ever it is of interest to use our data for the aluminum fluoride complex ions to evaluate the charge effect for this series of reactions. For the over-all reaction $Al(H_2O)_6^{+++} + 6F^- = AlF_6^{---} + 6H_2O$, $\Delta S^0 = 91$. In our discussion above, we calculated 15.6 entropy units for the replacement of a water molecule by fluoride. For six fluorides this would be 93.6. The agreement with the experimental value of 91 is, of course, accidental but the calculation does show that in this case the charge effect is small. From the Powell and Latimer equation, one would predict about -15 for the effect since in general the solvation of negative ions is greater than positive ions because of the smaller value of x and the radii of $Al(H_2O)_6^{+++}$ and AlF_6^{---} are about equal. It is not surprising that the hydration of AlF_6^{---} is less than that predicted by the equation, as the effective charge on the surface of the ion is doubtless less than -3.

In the last column of Table VI the charge effect has been calculated for each step by subtracting the replacement entropy from the experimental entropy. It will be noted that the charge effect is symmetrical about the neutral molecule, again indicating that the effect is the same for the positive and negative ions. At present we have no method of estimating the hydration entropy for ions such as AlF^{++} or AlF_2^+, but the values calculated in Table VI form a basis for future comparisons.

The recent work of Jonte and Martin[10] on AgCl and $AgCl_2^-$ may be employed for such a comparison. These authors give

$$Ag^+ + Cl^- = AgCl(aq) \qquad \Delta S^0 = 6$$
$$AgCl(aq) + Cl^- = AgCl_2^- \qquad \Delta S^0 = 5$$

Using 10 for the entropy of bound Cl^- in AgCl and 11 for the value in $AgCl_2^-$, we calculate the replacement entropy as 4 for the first reaction and 6 for the second. The charge effect thus is 2 for the first and -1 for the second. These values are to be compared with 3 and -3 for the corresponding reaction of AlF_2^+ and AlF_3 with F^-. One would not expect that the charge effect would be exactly the same for ions of different size, such as $AgCl_2^-$ and AlF_4^-, but the agreement appears to confirm our interpretation that the contribution from the charge effect is small for reactions of this general type.

[10] J. H. Jonte and D. S. Martin, THIS JOURNAL, **74**, 2052 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Acid Strength of Halogens

BY ROBERT L. SCOTT

RECEIVED NOVEMBER 3, 1952

A consideration of the free energy of trihalide ions shows that the halogens can be classed as Lewis acids (electron acceptors) with decreasing acid strength as: $ICl >> BrCl > IBr >> I_2 > Br_2 >> Cl_2$, a classification which agrees with measurements on halogen complexes with aromatic hydrocarbons as well. A calculation of the free energy of isomerization of trihalide ions illuminates the fact that only those trihalide ions which have the heaviest atom in the middle position are known.

The molecular complexes between aromatic hydrocarbons and halogens which have been the subject of much interest in the last few years[1-6] are generally accepted to be examples of Lewis acid-base interactions in which the benzene, etc., acts as an electron donor ("base") and the halogen as an electron acceptor ("acid").

Of the three halogens whose complexes with benzene and other aromatic "bases" have been studied, ICl is the strongest "acid," followed by I_2 and then Br_2. This general rule is illustrated in Table I, which gives equilibrium constants[4,6] for the reaction

$$Ar + X_2 = Ar{\cdot}X_2$$

The formation of trihalide ions can also be regarded as a similar complexing reaction between a halide ion (base) and a halogen molecule (acid). Superficially, however, no regularity is found; for example, I_3^- is the stablest trihalide ion, although we might expect I_2Cl^- to be more stable since ICl is a stronger acid than I^-. As a result, the stability of the trihalides is usually discussed in terms of a number of empirical rules.[7]

TABLE I

EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION

	K_c in liters/mole CCl_4 solution at 25°			
Base → Acid	Benzene	*p*-Xylene	Hexamethylbenzene	Naphthalene
ICl	0.54	1.51	22.7	1.39
I_2	.15	0.31	1.35	0.25
Br_2	.11	.23		

This difficulty is resolved when we recognize that an unsymmetrical trihalide ion can be formed (and conversely, decompose) in two different ways

$$X\text{-}Y + Z^- \underset{}{\overset{K_1}{\rightleftarrows}} [X\text{-}Y\text{-}Z]^-;\quad X^- + Y\text{-}Z \overset{K_2}{\rightleftarrows} [X\text{-}Y\text{-}Z]^-$$

The equilibrium constant K_1 measures the acid strength of XY and the base strength of Z^-; K_2, on the other hand, measures the acid strength of YZ and the base strength of X^-. The experimentally reported values are invariably for the reaction with smaller K; the other one can however be calculated by standard thermodynamic methods if the free energies of

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[1] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); **71**, 2703 (1949).

[2] R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952).

[3] T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950).

[4] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677, 5170 (1950).

[5] N. W. Blake, H. Winston and J. A. Patterson, *ibid.*, **73**, 4337 (1951).

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

[7] See, for example, N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, pp. 1190-1197.

formation of the halogens and the monohalide ions are known.

A third reaction also can be envisaged

$$X\text{–}Z + Y^- \overset{K_3}{\rightleftarrows} [X\text{–}Y\text{–}Z]^-$$

and its equilibrium constant or standard free energy change could also be calculated, but it is evident that this is not a simple acid–base reaction since it involves getting the Y atom into the central position in the trihalide ion.

Table II shows the free energies of formation of trihalides from various "acids" and "bases," calculated from the accepted values of the free energies.[8]

TABLE II

FREE ENERGIES OF TRIHALIDE FORMATION

Base → Acid	ΔF° in kcal./mole at 25° $I^-(aq)$	$Br^-(aq)$	$Cl^-(aq)$
ICl(aq)	−11.6	−5.9	−3.02
BrCl(aq)		(−3.8)	?
IBr(aq)	−8.85	−3.49	−2.23
I_2(aq)	−3.89	−1.46	−0.44
Br_2(aq)		−1.67	−0.19
Cl_2(aq)			+2.7

The value of −3.8 kcal./mole for $Br^- + BrCl$ is somewhat uncertain since it depends upon an estimate of the standard free energy of solution of BrCl(g). No quantitative data whatever exist for the ion $BrCl_2^-$. The blanks in the table correspond to reactions of the third type (not acid–base) cited above, since no trihalide ions are known in which the middle atom is of lower atomic weight than one of the extremes.

Table II permits an unequivocal ordering of the halogens in decreasing acid strength, but since the aqueous halogen can be regarded as already interacting with the base H_2O, it is perhaps more illuminating to refer the free energies of formation to the gaseous halogen at 1 atm. and 25° as a standard state. Table III shows the result of such a calculation, and includes the acid–base reaction $XY(g) + Aq \rightarrow XY(aq)$.

TABLE III

FREE ENERGIES OF COMPLEX FORMATION

Base → Acid	ΔF° in kcal./mole at 25° $I^-(aq)$	$Br^-(aq)$	$Cl^-(aq)$	$H_2O(l)$
ICl(g)	−14.3	−8.6	−5.7	−2.7
BrCl(g)		−5.78	?	(−2.0)
IBr(g)	−10.66	−5.30	−4.04	−1.81
I_2(g)	−4.59	−2.16	−1.14	−0.70
Br_2(g)		−1.44	+0.04	+0.226
Cl_2(g)			+4.4	+1.65

The "acids" in order of decreasing strength are thus $ICl \gg BrCl > IBr \gg I_2 > Br_2 \gg Cl_2$ whether gases at 1 atm. or 1 *M* aqueous solutions are chosen as standard states. These results are now in complete accord with the relative strength of complexes of halogens with aromatic hydrocarbons where a similar ICl, I_2, Br_2 situation was found (Table I).

Similarly the "bases" can be ordered: $I^-(aq) \gg Br^-(aq) > Cl^-(aq) > H_2O(l)$. (Note that the standard state of water is the pure liquid; were it referred to an equivalent concentration, the free energies in the last column of Table III would all be increased by $RT \ln 55 = +2.4$ kcal., and water would be seen to be a much poorer base than even Cl^-.)

By interpolation, we estimate ΔF° and K for the formation of $BrCl_2$(aq) as

	ΔF°, kcal.	K
$Cl^-(aq) + BrCl(g) = BrCl_2^-(aq)$	−4.3	1.5×10^3 atm.$^{-1}$
$Cl^-(aq) + BrCl(aq) = BrCl_2^-(aq)$	−3.3	260 liters mole^{-1}

Aside from the fact that BrCl is itself not very stable (although more so in solution than as a gas), $BrCl_2^-$ should be one of the stabler trihalide ions.

The figures in Tables II and III can be used to explain the non-existence of trihalide ions in which one or both of the outside atoms is heavier than the central atom. We interpolate and extrapolate to estimate ΔF°'s for the following hypothetical reactions

	ΔF° (est), kcal.
$I^-(aq) + BrCl(g) = [I\text{–}Br\text{–}Cl]^-(aq)$	−11
$I^-(aq) + Br_2(g) = [I\text{–}Br\text{–}Br]^-(aq)$	− 3
$I^-(aq) + Cl_2(g) = [I\text{–}Cl\text{–}Cl]^-(aq)$	+ 1
$Br^-(aq) + Cl_2(g) = [Br\text{–}Cl\text{–}Cl]^-(aq)$	+ 3

With these estimates we can now compute free energies of isomerization

	ΔF°, kcal.
$[I\text{–}Br\text{–}Cl]^-(aq) = [Br\text{–}I\text{–}Cl]^-(aq)$	−16
$[I\text{–}Br\text{–}Br]^-(aq) = [Br\text{–}I\text{–}Br]^-(aq)$	−18
$[I\text{–}Cl\text{–}Cl]^-(aq) = [Cl\text{–}I\text{–}Cl]^-(aq)$	−32
$[Br\text{–}Cl\text{–}Cl]^-(aq) = [Cl\text{–}Br\text{–}Cl]^-(aq)$	−14

From these figures it is obvious why these trihalide ions have never been observed, particularly so since it is easy to envisage a simple displacement mechanism for the isomerization process in any solution where the monohalide ions are present even in trace amounts.

The above calculations merely demonstrate the thermodynamic consistency of the Lewis acid–base model. We still need a molecular explanation for these phenomena, an explanation which will adequately answer at least two questions: (1) Why are configurations with the heavy atom central much more stable than other isomeric configurations? A crude explanation,[7] generally accepted, is that the halogen atoms of higher atomic number can more easily expand their "octet" of valence electrons, which the central atom must do. (2) Why is ICl a stronger acid than I_2? A possible answer may lie in the polarity of ICl; the iodine might more easily accept electrons from the base if it can shunt some electrons to the more electronegative chlorine end of the molecule. On the other hand, such an explanation is not entirely consistent with that offered for (1) and moreover, appears inadequate to explain the halogen-aromatic complexes where the end-on

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(8) W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, N. Y., 1952.

configuration with the halogen–halogen axis perpendicular to the plane of the ring at its center has been excluded.[2]

A careful study of these systems, possibly along the lines of the molecular orbital approach suggested by Pimentel[9] appears very desirable.

(9) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Reaction between Ferric Sulfate and Calcium Chloride in the Solid State[1]

BY J. FRED HAZEL, WALLACE M. MCNABB AND WILLIAM D. COOKE[2]

RECEIVED DECEMBER 22, 1951

The reaction between solid ferric sulfate and calcium chloride to form ferric chloride and calcium sulfate has been studied with particular reference to the effects of temperature, particle size, reactant ratio and the presence of water and ferric chloride as catalysts. When the materials were strictly anhydrous the reaction was found to occur only above 300°. The addition of small amounts of ferric chloride or of water caused the reaction to be initiated at much lower temperatures. The reaction was slow between 80 and 90°. At 118° a yield of 22% was obtained in five minutes while a maximum conversion of 43% was found in one hour. The percentage reaction was 88% in five minutes at 225° and 96% for the same period at 340°. At low temperature the presence of an induction period indicated that the reaction was autocatalytic. The percentage conversion decreased rapidly with increase in particle size. Mixtures containing an excess of one of the reactants had higher rates of reaction and gave greater yields than stoichiometric mixtures. The reaction could not be reversed.

The reaction between solid calcium chloride and ferric sulfate to form ferric chloride and calcium sulfate has been studied quantitatively by taking advantage of the solubility of one of the products, ferric chloride, in ether. The effects of temperature, pressure, particle size and reactant ratio on the reaction have been investigated.

Experimental

Materials.—Baker C.P. ferric sulfate and calcium chloride were used in the experiments. Petrographic analysis of the ferric sulfate revealed that it contained between 1 and 2% ferric oxide. When heated in the air to 550° it showed evidence of decomposition. A decomposition pressure of 23 mm. at 553° has been reported for this compound.[3] In preliminary experiments it was found that ferric sulfate from two other sources contained ferric oxide to about the same extent.

Heat Source and Temperature Control.—The temperature at which the reaction was studied ranged from 82 to 340°. Temperature control up to 200° was realized by the use of boiling liquids.[4]

By means of a thermocouple inserted in the powder, it was found that the time required for the reaction mixture to be heated from 90°, the temperature at which the reaction begins, to 118° was 15 seconds. To reach 182°, 180 seconds were necessary.

An electric heater was used for temperature control above 200°.

To obtain rapid heating, an electrically heated brass block with a hole drilled to accommodate the reaction tube was used as a preheater. The temperature of the block was adjusted about 75° above the temperature at which the reaction was to be carried out. The reaction mixture was allowed to remain in the preheater long enough for the temperature to approach the desired value. It was then transferred to the heater. In this manner mixtures could be heated to the reaction temperature in about one minute.

Procedure.—The materials were screened with Tyler Standard Screens to obtain size fractionation. They were weighed out approximately in the desired ratio and dried at 325° for 12 hours.

The dried reactants were placed in screw-cap bottles and conveyed to a dry-box charged with phosphorus pentoxide. A positive pressure was maintained in the box with air which had been dried by passing through sulfuric acid, calcium chloride and magnesium perchlorate. The materials were screened again in the dry-box and then mixed. To obtain uniform mixing the container was placed for one-half hour on a high frequency vibrator which kept the material in a semi-suspended state.

The exact ratio of the two reactants was found by determining the percentage iron in the mixture. In some reactions, a small amount of water was added as a catalyst. To accomplish this a weighing bottle containing a known quantity of the mixture was opened while on a balance, and allowed to pick up the desired amount of water from the atmosphere. The material was remixed as described above.

Reactions were carried out with about 0.15 g. of mixture in 9-mm. Pyrex tubes. After being heated for the desired length of time the contents of the tube was transferred to a small vial, weighed and extracted with ether.

Method of Analysis.—Ferric chloride was extracted from the reaction mixture with anhydrous ethyl ether. The ether layer was evaporated and the iron determined by a method previously described.[5] From the amount of iron in the sample, the completeness of the reaction was calculated.

The reliability of the extraction process as a quantitative method for following the course of the reaction was tested. It was found that ferric chloride was completely extracted from synthetic reaction mixtures and that no iron was extracted from ferric sulfate. However, when a 250-mg. sample of reactants was extracted with anhydrous ether (0.01% water) a small amount of iron, 0.09 mg., was found in the extract. This value was reproducible and was considered to be the blank determination of the reagents used.

Experiments in Open Tubes.—In open tubes protected from moisture with reactants dried at 325° for 12 hours, reactions occurred only at temperatures greater than 300°. Small amounts of water caused the reaction to proceed at much lower temperatures. The reaction was also catalyzed by ferric chloride. A striking demonstration of this was obtained by heating a layer of the unreactive mixture in an open Petri dish at 250°. No reaction occurred until a few crystals of anhydrous ferric chloride were added. The reaction then proceeded rapidly with the formation of the ferric chloride being evidenced by the widening, dark circle spreading out from the spot at which the catalyst was added.

Autocatalytic effects in reactions between solids are not uncommon.[6] Another indication of the autocatalytic na-

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(1) Presented before the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 10-13, 1951.

(2) From a dissertation by William D. Cooke presented to the faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIV, Longmans, Green and Co., London, 1935, p. 311.

(4) C. D. Hodgman, "Handbook of Chemistry and Physics," 28th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1944, p. 528.

(5) W. D. Cooke, J. F. Hazel and W. M. McNabb, *Anal. Chem.*, **21**, 643 (1949).

(6) A. Sieverts and H. Theberath, *Z. physik. Chem.*, **100**, 463 (1922); J. Kendall and F. J. Fuchs, THIS JOURNAL, **43**, 2017 (1921); C. N. Hinshelwood, *J. Chem. Soc.*, **119**, 721 (1921); H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand, Co., Inc., New York, N. Y., 1925, p. 981.