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THERMOCHEMISTRY OF FLUORINE COMPOUNDS.
PART III. HEATS OF SOLUTION AND NEUTRALIZATION IN BROMINE TRIFLUORIDE

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SUMMARY

The heats of solution of fluorides, and of their adducts with bromine trifluoride, have been measured in bromine trifluoride. The heats of mixing of "acid" and "base" adducts, with either "acid" or "base" in excess, have also been determined. The heats of formation of stannic and antimonic fluorides were found by dissolving tin and antimony in a bromine trifluoride–bromine mixture. The heats of formation of acids and bases in the bromine trifluoride solvent system have been calculated from these data. When combined with heats of neutralization and solution these yield values for the heats of formation of ternary fluorides. The stability sequences, derived thermochemically for acids and bases in the solid state and in solution, accord with previous observations. The low values for heats of neutralization in bromine trifluoride are compatible with a high intrinsic electrical conductivity of the solvent. There is no need to postulate extrinsic impurity conduction.

INTRODUCTION

The application of bromine trifluoride in reaction calorimetry was introduced in Part II[1]. In fluorination reactions the valency state of the bromine in the trifluoride is reduced, and complications arise in non-adiabatic calorimetry because of slow equilibration between the different valency states of bromine. This was circumvented by using a pre-equilibrated bromine trifluoride–bromine mixture. It was shown that a consistent heat of formation could be obtained for such a mixture without having to specify the exact quantity of each species in solution. In this paper we report the heats of formation of bromine trifluoride adducts with fluorides, the so-called "acids" and "bases" in the bromine trifluoride solvent system[2], together with their heats of neutralization. Pure bromine trifluoride could be used for these measurements because no redox reaction was involved. Hence these results are independent of any assumptions made for the mixed solvent[1].

EXPERIMENTAL

The experimental techniques and conventions are described in Part II. Fluorides were prepared and purified by conventional methods.

Heats of formation of stannic and antimonic fluorides

These were measured in the twin-cell calorimeter by reacting tin and antimony with excess of the equilibrated BrF_3–Br_2 mixture (mole ratio = 7.04). Combining these heats of reaction with the heat of formation of the BrF_3–Br_2 mixture (—321.7 kJ mole^{-1}) gives the heats of formation of stannic and antimonic fluorides in the calorimetric medium as —1,195 kJ mole^{-1} and —1,471 kJ mole^{-1} respectively. (ΔH_f^0 SnF_4(s) —1,136 and SbF_5(l) —1,379 kJ mole^{-1} can be calculated after deducting the heats of solution).

Heats of solution of compounds forming "bases" in bromine trifluoride

Some alkaline fluorides and an alkaline earth fluoride were dissolved in pure bromine trifluoride in the larger metal calorimeter described previously[1]. Silver bromide was dissolved in the BrF_3–Br_2 mixture because of the difficulty in preparing pure silver fluoride. The heat of solution of the adduct $KF{\bullet}BrF_3$ was also found. The precision of measurements in the pure solvent was better than in the mixed one. A number of experiments with lithium fluoride gave lower heats of solution because of incomplete reaction. (The solubility of lithium fluoride is only about 0.5 g in the volume of trifluoride used.)

Heats of solution of compounds forming "acids" in bromine trifluoride

Antimony and tantalum pentafluorides, prepared by direct fluorination, were purified by vacuum distillation and sublimation respectively. Stannic fluoride, was made from stannous chloride and bromine trifluoride, the adduct being decomposed at 180° *in vacuo*. Because the stoichiometric adduct $SnF_4{\bullet}2BrF_3$ cannot be isolated at 25°, a heat of solution must be estimated.

Heats of solution of fluorides incapable of neutralization in bromine trifluoride

Molybdenum hexafluoride and iodine pentafluoride were made from the elements, and purified by vacuum distillation.

Heats of "neutralization" in bromine trifluoride

These were measured by either (a) addition of the "base" fluoride or adduct to excess of the "acid" fluoride dissolved in the calorimetric medium, or (b) addition of the "acid" fluoride to an excess of the "base" fluoride in the solvent.

When a sparingly soluble ternary fluoride was produced, method (a) may give incomplete reactions because of surface coatings. If this occured, any slow dissolution would not be readily measured in the type of calorimeter used.

Heats of solution of ternary complexes were measured when required for calculation of heats of neutralization.

RESULTS AND DISCUSSION

The primary purpose of this work was to derive heats of formation of substances which can react with bromine trifluoride. Because a variety of salts can be prepared in this medium by neutralization reactions, it was hoped that the determination of the heats of formation of a relatively small number of acids and bases, together with a single heat of neutralization, would lead to a large number of salt values without the necessity of carrying out individual determinations. However, it appears that bromine trifluoride is too differentiating a solvent, and a constant heat of neutralization was not obtained. Nevertheless, approximate values for heats of formation of salts are calculable because heats of neutralization are small. Of secondary interest is the relevance of the thermochemical results to the solvent system concept originally proposed[2].

TABLE 1

HEATS OF REACTION OF TIN AND ANTIMONY IN BROMINE TRIFLUORIDE–BROMINE SOLUTIONS

	Metal (M) (g)	BrF_3–Br_2 (g)	Mole ratio BrF_3/M	Heat (kJ mole^{-1} of M)
Sn	0.2541	29.7	101	—759.0
	0.1702	21.3	109	—763.6
	0.2643	41.1	135	—765.7
				Mean—762.7 ±2.2
Sb	0.3033	23.0	68	—939.7
	0.2420	27.0	100	—922.6
	0.2850	36.0	114	—934.3
	0.1955	32.1	148	—931.8
				Mean—932.1 ±4.9

TABLE 2

HEATS OF SOLUTION OF COMPOUNDS FORMING "BASES" IN BROMINE TRIFLUORIDE

Base	(g)	BrF_3 (g)	Mole ratio BrF_3/base	Heat (kJ $mole^{-1}$ of base)
KF	0.2383	416.2	739	—91.0
	0.2159	414.6	811	—91.9
	0.1922	418.1	922	—92.9
				Mean —91.9 ±0.6
NaF	0.3637	419.4	353	—50.8
	0.2626	421.4	492	—49.2
	0.1953	424.5	667	—50.5
				Mean —50.5 ±0.5
LiF	0.0757	409.0	276	—11.7
BaF_2	0.3823	414.0	1380	—88.8
	0.3168	416.1	1680	—88.7
				Mean 88.7(5) ± 0.0(5)
AgBr*	1.9458	36.5	25.7	—36.4
	1.8464	35.7	27.0	—35.9
				Mean —36.1(5) ± 0.2(5)
$KF{\bullet}BrF_3$	0.7048	411.2	830	+ 1.38
	0.6184	412.8	951	+ 1.55
				Mean + 1.46 ± 0.08

* Determined in twin-cell calorimeter with BrF_3–Br_2 mixture.

TABLE 3

HEATS OF SOLUTION OF COMPOUNDS FORMING "ACIDS" IN BROMINE TRIFLUORIDE

Acid	(g)	BrF_3 (g)	Mole ratio BrF_3/acid	Heat (kJ $mole^{-1}$ acid)
SbF_5	1.1616	355.2	485	—92.3
	1.1868	368.9	495	—92.8
	0.8088	357.4	700	—91.8
				Mean —92.3 ± 0.3
TaF_5	3.5704	383.6	217	—46.0
	1.2160	380.1	628	—44.4
				Mean —45.2 ± 0.8
SnF_4	0.4219	411.2	1390	—57.7
	0.3663	415.8	1620	—59.1
	0.3437	406.7	1680	—59.5
				Mean —58.8 ± 0.7
$SbF_5{\bullet}BrF_3$	2.8280	367.8	490	— 4.90
	1.4398	369.4	662	— 4.98
				Mean — 4.94 ± 0.04
$TaF_5{\bullet}BrF_3$	1.9394	413.0	642	— 1.34
	1.8678	411.2	663	— 1.46
				Mean — 1.40 ± 0.06

TABLE 4

HEATS OF SOLUTION OF "NON-NEUTRALISABLE" FLUORIDES IN BROMINE TRIFLUORIDE

Fluoride	(g)	BrF_3 (g)	Mole ratio BrF_3/fluoride	Heat (kJ mole^{-1} fluoride)
MoF_6	0.9503	287.3	463	+2.93
	0.8146	291.4	547	+3.14
				Mean +3.03 ± 0.10
IF_5	1.1770	324.4	445	—7.36
	1.1120	320.6	469	—7.16
				Mean —7.26 ± 0.10

TABLE 5

HEATS OF NEUTRALIZATION IN ANTIMONY PENTAFLUORIDE–BROMINE TRIFLUORIDE SOLUTIONS

a) Base additions

Solute added	(g)	Solvent BrF_3 (g)	+ SbF_5 (g)	Mole ratio BrF_3/acid/base	Heat (kJ mole^{-1} base)
KF	0.2100	408.0	17.5	1040/28.7/1	—107.2
	0.1349	412.4	18.0	1300/36.0/1	—110.0
$KF \cdot BrF_3$	1.8117	392.4	5.0	308/2.5/1	— 16.4
	1.7741	396.7	7.1	290/3.58/1	— 18.4
	2.1229	420.2	9.0	284/6.0/1	— 19.0
	1.5612	421.8	10.5	303/8.0/1	— 16.9
AgBr	1.3769	437.2*	20.0	600/12.6/1	— 53.9
	0.8008	439.6*	21.0	758/17.9/1	— 56.9
BaF_2	0.2235	364.8	14.5	2010/52.8/1.0	—139.3

* Mixed solvent BrF_3/Br_2 (7.04/1).

TABLE 6

HEATS OF NEUTRALIZATION IN BASIC SOLUTIONS OF BROMINE TRIFLUORIDE

b) Acid addition (SbF_5)

Base	Solvent (g)	in BrF_3 (g)	Acid (g)	Mole ratio BrF_3/base/acid	Heat (kJ mole^{-1} of SbF_5)
$KF \cdot BrF_3$	3.2	320.0	0.9640	522/12.2/1	—111.5
	4.1	324.4	0.9600	530/15.8/1	—112.0
$NaF \cdot BrF_3$	3.5	322.9	1.3006	394/13.5/1	—106.2
	4.3	337.6	0.8928	595/24.1/1	—107.1
$AgF \cdot BrF_3$	1.9	383.3	1.4304	424/1.58/1	—109.0
	1.4	296.7	0.4727	1000/3.45/1	—110.5
$BaF_2 \cdot 2BrF_3$	1.8	291.6	0.6025	767/3.72/1	—107.1
	2.8	301.3	0.5250	990/6.7/1	—106.6

TABLE 7

HEATS OF NEUTRALIZATION OF STANNIC AND TANTALIC FLUORIDES IN BROMINE TRIFLUORIDE WITH ALKALI FLUORIDES

Solute added (g)		Solvent (g) BrF$_3$ (g)	+ acid	Mole ratio BrF$_3$/acid/base	Heat (kJ mole^{-1} base)
			SnF$_4$		
KF	0.1592	398.2	2.5	804/4.3/1	—99.3
	0.2964	400.0	2.0	394/2.23/1	—97.8
NaF	0.1737	389.6	2.0	705/2.72/1	—56.6
	0.1147	388.2	2.6	1020/4.85/1	—56.1
			TaF$_5$		
KF•BrF$_3$	1.5837	392.7	4.2	355/1.87/1	—14.7
	1.7868	394.0	6.7	303/2.65/1	—13.1

TABLE 8

HEATS OF SOLUTION OF TERNARY COMPLEXES IN BROMINE TRIFLUORIDE

Complex	(g)	BrF$_3$ (g)	Heat (kJ mole^{-1} of complex)
NaSbF$_6$	0.6529	414.9	— 1.67
	0.5155	417.2	— 2.13
	0.4634	420.4	— 2.25
			Mean — 2.02 ± 0.23
AgSbF$_6$	0.6285	410.1	—56.9
	0.3936	412.6	—56.1
	0.3892	406.9	—55.1
			Mean —56.0 ± 0.6
K$_2$SnF$_6$	0.7365	375.5	—15.7
	0.5738	386.2	—16.7
			Mean —16.2 ± 0.5
Na$_2$SnF$_6$	1.0923	388.2	—10.1
	0.8777	390.8	—10.8
			Mean —10.4(5) ± 0.3(5)
KTaF$_6$	0.6101	387.7	— 6.61
	0.5980	390.2	— 8.37
			Mean — 7.49 ± 0.88

The heats of formation of potassium, sodium, and barium tetrafluorobromates were obtained from the heats of reaction of the corresponding fluorides with pure bromine trifluoride and the heats of solution of the fluoro-bromates in the solvent. The heat of solution of $KBrF_4$ found at 25° (1.46 kJ mole^{-1}) was in reasonable agreement with that calculated from the variation of solubility with temperature (2.55 kJ mole^{-1}), which was an average value over the range 25–75°[3]. The heat of formation of $AgBrF_4$ was obtained by measuring the heat of reaction of silver bromide with the BrF_3–Br_2 mixture, and used the heat of formation of the latter obtained in Part II. The results are collected in Table 9, the heats of solution derived from solubility data being employed.

TABLE 9

HEATS OF FORMATION OF BASE ADDUCTS

	Heat of solution (kJ mole^{-1})		Heat of formation of base (kJ mole^{-1})
Adduct	Fluoride	Adduct	
$KF{\bullet}BrF_3$	-91.9 ± 0.6	$+1.46$* $+2.55$	-967.3
$NaF{\bullet}BrF_3$	-50.5 ± 0.5	$+3.80$	-933.9
$BaF_2{\bullet}2BrF_3$	$-88.7(5) \pm 0.0(5)$	$+9.41$	-1661
$AgF{\bullet}BrF_3$	$-36.1(5) \pm 0.2(5)$	$+5.06$	-560.2

* Calorimetric value at 25°: other values from solubility data[3].

A heat of dissociation (142 kJ mole^{-1}) of the potassium fluorobromate for the process $KBrF_4(s) \rightleftharpoons KF(s) + BrF_3(l)$ can be calculated from the heat of formation of the fluorobromate.

The relative stability of fluorobromates has been qualitatively assessed. Thus, the potassium compound lost 30% of its weight after heating for 5 min at 200°, whilst the sodium compound was completely decomposed to sodium fluoride and bromine trifluoride. The silver compound was more reactive with organic liquids than the potassium one[4]. The sum of the heats of solution in Table 9, with the sign reversed, confirms the order of stability $K > Na > AgBrF_4$. Enthalpies can be used to establish the stability sequence along the dissociative series,

$$MF{\bullet}BrF_3(s) \rightleftharpoons MF(s) + BrF_3(l)$$

because entropy changes are almost constant. The entropy increment in generating the liquid trifluoride more than compensates for the loss of entropy between the solid complex and simple fluorides. This loss would also hardly change in a structurally-related series.

The heats of formation of acid adducts are collected in Table 10. The value for the tantalum compound involves the heats of formation of bromine trifluoride[5] and tantalum pentafluoride[6] measured by fluorine bomb calorimetry. The heats of formation of stannic and antimonic fluorides are derived from calorimetry in the BrF_3–Br_2 mixture, and the heat of formation of "BrF_3" appropriate to this mixture[1]

$$3Sb + 5BrF_3 = 3(SbF_5) + 2.5(Br_2)$$
$$3Sn + 4BrF_3 = 3(SnF_4) + 2(Br_2)$$

The products are in solution in BrF_3–Br_2.

TABLE 10

HEATS OF FORMATION OF ACID ADDUCTS

Adduct	Heat of solution (kJ mole^{-1}) Fluoride	Adduct	Heat of formation of acid (kJ mole^{-1})
SbF_5•BrF_3	—92.3 ± 0.3	—4.9	—1,773
TaF_5•BrF_3	—45.2 ± 0.8	—1.4	—2,251
SnF_4•$2BrF_3$	—58.8 ± 0.7	—2*	—1,505

* Estimated assuming same order as for fluoride heats.

Since this work was completed (1967), the existence of ionic solids containing the Br_2^+ and Br_3^+ cations has been established[7,8]. The possibility arises that unsubstituted bromonium complexes may be present to some extent in the BrF_3–Br_2 calorimetric mixture in the presence of "acid" fluorides, and that this would invalidate the above procedure. It is true that the tin and antimony acids were prepared in BrF_3–Br_2 mixtures, but these were generally heated before isolating the adducts. Thus, the presence of Br_2^+ and Br_3^+ ions depends on their stability relative to BrF_2^+ in our medium at 25°, a matter which could be decided calorimetrically (*i.e.* by dissolving the new compounds in BrF_3 and the BrF_3–Br_2 mixture).

However, the derived heats of dissociation, and relative stabilities of the acids, are not affected because the requisite data were obtained in pure bromine trifluoride. The thermal stabilities, measured by weight losses at temperatures from 100–150°, were in the same order ($Sb > Ta > Sn$) as that of the heats of solution. (The values for the tin acid must be halved if the partial pressures of bromine trifluoride in equilibrium are to be compared.)

A heat of dissociation for the antimony acid (115 kJ mole^{-1}) can be calculated from vapour pressure measurements[9] over a temperature range (130–350°). It was assumed that the vapour was completely dissociated above the melt. A heat of dissociation (186 kJ mole^{-1}) from the solid at 25° to the gaseous fluorides can be calculated from our figures. The heat of vaporization of antimony pentafluoride was estimated to be 42 kJ mole^{-1}, and the published value taken for the heat of formation of gaseous bromine trifluoride[5].

The formation of a salt in bromine trifluoride was regarded as a neutralization reaction between an acid component, which generated the BrF_2^+ cation in solution, and a basic component which formed BrF_4^- anions, *i.e.* $BrF_2^+ + BrF_4^- = 2BrF_3$. Hence, mixing strong acids and bases should produce a maximum value for a neutralization heat. The variation of self-ionization of the solvent during neutralization reactions was avoided by initial suppression with either excess acid or base. The heats of neutralization measured are listed in Table 11. The heat of neutralization of the potassium base and the antimony acid, with either in excess, was

TABLE 11

HEATS OF NEUTRALIZATION IN BROMINE TRIFLUORIDE

Acid	Base	Heat of neutralization ($kJ\ mole^{-1}$ of added solute)
Excess SbF_5 in BrF_3	KF	16.7 ± 1.5
Excess SbF_5 in BrF_3–Br_2	AgBr	19.2 ± 1.3
Excess SbF_5 in BrF_3	$KBrF_4$	19.1 ± 1.0
SbF_5	Excess KF in BrF_3	19.4 ± 0.5
	Excess NaF in BrF_3	14.4 ± 0.5
	Excess AgF in BrF_3	17.4 ± 0.8
	Excess BaF_2 in BrF_3	14.6 ± 0.4
Excess SnF_4 in BrF_3	KF	6.5 ± 1.1
Excess SnF_4 in BrF_3	NaF	6.2 ± 0.7
Excess TaF_5 in BrF_3	$KBrF_4$	15.3 ± 0.8

consistent. The lower value obtained on addition of solid potassium fluoride was caused by this material being coated to some extent with the less-soluble ternary salt. This slowed the dissolution enough to make the thermal effect indistinguishable from the thermal background. The coating effect was especially noticeable with sodium fluoride additions, and these results have been omitted. Similarly with the silver base, the neutralization heats with acid or base in excess were consistent within experimental error. (It should be noted that this consistency obtains even though the heat of formation of the mixed solvent is involved.) Hence an average value of -19 kJ $mole^{-1}$ was taken for the heat of neutralization in bromine trifluoride. Lower values indicated acid or base strengths below the maximum and partial solvolysis, *i.e.* reversal of neutralization. The base strengths, found with respect to the antimony acid, were in the order $K \simeq Ag > Na > Ba$; the acid strengths, with respect to the potassium base, were in the order $Sb > Ta > Sn$. These sequences accord with previous experimental observations made during the preparation of complex fluorides. Salts prepared from weak acids or bases retained bromine trifluoride when excess solvent was removed *in vacuo* at room temperatures. The calorimetric order of base strength is also in agreement with the sequence of electrical conductivities of bases in bromine trifluoride. (The equivalent conductivities of bases measure essentially the number of BrF_4^- ions which are far more mobile than the equal number of cations present.)

Some values for the heat of formation of ternary fluorides are collected in Table 12. These were calculated with the maximum value of neutralization heat (-19 kJ $mole^{-1}$) in order to compensate for solvolysis which would occur in solution during some of the neutralizations.

The magnitude of the neutralization heat has a bearing on the intrinsic electrical conductivity of bromine trifluoride. The high values obtained for the solvent conductivity by numerous investigations (*ca.* 10^{-3} ohm^{-1} cm^{-1} at room temperature) have been disputed because the trifluoride is so reactive. Values in

TABLE 12

HEATS OF FORMATION OF TERNARY FLUORIDES (KJ MOLE^{-1})

$KSbF_6$	2,143	$KTaF_6$	2,625	K_2SnF_6	2,528
$AgSbF_6$	1,685	$AgTaF_6$	2,220	Ag_2SnF_6	2,072
$NaSbF_6$	2,110	$NaTaF_6$	2,594	Na_2SnF_6	2,473
$Ba(SbF_6)_2$	4,267	$Ba(TaF_6)_2$	5,232	$BaSnF_6$	2,499

the range 10^{-6} to 10^{-9} ohm^{-1} cm^{-1} have been considered more probable[10]. Differentiating intrinsic from extrinsic properties can be a difficult and unrewarding task, because, at the end of the purification process, the critic can always maintain that the purification had not been rigorous enough. An assessment is required which is not dependent on extreme purity (*e.g.* a property to which impurities only contribute linearly in proportion to their concentration).

Consider a solvent ionization brought about by ion-transfer $XY + XY \rightleftharpoons X^+ + XY_2^-$. The equilibrium constant for this process $K \simeq \alpha^2$, where α, the fractional dissociation of the solvent, is small. The specific conductivity of the solvent (κ) equals the product of the number of ions and the sum of cation and anion mobilities. For many ionizing solvents, it is known that the ions produced by self-dissociation of the solvent have the maximum mobility of all the ions which exist in that solvent. Indeed the mobilities of solvent ions remain high in spite of viscosity differences, because of co-operative movements by "Grotthus" mechanisms. The available figures show that the sum of solvent-ion mobilities fall in a narrow range. Hence, in comparing a series of ionizing solvents, the following proportionalities should be roughly true.

$$\kappa^2 \propto n^2 \propto K \propto \exp(-\Delta G/RT)$$

where n is the number of cations or anions and ΔG is the free energy change on ionization. Hence, a roughly linear relation between pκ and ΔG would be expected (pκ = $-\log\kappa$), and such a plot is shown in Figure 1 for some protonic solvents. (The free energy values for some solvents may have been derived from conductivities rather than cell potentials, and for these the relationship is implicit in the measurement.)

The free energy values can be further divided into major enthalpy and minor entropy terms for which the relation between pκ and energy is non-linear. Whatever the exact form of the relationship between conductivity and heat of neutralization, it remains true that low values of heats of neutralization are associated with high solvent conductivities, and vice versa. This correlation should remain valid for halide ion transfer as well as proton transfer, but no confirmatory data are available at present.

It can be concluded that the low value for the heat of neutralization in bromine trifluoride is compatible with a high intrinsic solvent conductivity.

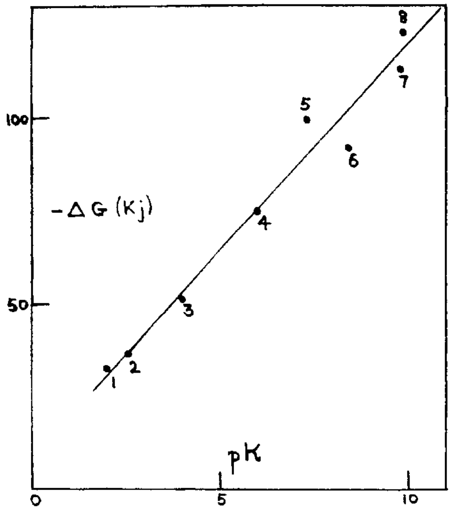

Fig. 1. Relation between specific conductivity and free energy of auto-protolysis at 25°.

1	H_2SO_4	5	H_2O
2	D_2SO_4	6	CH_3COOH
3	HSO_3F	7	CH_3OH
4	HF (10°)	8	C_2H_5OH

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