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Thermochemistry of disulphur oxyfluorides

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Abstract

The formation enthalpies of $S_2O_6F_2$, $S_2O_5F_2$ and the unknown $S_2O_4F_2$, the fluoro analogues of persulphuric, disulphuric and dithionic acids respectively, are predicted using some new data to show the stability order $S_2O_5F_2 > S_2O_4F_2 > S_2O_6F_2$. Estimated enthalpies of the other isomers of $S_2O_4F_2$ lead to a similar sequence, $FOS{-}O{-}SO_2F > FO_2S{-}SO_2F > FOS{-}O{-}O{-}SOF$. A synthesis is suggested for $S_2O_4F_2$ and its boiling point is predicted to be intermediate between $S_2O_6F_2$ and $S_2O_5F_2$ with the same interval as in the known series where trifluoromethyl replaces the SO_2F group. Optimized geometries of the $S_2O_4F_2$ isomers are reported and the large electron affinity of the fluorosulphate radical confirmed via a semi-empirical calculation.

Introduction

The fluorides listed in Table 1 can be considered either as SO_2 and SO_3 insertions into difluorine, or as the fluoro analogues of proton acids in which OH is replaced by F. Both viewpoints have utility in property estimations. Benson [1] has reviewed the thermodynamic properties of sulphur-containing

TABLE 1

Estimates of the formation enthalpies of sulphur oxyfluorides

Compound	Ideal symmetry	Acid analogue	Estimates (kJ mol^{-1})		B.p. (K)
			Benson [1]	New	
$FO_2S{-}O{-}O{-}SO_2F$	C_{2h}[a]	peroxo disulphuric	[−1150 (g), −1156 (g)]	[−1154 (g)] [−1190 (l)]	340
$FO_2S{-}O{-}SO_2F$	C_{2v}	disulphuric	–	[−1238 (g)] [−1260 (l)]	324
$FO_2S{-}SO_2F$	C_{2h}	dithionic	[−1037 (g)]	[−1092 (g)] [−1118 (l)]	[307]
$FOS{-}O{-}SO_2F$	C_1	–	–	[−1168 (g)]	[307]
FSO_2F	C_{2v}	sulphuric	−770 (g)	[−789 (l)]	218

[a] Raman spectrum indicates C_2 symmetry. Estimates are in square brackets.

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molecules and radicals. Additional data are now available for re-examining the values for the above fluorine compounds. Benson's estimates relied on group additivity, bond dissociation energies from kinetic experiments and, most·importantly, on the near thermal equivalence between corresponding fluoro and hydroxo compounds which he named 'homothermal pairs'. This correspondence has also been referred to as 'isoelectronic heats' [2] and applies to ionic as well as covalent compounds with small differences within pairs accounted for by the extent of hydrogen bonding.

Results and discussion

Peroxo disulphuryl difluoride

Although this fluoride, first reported in 1955 [3], has been the most extensively studied of the fluorides there is no experimental enthalpy value. Benson estimated it in two ways. Firstly, he compared it with its hydroxy analogue persulphuric acid, for which $\Delta H_f^0[H_2S_2O_8\ (aq.)]$ is known [4]. A gas-phase value was derived assuming a larger energy to convert to the gas than with sulphuric acid and then an added stabilization energy for replacing OH by F (i.e. $-1339+197-8=-1150$) [for brevity the units (kJ mol^{-1}) are omitted after all heats]. Secondly, by assuming the bond energy $D(HOSO_2O-H)$ in sulphuric acid was the same as $D(RO-H)=435$ in aliphatic alcohols, he derived $\Delta H_f^0(SO_3OH)=-523$ and hence $\Delta H_f^0(SO_3F)=-531$. Because a mean dissociation energy of $S_2O_6F_2$ into radicals has been established as 94 by a variety of methods [5–7], a value $\Delta H_f^0(S_2O_6F_2)=-1156$ follows. An apparently independent route is to use a Born–Haber cycle. Jenkins calculated a lattice energy (U) for NH_4HSO_4 and quoted $\Delta H_f^0(SO_3OH^-)=-1012$ [8]. Using this figure, $U(KHSO_4)$ would be -660 as shown:

$$\begin{tikzcd}
K^+\ (g) & + & SO_3OH^-\ (g) \arrow[ddrr, "U=-660"] & & \\
& & & & \\
K \arrow[uu, "514"] & + S + & 2O_2 \arrow[uu, "-1012"] + 0.5H_2 \arrow[rr] & & KSO_3OH\ (cryst.)\ (\Delta H_f^0=-1158)
\end{tikzcd}$$

We assume $\Delta H_f^0[SO_3OH^-\ (g)] \sim \Delta H_f^0[SO_3F^-\ (g)]$ similar to the almost identical heats of alkali fluoro and hydroxo sulphates [2], e.g. $\Delta H_f^0[KSO_3F\ (cryst.)]=-1162$. This together with a recently measured electron affinity $EA_{298}(SO_3F)$ of 4.9 eV [9], corrected to 5.0 eV (see later), yield $\Delta H_f^0[SO_3F\ (g)]=-530$ and $\Delta H_f^0[S_2O_6F_2\ (g)]=-1154$ in good agreement with Benson's values. However the EA value is not an independent value because it is computed from the heats of deprotonation, ΔH_{dp}, between strong acids and their weak conjugate bases via the relationship:

$$\Delta H_{dp}=IE(H)+D(FO_2SO-H)-EA(SO_3F)$$

in which the dissociation energy had been obtained from Benson's $\Delta H_f^0(SO_3F)$ values. Because of a revision to $\Delta H_f^0[HSO_3F\ (g)]=-763$ [10], $D(FO_2SO-H)=$

449 and the electron affinity value increases to 5.00 eV. At least there is a self-consistency when the new data are introduced.

In view of the accumulated uncertainties in these estimations, as well as the assumptions made, a direct experimental verification is needed. This could be effected by contacting NO with $S_2O_6F_2$, perhaps in a fluorocarbon or fluorocarbon ether solvent, in the bell-type apparatus described previously [11]. Nitrosonium fluorosulphate would precipitate after an exothermic reaction with a calculated heat evolution of 454 per mol $S_2O_6F_2$. Although the reaction would be a radical one, the amount of SO_3F in equilibrium at room temperature would be too small to warrant any heat correction.

Disulphuryl (pyrosulphuryl) difluoride

Enthalpy estimation of this compound in the gas state is relatively straightforward. A value exists for the solid acid analogue, $\Delta H_f^0[H_2S_2O_7$ (cryst.)$] = -1274$ [4], which taken together with a ΔH_{vap} value of 32 (from the vapour pressure/temperature curve for $S_2O_5F_2$) and a ΔH_{fusion} value of 12 (using Walden's entropy of fusion constant, 54 J K^{-1} mol^{-1}) yields $\Delta H_f^0[S_2O_5F_2$ (g)$] = -1238$, allowing for an extra stabilization (8) when F replaces OH. The corresponding figures for the monosulphur pair $\{\Delta H_f^0[SO_2F_2$ (g)$] = -770$ and $\Delta H_f^0[HSO_3F$ (g)$] = -763\}$ support the assumption of a nearly athermal exchange of OH by F.

Thus it appears that $S_2O_5F_2$ is more stable than $S_2O_6F_2$ by about 84, a quantity comparable with the enthalpy difference between the salts $K_2S_2O_7$ (cryst.) and $K_2S_2O_8$ (cryst.) of 74 [4]. These estimates are also compatible with the observed deoxygenation reactions in the gas phase at room temperature which should be highly exothermic:

$$S_2O_6F_2 + X \longrightarrow S_2O_5F_2 + XO$$

where $X = CO, PF_3, SOF_2, COCl_2$.

Dithionyl difluoride

This fluoride, named after the corresponding dithionic acid, has yet to be prepared, but as usual with fluorides it should be more kinetically stable than dithionic acid which has only been isolated in aqueous solution. Again Benson derived $\Delta H_f^0[HO(SO_2)_2OH$ (g)$] = -1029$ from the aqueous value assuming the same difference between aqueous and gas phase enthalpies of 167 as for sulphuric acid which is probably an overestimate.

The alternative approach is via the dimerization of the fluorosulphite radical. The most direct route is to employ the experimentally determined $D(FO_2S-F)$ from shock tube studies [13]. Possible values of 339 and 397 were obtained. The former value was selected as giving a better fit to the data, but Benson queried the choice because the pre-exponential factor appeared too small. However a value of 389 can be extrapolated from the consideration of $D(S-F)$ as a function of bond length (Fig. 1). The shorter the bond the greater the double bond character and bond strength. Dissociation energies were taken from the two data sets for the stepwise defluorination

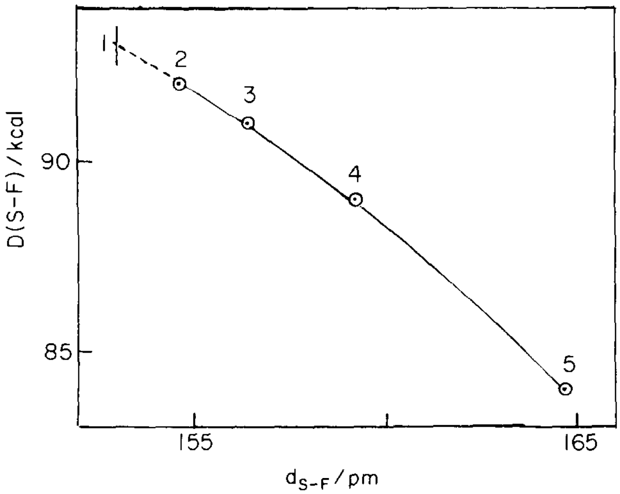


Fig. 1. Dissociation energies of the S−F bond, D(S−F), as a function of bond length, d_{S-F} [1, SO_2F_2; 2, SF_4 (equatorial); 3, SF_6; 4, SF_2; 5, SF_4 (axial)].

TABLE 2

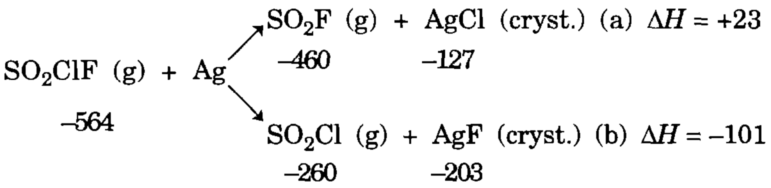
Derivation of the enthalpy of formation of the SO_2F radical

Energies	Derivation
$D(FO_2S-F) = 389$	see Fig. 1.
$\Delta H_f^0 SO_2F = -460$	$SO_2F_2 \rightarrow SO_2F + F + D(S-F)$ $-770 \quad 79 \quad -389$
$D(FO_2S-Cl) = 225$	$SO_2ClF \rightarrow SO_2F + Cl + D(S-Cl)$ $-564 \quad -460 \quad 121$
$\Delta H_f^0 SO_2Cl = -260$	$SO_2Cl_2 \rightarrow SO_2Cl + Cl + D(S-Cl)$ $-364 \quad 121 \quad -225$
$D(ClO_2S-F) = 383$	$SO_2ClF = SO_2Cl + F + D(S-F)$ $-564 \quad -260 \quad 79$

of SF_6 to SF [14, 15]. For SF_4, the weaker axial (longer) bond is assumed to break first. A value for the equatorial bond is estimated as 10% greater by comparison with a similar estimate on PF_5. Finch partitioned the average D(P−F) value over the equatorial and axial bonds in proportion to their force constants [16]. The enthalpy value $\Delta H_f^0[SO_2F\ (g)] = -460$ follows from $D(FO_2S-F)$. The consistency of the D(S−F) value can be tested using experimental heats of formation of other sulphuryl halides [10] as shown in Table 2.

This derivation shows the transferability of S−Cl and S−F bond energies between the sulphuryl halides. The initial and final D(S−F) values differ by no more than the sum of uncertainties in the enthalpy values. The experimental values $\Delta H_f^0(SO_2Cl^-) = -565$ and the electron affinity $EA(SO_2Cl) = 2.55$ eV, obtained mass spectrometrically from the $Cl^- + SO_2Cl_2$ reaction [12], yield $\Delta H_f^0(SO_2Cl) = -319$ and give inconsistent $D(S-F)$ values when taken through a similar derivation to that in Table 2. Both experimental values must be erroneous (see later).

A dissociation energy $D(FO_2S-SO_2F)$ is all that is required to complete the estimation. An approximate value of 172 can be taken from the S−S bond-breaking energy in diaryl sulphones leading to $\Delta H_f^0[S_2O_4F_2\ (g)] = -1092$ in fair agreement with Benson's estimation. The uncertainties in both estimates cannot be resolved until $S_2O_4F_2$ has been prepared and a heat of formation determined by, for example, alkaline hydrolysis to KF and $K_2S_2O_6$. A reasonable preparation would be by abstraction of chlorine from SO_2ClF with a 'class-b' metal vapour such as silver. The S−Cl bond should cleave preferentially since $D(S-Cl)$ is much weaker than $D(S-F)$. The feasibility of forming the SO_2F radical is shown by the exothermicity of reaction (a) as compared with the endothermicity of forming SO_2Cl in (b). With other metals, both reactions are exothermic. This accords with the experimental observation (unpublished work) that both $NiCl_2$ and NiF_2 form when SO_2ClF reacts with excess Ni at room temperature, admittedly in MeCN solution.



A low-pressure hydrogen discharge with SO_2ClF vapour would also favour SO_2F production over SO_2Cl.

An estimate of the boiling point and vapour pressure of $S_2O_4F_2$ should help in the choice of an experimental procedure for its preparation. The former can be estimated as 34 °C from the $\Delta = A + BR$ line [17] for the insertion of SO_2 into the fluorides and other molecules listed in Fig. 2. Thus the boiling points of $S_2O_6F_2$, $S_2O_5F_2$ and $S_2O_4F_2$ are equally spaced as in the sequence CF_3SO_3OF, CF_3SO_2OF and CF_3SO_2F where CF_3 replaces SO_2F and again the same 17 °C interval is encountered. A heat of vaporization and vapour pressures can be obtained from the boiling point using the numerous extant relations listed in ref. 22.

From the relative enthalpies of $S_2O_4F_4$, $S_2O_5F_2$ and $S_2O_6F_2$ it should be possible to oxidize $S_2O_4F_2$ with $S_2O_6F_2$ providing the kinetic barrier to oxygen transfer is not excessive, i.e.

$$S_2O_4F_2 + S_2O_6F_2 \longrightarrow 2S_2O_5F_2 \qquad \Delta H = -230$$

This compares with the $S_2O_6F_2$ oxidation of SOF_2 to SO_2F_2 ($\Delta H = -310$).

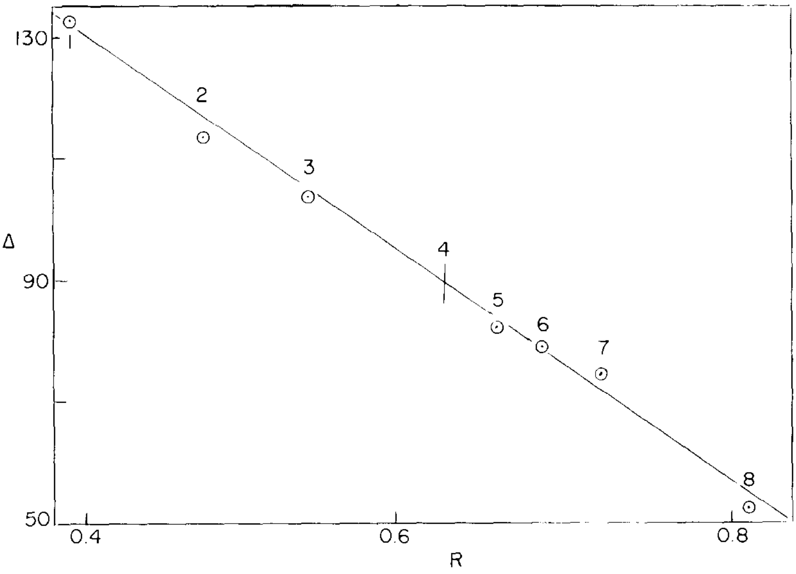


Fig. 2. Elevation of boiling point, Δ, on insertion of SO_2 into molecules as function of the mass ratio, R, before and after insertion. [Inserted molecules: 1, F—F; 2, FOF; 3, Cl—Cl; 4, FSO_2F; 5, FSO_3F; 6, FSO_2NF_2; 7, $FOSF_5$; 8, SF_5OOSF_5. $\Delta = 197.7 - 175.8R$, $r = -0.994$.]

Isomers of $S_2O_4F_4$

Unlike SO_3F radicals, the fluorosulphite radical can dimerize in more than one way, namely by O—S, S—S and O—O links giving decreasingly less stable molecules in line with decreasing bond energies. The weakest bond strength $D(O-O)$ should be between $D(F_5SO-OSF_5) = 155$ [18] and $D(FSO_2O-OSO_2F) = 94$ in persulphuryl difluoride. The strongest bond strength $D(S-O) = 248$ is derived from:

$$\begin{array}{llll} S_2O_5F_2 & \longrightarrow SO_2F & + SO_3F & + D(S-O) \\ -1238 & \quad -460 & \; -530 & \end{array}$$

The $D(S-S)$ value of 172, quoted earlier, lies between them. Hence the stability order expected is $FOSOSO_2F(II) > FO_2S-SO_2F(I) > FOS-O-O-SOF(III)$. The polarity within the SO_2F radical, making sulphur positive with respect to O and F, should favour dimerization to the most stable form (II). Alternatively, the thermodynamically favourable dismutation to SO_2F_2 and SO_2 may be preferred.

Semi-empirical molecular orbital calculations

Stewart has recently reparameterized the MNDO programme and claims his PM3 programme [19] considerably reduces errors with hypervalent molecules containing S or P atoms. (However the parameters may not be fully optimized. Over a fifth of the quoted enthalpy values, which were compared with calculated ones, must be estimates since they refer to unknown molecules or their fragments.) It is of interest to compare our estimated values with the PM3 calculations. The three $S_2O_4F_2$ isomers were geometrically optimized and perspective views, together with Newman projections viewed along the S to S links, are collected in Fig. 3. The symmetrical structures I and III, with both sulphurs in the same oxidation state, have the expected *anti* conformation of fluorines whereas the unsymmetrical structure II with S^{IV} and S^{VI} has a gauche conformation with the fluorines at 86°. This is probably an example of an 'anomeric effect' [20]. An electron transfer is seen in the lengthening of S_1-O_1 relative to the other terminal S–O bonds

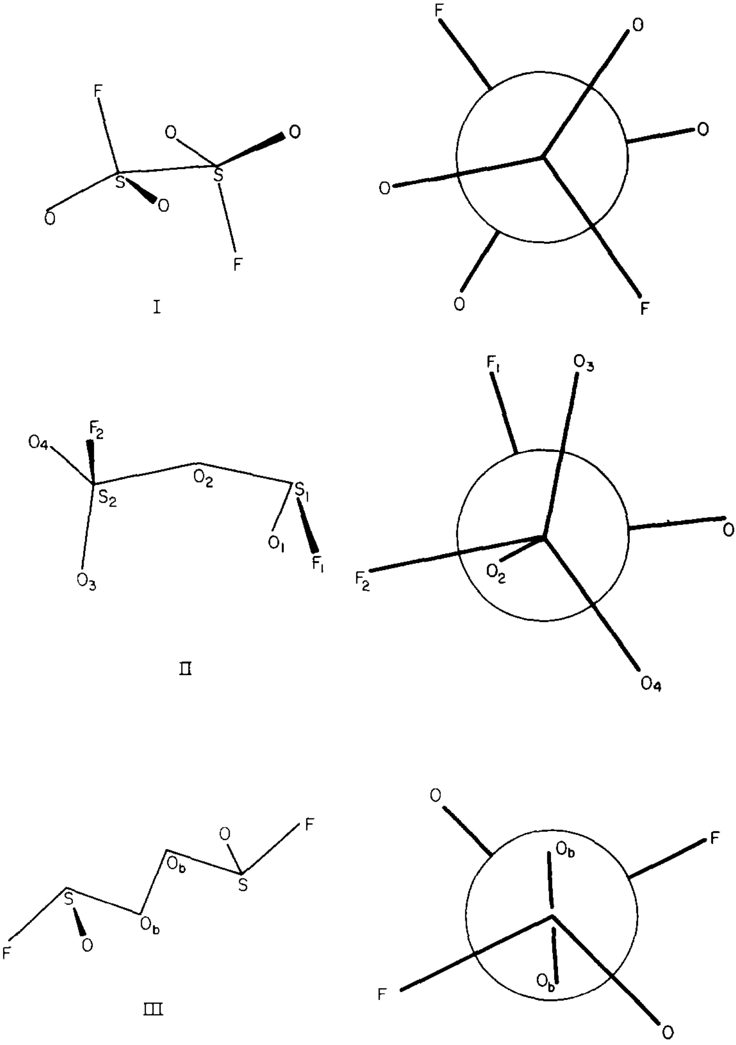


Fig. 3. Optimized geometries of $S_2O_4F_2$ isomers: [bond lengths (pm) and angles (to nearest degree)]. I: SF 157, SO 144; FSO, 106, OSO 122, FSS 103, OSS 109. II: S_1F_1 157, S_2F_2 154, S_1O_1 145, S_2O_2 140, SO (bridge) 167; $F_1S_1O_1$ 100, $F_2S_2O_3$ 108, $O_4S_2O_3$ 126, $F_1S_1O_2$ 96, $S_1O_2S_2$ 152. III: SF 157, SO 146, SO (bridge) 172, O_bO_b 152; FSO 101, OSO_b 96, SO_bO_b 107.

TABLE 3

Comparison of calculated and experimental electron affinities (*EA*)

Species	ΔH_f^0 [a]	Electron affinity			Difference (2) − (1)
		Calc. (1)	Expt. (2)		
SO_3F SO_3F^-	−486 −978	492	483 [9]		−9
SO_2Cl SO_2Cl^-	−240 −582	342	−260[b] −618 [21]	358	+16
SO_2F SO_2F^-	−429 −715	286	−460[b] −731 [21]	271	−15

[a] PM3 calculations.

[b] See Table 2 for derivation.

and a shortening of the *anti* S_2-F_2 bond compared with the other S_1-F_1 bond. A similar explanation has been advanced to explain gauche fluorines in 1,2-difluoroethane.

The S—F, S—O and O—O bond lengths are near to the experimental values found in other molecules, but the bridging SOS angle in II is much more obtuse than the 124° angle observed in the more symmetrical $S_2O_5F_2$ or disulphate anion. The calculated $\Delta H_f^0 = -1142$ for II is in reasonable agreement with our estimate of −1168. However, values for isomers I and III, at −770 and −774 respectively, are obvious underestimates for the true values which must be greater than twice that of $\Delta H_f^0(SO_2F)$, i.e. −920. At least, the calculations confirm that the most stable isomer is the unsymmetrical one. The electron affinities, referred to earlier, can be found from the difference between the calculated heats of formation of the radical and anion. Errors in individual 'PM3' values will tend to cancel when differences are calculated between similar species with approximately matching geometries (see Table 3).

There is quite good agreement between the calculated and experimental values. The SO_2X^- values were determined by ion cyclotron resonance as X^- equilibrated with SO_2. The electron affinity of SO_2Cl is about 1 eV greater than claimed previously [12] and interestingly much larger than the electron affinity of SO_2F.

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