Heats of Formation of Sulphuryl Chlorofluoride and Lead Chlorofluoride †

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Standard heats of formation of PbClF and SO_2ClF have been determined from heats of precipitation and hydrolysis respectively. The enthalpy of PbClF is more negative than the mean of the corresponding difluoride and dichloride, whereas the opposite is true for SO_2ClF. These results can be used to controvert the claim that reaction of PbF_2 with SO_2Cl_2 produces SO_2ClF exclusively. Heats of formation of SO_2Br_2, SO_2BrF, and HSO_3Br have been estimated and shown to be compatible with their formation and decomposition modes. An explanation is given for the partial hydrolysis of SO_2F_2 as compared with the complete hydrolysis of SO_2ClF.

THE chemistry of sulphuryl chlorofluoride has not been examined in detail, apart from its use in fluorosulphonylation [1] and as a diluent [2] or solvent [3] for carbonium-ion formation using antimony pentafluoride. It is a potential source of fluorosulphite anions,[4] fluorosulphonium cations, and SO_2F radicals.[5] Thermodynamic data on SO_2ClF are needed to assess its possible role in preparative chemistry. The data are used in this paper first to examine the rationale of a recent preparation of sulphuryl chlorofluoride from lead(II) fluoride and sulphuryl chloride in acetonitrile [6] which is claimed to produce SO_2ClF and PbClF with the implication that the chlorofluorides cannot interact. Secondly the equivalence of heats of formation of isolectronic and isostructural F and OH compounds [7] can be further tested by contrasting SO_2ClF with chlorosulphuric acid [$SO_2Cl(OH)$].

EXPERIMENTAL

Different samples of SO_2ClF were used for calorimetric measurements. The first, prepared from NaF and SO_2Cl_2 in acetonitrile,[8] was purified by fractionation (1 atm,‡ 10 °C). The second, a commercial sample (Aldrich Specpure grade), was distilled *in vacuo* and a mid-fraction taken. Purity was checked by hydrolysing samples with excess of potassium hydroxide for 1 h. Aliquots of the hydrolysate were analysed for (1) total H^+ (back titration with HCl), (2) SO_4^{2-} as $Ba[SO_4]$, (3) Cl^- as AgCl, and (4) F^- (titration with $CeCl_3$).[9]

Calorimetry.—A conventional isoperibol calorimeter was used for solid and solution samples with a 'rotating-bell' device for gas samples.[10] Samples of SO_2ClF (*ca.* 0.3 g), condensed into a glass weighing tube fitted with a Teflon tap, were allowed to warm to room temperature and expand into a glass syringe (100 cm³) fitted with a three-way tap. The gas in the syringe was injected into the calorimeter under the gas holder. Aliquots of the hydrolysate were removed for analyses after the calorimetric measurements, and the heats released per mol of SO_2ClF (Table 1) were calculated from the analytical results.

The heat of precipitation of PbClF was found by adding solutions of KF from the sample holder to saturated solutions of lead(II) chloride in the calorimeter. The identity of the precipitate was proved by X-ray powder data as described below. The reactions involved were (1) and (2).

$$SO_2ClF(g) + 4K[OH](aq) \longrightarrow (K_2[SO_4] + KF + KCl)(aq) \quad (1)$$

$$PbCl_2(sat.) + KF(aq) \longrightarrow PbFCl + KCl(aq) \quad (2)$$

$\Delta H_f^{\ominus}(SO_2ClF, g)$ was calculated using the following auxiliary $\Delta H_f^{\ominus}$ values and assuming gas ideality: OH^-, −230.0; Cl^-, −167.4; F^-, −335.7; SO_4^{2-}, −907.5; and H_2O, −285.85 kJ mol⁻¹. $\Delta H_f^{\ominus}(PbClF, s)$ required knowledge of the heat of formation of the real saturated solution of lead(II) chloride and not that of the hypothetical standard state derived from ion values. This was obtained from solubilities of lead chloride.[11] All the data from 15 to 35 °C were collated and the average slope of a plot of the logarithm of solubility against $(T/K)^{-1}$ over 5 °C intervals was found. The average heat of solution was 14.4(8) kJ mol⁻¹ [σ = 0.8(3)] at 25 ± 10 °C. [The whole of the data from 0 to 100 °C gave an average value of 14.5(2) kJ mol⁻¹ but with a larger deviation because one set of data was inconsistent with the rest.]

TABLE 1

Heats of hydrolysis of *ca.* 0.3 g SO_2ClF in 0.226 5 mol dm⁻³ K[OH]

Amount of products (mmol)			Heat released (kJ mol⁻¹)			Mean *
H^+	Cl^-	SO_4^{2-}	H^+	Cl^-	SO_4^{2-}	(kJ mol⁻¹)
	2.135	2.148		499.3	496.3	497.8
3.294	3.257	3.304	495.4	500.7	494.7	496.6
3.552	3.548	3.560	500.2	500.8	499.1	500.1
3.198	3.188	3.206	500.2	501.8	499.0	500.3
3.989	4.013	4.004	498.4	494.8	495.9	496.9
						498.3
						(σ = 1.8)

* Weighted 2 : 1 : 1 to accord with the analytical accuracy of the H^+, Cl^-, and SO_4^{2-} analyses.

TABLE 2

Heats of precipitation of PbClF obtained by adding KF solutions to saturated $PbCl_2$ solution

Weight of KF solution * (g)	Weight of added KF (g)	Heat released (kJ mol⁻¹ of KF)
5.0766	0.4940	32.46
5.3783	0.5234	32.33
5.2632	0.5122	32.77
4.9363	0.4804	33.07
		Mean 32.66
		(σ = 0.33)

* Aliquot weights of a KF (30.178 H_2O) solution were added to 350 cm³ of saturated $PbCl_2$ solution.

Re-examination of PbF_2–SO_2Cl_2 *Reaction*.—Two samples of SO_2ClF were prepared by the lead(II) fluoride method.[6] The compositions of the solid residues were analysed from X-ray powder patterns by measuring the intensities of the

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† Systematic names for the title compounds are sulphonyl chloride fluoride and lead chloride fluoride, respectively.

‡ Through this paper: 1 atm = 101 325 Pa.

{211}, {102}, and {012} reflections for $PbCl_2$, PbClF, and PbF_2 respectively by means of a counter diffractometer. The relative proportions of pairs of components were determined using the relationship quoted in ref. 12. The PbClF : $PbCl_2$ ratio was 2 : 1 in one preparation and much less in the other preparation. (The only difference in the preparative conditions was in the drying of PbF_2 which may have partly converted the β into the α form in the preparation with the higher ratio.)

The purity of the PbClF precipitated in the calorimetric measurements was also checked by the same method. The mixed halide contained less than 1% of PbF_2 or $PbCl_2$ which corresponded to the limit of dectection as judged from synthetic mixtures of PbClF + 5% PbF_2 or $PbCl_2$.

Both samples after fractionation as described [6] contained residual sulphuryl fluoride. This was shown indirectly by the inconsistent heats of hydrolysis obtained with these samples. [The heat of alkaline hydrolysis of SO_2F_2(g) is 275.4 kJ mol^{-1} compared with 498.3 kJ mol^{-1} of SO_2ClF(g).] It was confirmed directly by observing the ^{19}F n.m.r. spectra at −50 °C.

Thermal Decomposition of SO_2ClF.—Samples were sealed in thick-walled tubes (previously degassed at 350 °C) and held at 300 °C for 5 d. The presence of 22% SO_2F_2 in the residue was estimated from the ^{19}F n.m.r. spectra. Free chlorine was also present.

Comparative rates of hydrolyses of the S–Cl and S–F bonds were followed by inserting a LaF_3 crystal electrode and a silver electrode in the calorimeter. A salt bridge ($K[NO_3]$ in an agar–agar gel) was used to connect with an external calomel electrode. The voltages generated between each electrode in the calorimeter and the external electrode were applied to separate pH meters and suitably amplified outputs applied to a dual X-t recorder. The response of each electrode system was checked with chloride and fluoride additions before and after each hydrolysis.

DISCUSSION

The heat of formation of lead chlorofluoride has not been measured previously. A reported [13] value of 534.7 kJ mol^{-1} is presumably derived from Hood and Woyski's free-energy data.[14] They measured HCl : HF ratios over a temperature range 610.5 ± 57.5 K for the forward and

$$HF(g) + PbCl_2(s) \rightleftharpoons PbClF(s) + HCl(g) \quad (3)$$

back reactions (3) and obtained a $\Delta G^{\ominus}$ value of 7.15 ± 0.35 kJ at *ca.* 600 K and a $\Delta H^{\ominus}$ value of 6.03 kJ over the above temperature interval. Assuming the $H_T^{\ominus} - H_{298}^{\ominus}$ function for PbClF is the mean of those for $PbCl_2$ and PbF_2, the overall enthalpy change at 298 K is only 0.2 kJ more negative than at 600 K and thus $\Delta H_f^{\ominus}$ (298) for PbClF is −535.6 kJ mol^{-1}.

The value derived from the heat of precipitation of 32.66 ± 0.33 kJ mol^{-1} for the stoicheiometry (4) is

$$1.30PbCl_2\ (1\,700\ H_2O) + KF\ (30\ H_2O) \longrightarrow PbClF(s) + KCl\ (1\,900\ H_2O) + 0.30PbCl_2\ (7\,000\ H_2O) \quad (4)$$

−538.4 kJ mol^{-1}. The main errors in this determination are associated with the heats of solution (−14.5 ± 0.8 kJ) and dilution of lead(II) chloride (0.3 kJ). The former was calculated from solubility data [11] and the latter assumed equal to twice the dilution heat of the chloride ion. The solubility of lead chlorofluoride is sufficiently depressed by the presence of lead and chloride ions that one can neglect any thermal effect of its solubility. The identity of the chlorofluoride was checked by a quantitative *X*-ray analysis.

Another value for the heat of precipitation of PbClF (36.6 kJ mol^{-1}) has been measured and applied in an enthalpic determination of fluoride.[15] It is 3.9 kJ more exothermic partly due to our use of a more concentrated fluoride solution. However, not enough information is available to calculate the heat of formation of PbClF since heats of dilution in the complicated salt mixture $Pb[ClO_4]_2$, $Na[O_2CMe]$, $MeCO_2H$, and NaCl were not measured.

Lead chlorofluoride is more stable than the mean of the dihalide values in agreement with its ready preparation from the latter in solution or melt. Reaction (5) is

$$\tfrac{1}{2}(PbF_2 + PbCl_2) \longrightarrow PbClF \quad (5)$$

exothermic by 26.7 kJ and exoergonic by 33.0 kJ at 25 °C.[14] The entropy change is small enough to be neglected when considering stabilities.

Conversely, the heat of formation of sulphuryl chlorofluoride is slightly less negative than the mean of the corresponding dihalide values. Hence the chlorofluoride cannot be obtained by equilibrating the dihalides, rather the mixed compound would tend to disproportionate as in (6). In practice the thermal decomposition of SO_2Cl_2

$$SO_2ClF(g) \longrightarrow \tfrac{1}{2}[SO_2Cl_2(g) + SO_2F_2(g)] + 11.9\ kJ \quad (6)$$

$$SO_2ClF(g) \longrightarrow \tfrac{1}{2}[SO_2(g) + Cl_2(g) + SO_2F_2(g)] + 30.7\ kJ \quad (7)$$

assists the reaction [equation (7)] shown by experiment. (The free-energy change would be smaller because of the increase in gas volume.)

The supposition that lead fluoride is a specific reagent for producing sulphuryl chlorofluoride [6] can be tested using the data collected in Table 3 since only minor entropy changes will be involved in the exchange reactions (8)—(10). Thus there is no thermodynamic

TABLE 3

Standard heats of formation (kJ mol^{-1}) of chlorofluorides in comparison with dihalides and hydroxy-halides

	Gas	Liquid	Solid	
SO_2F_2 (1) [a]	769.7	788.5	PbF_2 (3)	664.0
	6.9	9.4		
$SO_2F(OH)$ [b]	762.8	797.9	PbF(OH)	
SO_2Cl_2 (2) [c]	382.1	394.1	$PbCl_2$ (4) [c]	359.4
Mean of (1) and (2)	575.9	591.3	Mean of (3) and (4)	511.7
SO_2ClF	564.0	590.5	PbClF	538.4
	5.8	7.4		
$SO_2Cl(OH)$ [b]	558.2	597.9	PbCl(OH)	

[a] M. Cartwright and A. A. Woolf, *J. Fluorine Chem.*, 1977, **9**, 495, corrected by an *RT* term. [b] G. W. Richards and A. A. Woolf, *J. Chem. Soc.* (*A*), 1967, 1118. [c] Ref. 13.

barrier to complete replacement of chlorine although it is true that the intermediate PbClF is unable to fluorinate sulphuryl chloride. Experimentally we find that lead(II) chloride and sulphuryl fluoride accompany the chlorofluorides and hence reactions (8) and (9) occur. The

$$PbF_2(s) + SO_2Cl_2(l) \longrightarrow PbFCl(g) + SO_2ClF(g) + 44.3\ kJ \quad (8)$$

$$PbClF(s) + SO_2ClF(g) \longrightarrow PbCl_2(s) + SO_2F_2(g) + 26.7\ kJ \quad (9)$$

$$PbClF(s) + SO_2Cl_2(l) \longrightarrow PbCl_2(s) + SO_2ClF(g) - 9.1\ kJ \quad (10)$$

latter replacement is likely to be kinetically controlled and could be facilitated by changing to higher boiling solvents and longer contact times. There is no advantage in using lead(II) fluoride in place of sodium fluoride since both produce SO_2F_2 as a by-product.

The figures in Table 3 also confirm the expectation that the heat of formation of sulphuryl chlorofluoride can be predicted from the 'isoelectronic heat'[7] of chlorosulphuric acid. The analogy between these compounds is similar to that between sulphuryl fluoride and fluorosulphuric acid. Both acids are slightly more stable in the liquid state than the sulphuryl halides because of hydrogen bonding and this stability sequence reverses in the gas-phase comparisons. We can also predict that the heat of formation of PbCl(OH) will be close to that of PbClF and of PbF(OH) to PbF_2.

A thermochemical comparison with the corresponding bromo-compounds can be made since the heat of formation of thionyl bromide is known[13] (-74.1 kJ mol^{-1}). The heat of formation of sulphuryl bromide can be estimated by extrapolation of the series SO_2F_2, SO_2Cl_2, and SO_2Br_2 in comparison with the series SOF_2, $SOCl_2$, and $SOBr_2$. The average value obtained by plotting heats of formation against molecular weights on log-linear, linear-log, and linear-linear scales was -173 ± 14 kJ mol^{-1}. The heat of formation of sulphuryl bromofluoride or of bromosulphuric acid can then be approximated as the mean heat of SO_2F_2 and SO_2Br_2, *i.e.* -472 kJ mol^{-1}. The above values are consistent with the known properties of the bromo-compounds. Sulphuryl bromide is unknown because the reaction $SO_2Br_2 \longrightarrow SO_2 + Br_2$ is a mechanistically feasible endergonic reaction. Bromosulphuric acid can be formed from HBr and SO_3 but is unstable to disproportionation. Sulphuryl bromofluoride, made from BrF and SO_2, has been shown to undergo an analogous thermal decomposition.[16] Estimates of the heats of these reactions are given in Table 4.

TABLE 4

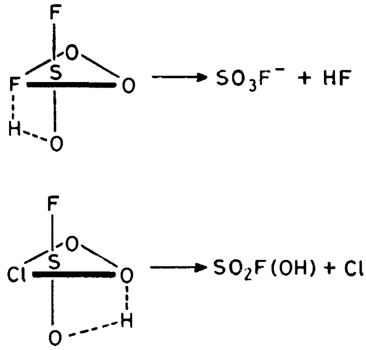
Estimates of exothermicity of reactions involving sulphuryl bromo-compounds

Reaction	$\Delta H^{\ominus}$/ kJ mol^{-1}
$SO_2Br_2(g) \longrightarrow SO_2(g) + Br_2(g)$	90
$BrF + SO_2 \longrightarrow SO_2BrF$	20
$HBr(g) + SO_3(g) \longrightarrow HSO_3Br(g)$	48
$HSO_3Br(g) \longrightarrow \frac{1}{2}[H_2SO_4(l) + SO_2(g) + Br_2(g)]$	67
$SO_2BrF \longrightarrow \frac{1}{2}[SO_2F_2(g) + SO_2(g) + Br_2(g)]$	45

The hydrolysis of sulphuryl chlorofluoride differs from that of sulphuryl fluoride which only proceeds as far as the fluorosulphate stage [equations (11) and (12)]. This result is perplexing because one would expect the same fluorosulphate ion (stable to alkali) to be formed as intermediate. In the mixed halide the S–Cl bond is much weaker than the S–F bond as can be seen by comparing bond energies in any analogous set of S–F and S–Cl compounds. Direct experimental evidence also shows that chloride ions are produced faster than fluoride ions during the hydrolysis, although absolute rates could not be measured because of the different response times of the specific ion electrodes used and the response of the fluoride electrode to hydroxide ions. Hence different intermediates or mechanisms must be involved.

$$SO_2F_2 + 2K[OH] \longrightarrow K[SO_3F] + KF + H_2O \quad (11)$$

$$SO_2ClF + 4K[OH] \longrightarrow K_2[SO_4] + KF + KCl + 2H_2O \quad (12)$$



SCHEME

One possibility is a covalent intermediate which is more susceptible to hydrolysis than the fluorosulphate ion. This is based on previous observations that aqueous fluorosulphuric acid can be produced quantitatively by ion exchange from an alkaline fluorosulphate solution, whereas hydrolysis of the predominantly covalent anhydrous fluorosulphuric acid gives major amounts of sulphate and fluoride in addition to some fluorosulphate ions.[17]

Assuming hydroxide-ion attack in both reactions is *trans* to the most electronegative ligand, the five-coordinate intermediates and their subsequent eliminations can be formulated as in the Scheme, where the covalent HSO_3F is hydrolysed very rapidly compared with SO_3F^-

[9/1078 *Received, 10th July, 1979*]

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