

THE HEAT OF FORMATION OF SULPHURYL FLUORIDE
AND THE STABILITY OF FLUOROSULPHATES

M. CARTWRIGHT and A.A. WOOLF

School of Chemistry, University of Bath, Bath BA2 7AY (Great Britain)

SUMMARY

A standard enthalpy of $-767.2 \text{ kJ mol}^{-1}$ was determined for sulphuryl fluoride from the heat of alkaline hydrolysis, and a standard free energy of $-720.8 \text{ kJ mol}^{-1}$ derived. The thermodynamically preferred product of ionic fluorosulphate decompositions is always sulphuryl fluoride. Kinetic control must predominate when sulphur trioxide is the main product.

INTRODUCTION

A direct measure of the heat of formation of sulphuryl fluoride was required to complete the series H_2SO_4 , HSO_3F [1], SO_2F_2 in which hydroxyl groups are replaced successively by fluorine. From previous work [2] we expected the heat of the difluoride to be close to that of fluorosulphuric acid. However, the only experimental value [3], obtained from electron impact studies, was considerably higher than expected even when the large experimental error was taken into account.

The thermal decomposition of fluorosulphates seems to depend on the cation and only a few salts decompose to sulphuryl fluoride. [4] A knowledge of the free energy of the difluoride is needed to check whether these are equilibrium situations before speculating on structural effects which could influence kinetically controlled decompositions.

EXPERIMENTAL

Sulphuryl fluoride (Matheson \star 99.5%) was further purified by fractionation in vacuo and the purity verified by infra-red spectra. Potassium fluorosulphate was prepared in anhydrous acetic acid [5] and dried in vacuo.

Calorimetric measurements

The calorimeter and measuring system have been described [6]. Modifications were made for introducing gas samples. The gas was contained in a glass cylindrical vessel closed by metal needle-valves (Hone) and could be displaced by mercury in an attached reservoir. The whole unit was immersed and equilibrated in the thermostat. In one set of experiments the gas was bubbled through a glass sinter about 5 cm below the liquid level in the calorimeter. Because the rate of gas absorption was slow in aqueous solutions the medium was changed to 2 M KOH in ethanol (95%) in which the gas could be dissolved at a rate of 10 ml min^{-1} and react within a time suitable for this type of isoperibol calorimetry. Some insoluble solid, a mixture of fluoride, sulphate and fluorosulphate, was produced and hence the heats of formation of these salts were determined in the alcoholic solution from the heats of neutralization of the corresponding acids.

In a second set of experiments it was possible to use aqueous 0.1 M KOH as the calorimetric medium by trapping the gas in a glass "bell" under the liquid and stirring through the gas-liquid interface to accelerate the gas absorption. The "bell" was of 5 cm diameter and 3.5 cm depth through the top of which was sealed a 1 cm tube of 3.5 cm length as a stirrer guide. The stirrer was U-shaped so that the arms agitated the annular space containing gas and liquid. Any air trapped under the "bell" was allowed to escape via a fine polythene tube before connecting this tube to the gas reservoir for the introduction of sulphuryl fluoride. Reactions were completed within 5 min. and homogeneous solutions resulted. Ancillary heats of solution were determined directly in situ. The calorimetric fluid was renewed for each experiment.

Analytical methods

As soon as thermal measurements were complete weight aliquots (circa 50 g) were removed and the alkali neutralized with the appropriate strength of HCl. Free fluoride was then determined by potentiometric titration with cerium(III) chloride using a glass - Ag/AgCl electrode system. The titrant was standardized against NaF solutions matched with the unknown. Fuller details are described in an accompanying paper. The time which elapsed between introducing the gas and the end of the fluoride titration was noted in order to extrapolate the fluoride value back to its value at the mean time of the primary reaction. This required a knowledge of the rate of hydrolysis in the alcoholic medium and was found in a separate experiment.

The amount of sulphuryl fluoride which had reacted was obtained from the total sulphur content in the remaining calorimetric fluid. This was determined by completing the hydrolysis, removing all fluoride with boiling hydrochloric acid and then precipitating BaSO_4 .

TABLE 1

Heats of reaction of SO_2F_2 in 2 M KOH in 95% EtOH

SO_2F_2 dissolved /mM	F^- produced /mM	H^+ /mM	Extrapolation time/min	F^{-*} /mM	$\text{F}^-/\text{SO}_4^{=}$	Heat released /kJ mol ⁻¹ of SO_2F_2
1.650	2.268	4.02	13.5	2.126	1.288	268.4
1.557	2.620	4.21	16.5	2.418	1.553	312.9
0.776	1.443	2.72	19.0	1.315	1.695	335.8
1.045	1.450	2.56	12.0	1.362	1.303	276.9
0.851	1.582	2.72	17.5	1.453	1.708	344.2

* Extrapolated value with indicated time interval and rate from Table 2.

TABLE 2

Time variation of secondary hydrolysis of SO_2F_2 in 2 M KOH in 95% EtOH

Time* /hrs.	F ⁻ /mM	Hydrolysis %	
		Total	Secondary**
0.39	1.93	56.8	13.6
0.80	2.13	62.6	25.2
1.05	2.33	68.3	36.6
1.42	2.58	75.8	51.6
2.72	3.04	89.5	79.0
26.0	3.40	100.0	100.0

* Time from start of gas absorption

** (Total - 50) x 2

TABLE 3

Heats of solution of KOH and H_2O in 2M KOH in 95% EtOH

KOH/g	Heat released /kJ mol ⁻¹	H_2O /g	Heat released /kJ mol ⁻¹
0.3900	25.81	4.899	0.696
0.5767	29.68	4.922	0.700
0.5867	28.95	5.084	0.697
0.5825	26.85		
Mean	27.82 ± 1.80	Mean	0.698 ± 0.011

TABLE 4

Heats of neutralization in 2 M KOH in 95% EtOH

HF solution [*] /g	H ₂ O added/g	Total heat released/J	Heat due to neutr'n/J	Heat released /kJ mol ⁻¹ HF
1.0529	4.5044	1181.8	968.7	45.57
0.8281	4.4551	1002.4	798.9	47.81

* HF solution 40.37 w/w HF. 1 g of this solution forms 0.3635 g H₂O on neutralization. The heat of solution of H₂O is deducted

H ₂ SO ₄ soln. [*] /g	Total H ₂ O in reaction/g	Total heat released/J	Heat due to neutr'n/J	Heat released /kJ mol ⁻¹ H ₂ SO ₄
5.3514	4.7479	1639.8	1455.9	149.56
5.1643	4.5815	1560.0	1382.5	147.18
2.3457	2.0810	687.5	606.9	142.23

* H₂SO₄ solution 17.84% w/w H₂SO₄. 1 g of this solution forms 0.3674 g H₂O on neutralization

HSO ₃ F [*] /g	Total heat released/J	Heat of H ₂ O dissolution/J	Heat released /kJ mol ⁻¹ HSO ₃ F
0.2469	425.4	1.72	171.7
0.3148	549.3(5)	2.20	173.8

* 100% HSO₃F

TABLE 5

Heats of reaction of SO_2F_2 in 0.1 M KOH in H_2O

SO_2F_2 dissolved/mM	KOH solution/g	F^- produced /mM	Heat released /kJ mol ⁻¹ of SO_2F_2
1.851	347.6	1.835	275.3
1.964	289.9	1.952	276.7
1.918(6)	318.7	1.909	275.3
2.055	326.0	2.014	274.9
2.000	345.4	2.025	274.6
			Mean 275.4 ± 0.7

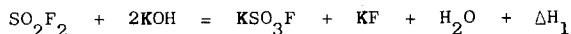
TABLE 6

Heats of solution of solids in 0.1 M KOH in H_2O

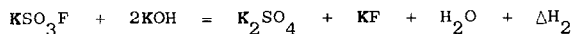
$\text{KSO}_3\text{F/g}$	Heat absorbed /kJ mol ⁻¹	KF/g	Heat released /kJ mol ⁻¹
0.4732	27.23	1.4781	17.10
0.5081	28.31	1.4100	16.47
0.6896	28.98		
0.6968	27.62		Mean 16.79 ± 0.31
0.6053	28.54		
	Mean 28.14 ± 0.57		

RESULTS AND DISCUSSION

The results are collected in Tables 1 to 6. In alcoholic solution the heat of primary hydrolysis ΔH_1



is accompanied by amounts of heat $f \cdot \Delta H_2$ from the partial secondary hydrolysis



where f is the fractional part of the second hydrolysis determined by the analytical ratio of free fluoride to total sulphur. The best values for ΔH_1 and ΔH_2 , evaluated by a least squares method, were 223.3 and 167.2 kJ mol⁻¹ respectively. The ancillary heats enabled the heats of formation of the potassium salts to be deduced in the state in which they existed in the alcoholic medium and thence to calculate $\Delta H_f^{\text{O}}(\text{SO}_2\text{F}_2)_g$ as -795.8 kJ mol⁻¹.

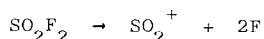
In aqueous solutions it was shown by analyses that the primary hydrolysis alone had occurred. The heat of this unique hydrolysis together with two ancillary heats yielded a $\Delta H_f^{\text{O}}(\text{SO}_2\text{F}_2)_g$ of -767.2 kJ mol⁻¹,

The hydrolysis of sulphuryl fluoride has been investigated by Cady and Misra [7] who report much higher gas solubilities in water than obtained previously. Although they state that the gas dissolved rapidly in water this was true when the gas-water interface was agitated vigorously in a closed system as in their own experimental procedure. In flow systems much of the gas passes through the liquid and this probably accounts for the low solubilities reported by previous workers. With the gas in solution hydrolysis was rapid and followed a rate law $d[\text{SO}_2\text{F}_2]/dt = -K[\text{SO}_2\text{F}_2][\text{OH}^-]$. The secondary hydrolysis was also pseudo-first order using excess alkali but with rate constants which were smaller by orders of magnitude [8]. In alcoholic solution the secondary rate increased and became more comparable with the primary one.

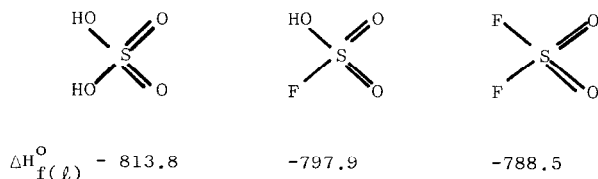
A reliable value for the heat of primary hydrolysis was obtained in deci-molar solutions of aqueous alkali. The rate-determining step in the calorimeter was the rate of solution of gas

because the above rate law indicated extremely rapid hydrolysis when it had dissolved. The value obtained in a flow system using alcoholic potash as the medium was not regarded as reliable because of the concomitant secondary hydrolysis which occurs at a slow rate almost from the start of the measurement. The extrapolation made to allow for secondary hydrolysis was based on fluoride analyses in media of changing alcohol and alkali contents and is imprecise. In addition the enthalpy values assigned to the partly soluble salts are uncertain although we attempted to produce them and measure heats in situ.

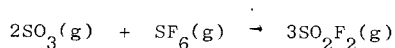
The only previous enthalpy value was derived from the appearance potential of SO_2^+ at 19.9 ± 0.3 eV resulting from electron impact on sulphuryl fluoride [3]. The suggested process



leads to $\Delta H_f^\circ (\text{SO}_2\text{F}_2)_g$ of -861.9 ± 30 kJ mol^{-1} assuming that fluorine atoms are produced in their ground state. The difference of 95 kJ mol^{-1} between values could indicate that the fluorine atoms are carrying excess kinetic energy. Credence can be given to the new value because it confirms an already established trend. Replacing a hydroxyl group by fluorine in hydrogen sulphates or sulphuric acid hardly alters the heats of formation [2]. A further replacement in fluorosulphuric acid would also be expected to continue the trend

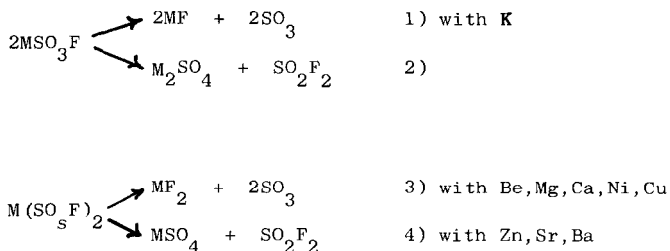


Because substances have to be compared in the same states a hypothetical liquid state for sulphuryl fluoride is quoted derived by adding the heat of vapourization [9]. A comparison can be made between gaseous molecules $\Delta H^\circ \text{HSO}_3\text{F}(g)$ -762.8 and $\Delta H^\circ \text{SO}_2\text{F}_2(g)$ -767.2 kJ mol^{-1} . A lower limit to the heat of formation is set by the occurrence of the reaction



which means that the free energy of sulphuryl fluoride is more negative than $\Delta G[(2\text{SO}_3 + \text{SF}_6)/3]$ and hence its enthalpy would be more negative than -675 kJ mol^{-1} . The free energy of the above reaction would have a very small temperature variation.

Muetterties and Coffmann [4], who made the most thorough study of the formation and pyrolysis of ionic fluorosulphates, found as had earlier workers that two modes of decomposition were available



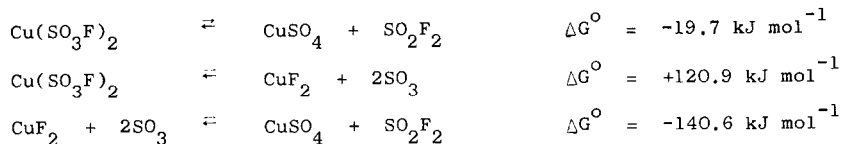
Mercuric and sodium salts yielded mixtures with appreciable amounts of sulphuryl fluoride. They suspected that the differences had a thermodynamic basis. This can now be evaluated by deciding if the products from 2) and 4) are more, or less, stable than the alternative products from 1) and 3). This amounts to comparing the free energy differences $\Delta G^\circ(\text{M}_2\text{SO}_4 - 2\text{MF})$ or $\Delta G^\circ(\text{MSO}_4 - \text{MF}_2)$ with $\Delta G^\circ(2\text{SO}_3 - \text{SO}_2\text{F}_2)$.

The entropy of sulphuryl fluoride [10] relative to the elements can be calculated as $\Delta S_{298}^\circ - 155.6 \text{ J mol}^{-1} \text{ K}^{-1}$ and hence $\Delta G^\circ(\text{SO}_2\text{F}_2)_g$ is $-720.8 \text{ kJ mol}^{-1}$ and $\Delta G^\circ(2\text{SO}_3 - \text{SO}_2\text{F}_2)_g$ is $-21.3 \text{ kJ mol}^{-1}$. A free energy difference (Δ) between sulphate and fluoride which is more negative than $-21.3 \text{ kJ mol}^{-1}$ means that the decomposition to sulphuryl fluoride is favoured. This is the situation with all the above salts (ΔNa , -184.9 ; K , -250.2 ; Mg , -159.4 ; Zn , -158.6 ; Ca , -158.6 ; Sr , -172.0 ; Ba , -204.6 ; Cu , -162.0 ; kJ mol^{-1}). The magnitude of these differences is too large for reversal in the temperature range used for pyrolysis.

It is significant that, although the figures for zinc, calcium and copper salts are close in value, only the zinc fluorosulphate produces sulphuryl fluoride on heating. It seems probable that in most experiments the continuous removal of product prevented equilibration. The only true equilibrium experiment, in which a mixture of calcium sulphate and sulphuryl fluoride remained

unaltered after 12 hours at 773 K [4], conforms with thermodynamic expectation. Kinetic control must predominate when sulphur trioxide is the main product. It should be noted that fluorination of sulphur trioxide by a fluoride would be thermodynamically feasible and hence mixed products would reflect an interplay of kinetic and thermodynamic factors.

Some figures for cupric salts illustrate the equilibrium possibilities [2].



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