylammonium chloride and bromide and tetrabutylammonium iodide were Eastman Kodak White Label products. Both compounds were recrystallized from ethanol and dried under vacuum at 40°. Solutions of the halide salts were prepared by weighing. Concentrated solutions of hydrogen chloride were obtained by saturation with Matheson anhydrous HCl gas after passage through a Dry Ice–acetone trap. The HCl concentration was determined by titration with standardized NaOH after flooding of the sample with water.

Apparatus and Procedure.—Heats of reaction were measured with an LKB-Produkter AB (Stockholm, Sweden) Model 8725-2 Isoperibol calorimeter. It consists of a 25-ml Pyrex reaction vessel equipped with a 1700 ohm thermistor, a 50 ohm heater, and a sample-holder stirrer. Sealed 1-ml glass ampoules filled with a 3 *M* HCl solution were attached to the holder. The reaction vessel containing the halide solution is enclosed in a chrome-plated submarine jacket, which, in turn, is kept in a thermoregulated bath maintained at 30.016 ± 0.001°. The calorimeter is calibrated electrically before and after each run by means of a Hewlett-Packard 740B standard calibrator. The current pulse into the heater is predetermined by a HP 5214L preset electronic timer followed by a flip-flop circuit driving a high-speed miniature Clare mercury wetted relay with a response time less than 1 msec.

The thermistor temperature sensor is connected in series with a Guildline 9801T temperature controlled four-terminal resistor (calibrated to 1 ppm) and a Keithley 225 constant-current source (set at 200 μA). The voltage drops at the thermistor and the four-terminal resistor are compared with a Guildline 9810L isolating potential comparator.[7] The difference signal between the thermistor and the resistance settings, in increments of 10 ohms (0.125°K), is recorded on a strip chart recorder, yielding a complete time–resistance curve.

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Heat calculations were made according to Dickinson's method. The extrapolations were carried out to the time corresponding to half the temperature rise in the case of electrical calibration measurements and to the time corresponding to 0.6 the temperature change in the case of heat of solution measurements. The performance of the calorimeter was checked by measuring the integral heat of solution of KCl in water and the heat of neutralization of tris(hydroxymethyl)aminomethane with aqueous 0.1 *M* HCl. In both cases, results fell within less than 0.3% from reported values.[8,9]

Solution vapor pressures were measured with a precision quartz gauge (Texas Instruments) whose quartz spiral was thermostated at 60°. The gauge was connected to a 70-ml cell by a thermally jacketed glass capillary. The cell, containing the magnetically agitated HCl solution, was kept in a water bath regulated to ±0.005°.

Results

The heat changes measured relate to the reaction between a known weight, corresponding to less than 1 ml, of 3.0 *M* HCl solution and a known weight, equivalent to approximately 26 ml, of halide solutions. The concentrations C_X' of the latter solutions were respectively 0.088 *M* for Cl^-, 0.096 *M* for Br^-, and 0.089 *M* for I^-. The calorimetric measurements were thus made at nearly constant ionic strength. The water concentration of the solutions, as determined by the Karl Fischer method, was 8×10^{-2} *M*. The solution volume V after reaction is calculated from the weight and density measurements. The concentration C_H of acid was determined after reaction by titration.

The calorimetric results are presented in Table I which includes solution data and corresponding heat changes Q.

TABLE I

CALORIMETRIC DATA FOR THE SYSTEMS HCl + X^-

Vol/ml	Mmol HCl	Mmol X^-	Q/cal
	(a) X = Cl		
25.54	0.460	2.253	3.70
26.09	0.722	2.340	5.61
25.98	0.860	2.331	6.69
26.04	1.333	2.271	10.26
26.22	1.596	2.277	11.80
25.88	1.922	2.244	13.82
26.47	2.482	2.266	15.90
26.75	3.133	2.337	17.55
26.60	3.211	2.318	17.34
	(b) X = Br		
26.28	0.497	2.507	2.30
26.23	0.754	2.501	3.51
26.54	0.944	2.521	4.24
26.64	1.421	2.514	6.45
26.75	1.658	2.514	7.41
27.08	2.398	2.517	9.57
28.00	2.479	2.515	9.86
27.32	3.253	2.517	10.91
	(c) X = I		
25.72	0.522	2.256	0.86
25.65	0.853	2.260	1.16
25.76	1.423	2.260	1.66
26.10	1.966	2.263	2.08
26.35	3.015	2.261	2.82
26.20	3.445	2.252	3.08

The equilibrium constants K and enthalpies ΔH of reaction 1 are related to concentrations by the following equations.

$$C_H = (HCl) + (HClX^-)$$

$$C_X = (X^-) + (HClX^-)$$

$$K = \frac{(HClX^-)}{(HCl)(X^-)}$$

$$Q = (HClX^-) \times V \times \Delta H = f(K, C_H, C_X)V \times \Delta H$$

The measured heat changes are corrected for the small heat of dilution of 3 *M* HCl estimated as −0.05 kcal mol^{-1}.

Approximate values of ΔH are obtained from the results corresponding to low concentrations of acid; they in turn lead to approximate values of K. Further calculations were carried out using a computer program similar to one previously described.[10] The approximate values of ΔH and K are refined simultaneously by the nonlinear least-squares method in order to minimize the residual function

$$\sum_i \left[\left(\frac{Q^{\text{exp}}}{V} - \frac{Q^{\text{calcd}}}{V}\right)^2\right]$$

A few least-squares cycles resulted in convergence and the refined values of K and ΔH are given in Table II.

TABLE II

THERMODYNAMIC RESULTS FOR THE EQUILIBRIA

$X^-(\text{solv}) + HCl(\text{solv}) \rightleftharpoons HClX^-(\text{solv})$

$HClX^-$	$-\Delta H$, kcal mol^{-1}	log K (cal)	log K (RMN)[a]
HCl_2^-	8.09 ± 0.18	2.54 ± 0.15	2.4 ± 0.3
$HClBr^-$	4.93 ± 0.24	2.3 ± 0.2	2.1 ± 0.3
$HClI^-$	2.3 ± 0.8	1.2 ± 0.4	0.9 ± 0.3

[a] See reference 6.

The errors set for the 99% confidence limit are equal to three times the standard deviation estimated from the diagonal elements of the inverse matrix corresponding to the last least-squares cycle. The low accuracy obtained for $HClI^-$ is due to the low heat changes measured. The results of the previous nmr study[6] are also quoted in Table II.

The data of the vapor pressure measurements are given in Table III. The sulfolane vapor pressure is less than 0.05 mm at the temperatures considered so that the HCl partial pressure is taken as the total vapor pressure. From these results the heat of solution of HCl corresponding to HCl(g) = HCl(solv) is calculated as $\Delta H = -5.8 \pm 0.1$ kcal mol^{-1}.

TABLE III

VAPOR PRESSURES OF HCl SOLUTIONS

0.83 *M* HCl	Temp, °C	29.53	36.44	40.3	
	p, mm	172.3	214.7	240.9	
1.76 *M* HCl	Temp, °C	27.42	30.95	35.84	41.26
	p, mm	353.0	392.6	456.0	536.9
2.29 *M* HCl	Temp, °C	26.76	32.25	37.87	41.58
	p, mm	464.7	554.1	662.1	742.1

Discussion

The values obtained here for K, the formation constants of the $HClX^-$ ions, are in good agreement with the values determined in the nmr study under somewhat different experimental conditions.[6] It can only be inferred that K is not very sensitive to the presence of

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small amounts of water (2×10^{-2} to 9×10^{-2} M) and to variations in ionic strength (0.09 to 0.6 M).

Comparisons with literature values for K_{HCl_2} in other solvents have already been made.[6] The value of the formation constant of HCl_2^- can be used to estimate the stability of HCl_2^- in water. Combining $(HCl_2^-)_s/((Cl^-)_s(HCl)_s) = 10^{2.6}$ with $p_{HCl} = k(HCl)_s$, where $k = 0.277$ when p is expressed in atmospheres and $(HCl)_s$ is in moles per liter, gives $(HCl_2^-)_s/(Cl^-)_s = 10^{3.2}p_{HCl}$. If we now assume that the energy of transfer of the related ions HCl_2^- and $AgCl_2^-$, from water to sulfolane, are not too different, the previously reported values[10] $(AgCl_2^-)_s/(Cl^-)_s = 10^{1.7}$ and $(AgCl_2^-)_w/(Cl^-)_w = 10^{-4.4}$ lead to $(HCl_2^-)_w/(Cl^-)_w = 10^{-2.9}p_{HCl}$. Thus at 30°, in a 10.8 M aqueous HCl solution ($p_{HCl} = 0.10$), the concentration of HCl_2^- ions would be $\sim 10^{-2.9}$ M. Although such values are only approximate, they at least explain qualitatively why HCl_2^- has not been detected by Raman spectroscopy in aqueous solutions even in the presence of added chloride.[11]

No ΔH values for the solvated $HClX^-$ ions appear to have been reported to date.[1] More fundamental enthalpy values can be deduced from the enthalpy changes for reaction 1 by adding the heat of solution of gaseous HCl in sulfolane, HCl(g) = HCl(solv) − 5.8 kcal mol^{-1}. The calculated enthalpies which correspond to the reactions

$$X^-(solv) + HCl(g) = HClX^-(solv) \qquad (2)$$

are given in the first column of Table IV.

TABLE IV

MINIMUM HYDROGEN BOND ENERGIES

$HClX^-$	ΔH, kcal mol^{-1}	
HCl_2^-	13.9[a]	14.2[b]
$HClBr^-$	10.7[a]	9.2[c]
$HClI^-$	8[a]	8.6[c]

[a] This work. [b] Reference 12. [c] Reference 13.

The enthalpy changes for reaction 2 are closely related to the hydrogen bond energies defined for

$$X^-(g) + HCl(g) = HClX^-(g) \qquad (3)$$

Although these latter values cannot be calculated as the solvation enthalpies for the nonspherical $HClX^-$ gaseous ions are not known, it is expected, on account of ion sizes[4] alone, that the solvation enthalpies of $HClX^-$ are smaller than that of X^-, so that the ΔH values for reactions 2 represent minimum values for the hydrogen bond energies corresponding to reactions 3. Some estimates of solvation enthalpies of halide and perchlorate ions,[4] respectively (Cl^-, 80.1; Br^-, 77.0; I^-, 72.1; ClO_4^-, 62 kcal mol^{-1}), indicate that the hydrogen bond energies may be substantially higher than the very minimum values quoted in Table IV.

Previous estimates of hydrogen bond energies for HCl_2^-, $HClBr^-$, and $HClI^-$ were made by McDaniel and Vallée[12] and Deiters[13] and are listed in the second column of Table IV. These authors determined the enthalpy changes for reactions

$$R_4NX(s) + HCl(g) = R_4NHClX(s) \qquad (4)$$

by calorimetric and manometric methods. It was argued that the lattice enthalpies of R_4NX and R_4NHClX would tend to be equal at some large cation size so that under these conditions, the enthalpy change of reaction 4 would approach the energy of the hydrogen bond in $HClX^-$. As expected, it was found that the heats of reaction of HCl with R_4NCl salts increased in the order Me_4N (11.3–12.0 kcal mol^{-1}), Et_4N (13.7 kcal mol^{-1}), Bu_4N (12.6–14.2 kcal mol^{-1}). This latter "limit value" 14.2 kcal mol^{-1} was thus taken as a minimum for the hydrogen bond strength in HCl_2^-. The values for $HClBr^-$ and $HClI^-$ given in Table IV were also obtained for the tetrabutylammonium salts.

The approximate agreement between both sets of ΔH values in Table IV is coincidental as the discrepancies merely reflect the apparently small differences (less than 2 kcal mol^{-1}) in heats of solution of the simple and complex halide salts. The validity of the assumption of McDaniel and Vallée,[12] *i.e.*, that the lattice enthalpies of Bu_4NCl and Bu_4NHCl_2 are nearly equal, is however open to question. Although the ionic radii of R_4N^+ and HCl_2^- are in doubt, the simple Kapustinskii formula indicates some appreciable difference in lattice enthalpies. Furthermore, later studies[14] with a similar assumption led to a value of −37 kcal mol^{-1} for the hydrogen bond strength in HF_2^- while Waddington's extensive calculations[15] gave −58 ± 5 kcal mol^{-1}. In summary, it can only be said that both sets of figures given in Table IV represent minimum values for the hydrogen bond strength in $HClX^-$ anions, the real values may be considerably higher but remain unattainable as long as solvation enthalpies of X^- and $HClX^-$ ions or lattice enthalpies of R_4NX and R_4NHClX cannot be predicted. Although direct gas-phase determinations of hydrogen bond strength in $HClX^-$ have recently been attempted,[16] they do not appear to be free from difficulties; the following values were obtained by extrapolation: HCl_2^-, 24; $HClBr^-$, 16 kcal mol^{-1}; while 30 ± 5 kcal mol^{-1} was recommended for HF_2^-. The first two values are respectively 10 and 5 kcal mol^{-1} higher than those obtained for equation 2. These differences, which represent the differences in solvation enthalpies between Cl^- and HCl_2^- and Cl^- and $HClBr^-$, are not unreasonable when the solvation enthalpies already quoted in the text for Cl^-, Br^-, I^-, and ClO_4^- are considered.

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