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ISOELECTRONIC HEATS OF FORMATION. A COMPARISON OF FLUORO AND  
HYDROXO-COMPOUNDS

A.A. WOOLF

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

SUMMARY

Enthalpies of formation of fluoro-compounds are compared with those of corresponding hydroxo-compounds to see how general is the equality of enthalpies found between ionic fluorosulphates and hydroxosulphates. A restricted correlation exists when one or two fluoro groups are interchanged with hydroxo groups. Differences can be rationalised in terms of hydrogen bonding. The survey indicates a lack of thermochemical data on organic isoelectronic pairs and on fluoro-substituted octahedral complexes. Examples of approximations which can be made with isoelectronic heats are given.

Estimating enthalpies of fluorides has been necessary both to make predictions about their stabilities and to check the reasonableness of experimental results with reactive materials. The methods employed have used interpolations or extrapolations of series. Thus Hoppe extrapolated along series such as  $\text{SbF}_3$ ,  $\text{TeF}_4$ ,  $\text{IF}_5$  to predict stabilities of xenon fluorides [1]. Alternatively heats can be derived from electronegativities, the inverse operation to obtaining electronegativity values from limited sets of heat data. Sanderson has carried the use of electronegativities to an extreme in deriving atomization heats [2] but this method, like the data fitting of Wilcox and Bromley [3], carries a number of arbitrary parameters. In one form or another these methods are related to periodicity and hence the underlying atomic structure.

Another relation which could provide estimates of formation enthalpies of fluoro-species was encountered when fluorosulphuric acid was introduced as a calorimetric medium [4]. It was found that salts of hydrogen sulphates had almost identical heats of formation with fluoro-sulphates of the same cation. (See Table 1). The array is self-consistent in that differences between corresponding pairs of salts agree within a few Kcal.mol<sup>-1</sup>.

TABLE 1

Comparison of heats of formation of fluorosulphates with corresponding salts (Kcal.mol<sup>-1</sup> at 298K)

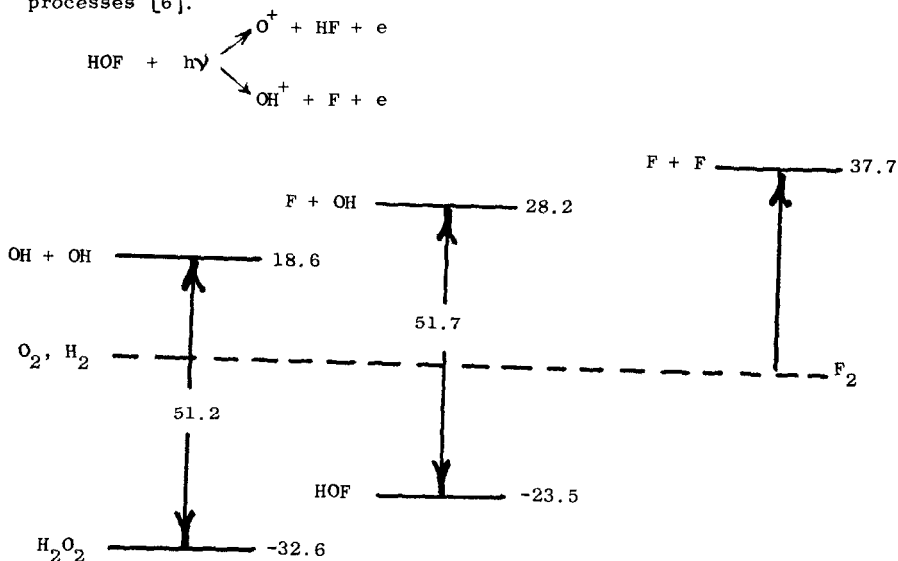
NO <sub>2</sub> SO <sub>3</sub> F	-162.2	NO <sub>2</sub> (SO <sub>3</sub> OH) <sup>a</sup>	-	NO <sub>2</sub> ClO <sub>4</sub>	8.7
NOSO <sub>3</sub> F	-180.8	NO(SO <sub>3</sub> OH)	-182.5	NOCLO <sub>4</sub>	-9.0
KSO <sub>3</sub> F	-276.8	K(SO <sub>3</sub> OH)	-276.8	KClO <sub>4</sub>	-103.2
NaSO <sub>3</sub> F	-268.9	Na(SO <sub>3</sub> OH)	-269.1	NaClO <sub>4</sub>	-91.5

<sup>a</sup>Dissociates to (NO<sub>2</sub>)HS<sub>2</sub>O<sub>7</sub> + HNO<sub>3</sub>

Thus interchanging OH with F in these salts does not appreciably change the enthalpy value. Now it is well known that such interchanges can be readily carried out between some types of isostructural compounds which indicates small free energy, and hence enthalpy, changes because the entropy differences are small.

Thus in many minerals the F/OH ratio can vary between wide limits. Indeed the partial replacement of OH by F in hydroxo-apatites is the basis for producing the protective enamel on teeth; the "specific" ion lanthanum fluoride electrode responds similarly to hydroxyl ions; in pharmaceutical chemistry the replacement of OH by F has been widely practised. It seemed reasonable to postulate that the constancy of enthalpies was connected with the isoelectronic nature of fluorine and hydroxyl in ionic or covalent forms, although it was recognized that direct comparisons could be misleading because of the thermochemical reference state. In addition hydrogen-bonding would be expected to stabilize compounds when such bonding was possible.

The simplest example is provided by a comparison of gaseous  $F_2$ ,  $H_2O_2$  and HOF. Arguments for regarding the latter as a hydroxo-fluoride have been advanced [5]. The heat of formation of the unstable HOF ( $-23.5 \pm 1 \text{ Kcal.mol}^{-1}$ ) has been estimated indirectly from photo-ionization processes [6].



Although the heat of formation of HOF is less than that of  $H_2O_2$ , the heats of dissociation to isoelectronic radicals are equal within experimental error. In this comparison the reference levels are eliminated. The facile dissociation of fluorine, which is anomalous with respect to the other dihalogens in a group comparison, can be regarded as an extrapolation of an isoelectronic series  $CH_3-CH_3$ ,  $H_2N-NH_2$ ,  $HO-OH$ . However a direct comparison of  $H_2O_2$  with  $F_2$  is not possible because the arbitrary zero level of the latter is not eliminated.

The effects of hydrogen bonding can be seen in a comparison of the enthalpies of  $H_2O$  with HF in different phases.

$H_f^o / \text{Kcal.mol}^{-1}$	$H_2O$	HF	
Gas	-57.80	-65.32	8.5
Liquid	-68.32	-72.55	4.2
Solid <sup>a</sup>	-69.7	-73.5	3.8

<sup>a</sup>The latent heat of fusion has been added to obtain this state.

An interpretation of these figures is that gaseous hydrogen fluoride remains polymerised unlike water vapour. In the liquid phase the difference is narrowed; the lesser polymerisation, which is likely with two dimensional F---H---F bonding compared with the three dimensional network in water, is more than compensated by the greater strength of the fluorine hydrogen-bonding.

Bearing these points in mind the comparison of ionic fluorosulphates and hydrogen sulphates can be extended to covalent species and to the neighbouring oxy-acids and their derivatives viz.

$OP(OH)_3$	$O_2S(OH)_2$	$O_3Cl(OH)$	
$OAs(OH)_3$	$O_2Se(OH)_2$	$O_3Br(OH)$	$(O_4Kr)$
$HSb(OH)_6$	$Te(OH)_6$	$OI(OH)_5$	$O_2Xe(OH)_4$

Available data on heats of formation in the liquid state are as follows:

$OP(OH)_3$	-304.4	$O_2S(OH)_2$	-194.5	$O_3Cl(OH)$	-9.7
$OP(OH)_2F$	-	$O_2S(OH)F$	-190.7	$O_3ClF$	-10
$OP(OH)F_2$	-	$O_2SF_2$	-188.5		
$OPF_3$	-300				
$OAs(OH)_3$	-215	$O_2Se(OH)_2$	-123	$O_3Br(OH)$	+24.5 <sup>b</sup>
$OAs(OH)F_2$	-	$O_2Se(OH)F$	-125 <sup>a</sup>	$O_3BrF$	-
$OAs(OH)_2F$	-	$O_2SeF_2$	-118 <sup>a</sup>		
$OAsF_3$	-				

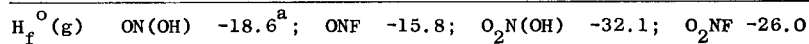
<sup>a</sup> Unpublished measurements

<sup>b</sup> Estimated from  $H_f(HClO_4 + KClO_4 - KBrO_4)$

The heats of formation of the sulphur oxo-compounds decrease slightly in the liquid state as the extent of hydrogen bonding lessens (Sulphuric acid has a sheet like structure  $SO_4 \cdot 4H/2$  compared with a chain like fluorosulphuric acid  $SO_3F \cdot 2H/2$ ). Hydrogen-bonding of fluorosulphuric acid is lessened in the gas phase when the enthalpies of  $HSO_3F$  and  $SO_2F_2$  converge. (-182.3 and -183.4 respectively). Only the end members of the phosphorus series have been measured and again are almost equal.

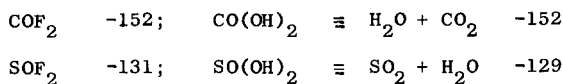
The selenic acid series is another complete set which confirms the pattern in the tetrahedral iso-structures. Unfortunately there are no sets of measurements on the octahedral oxo-anions or acids. (The salts  $\text{KSb}(\text{OH})_6$ ,  $\text{KSb}(\text{OH})_2\text{F}_4$ ,  $\text{KSBF}_6$ , and the acid  $\text{OI}(\text{OH})\text{F}_4$  are known). All that can be done is to compare solid telluric acid with tellurium hexafluoride, the end members of a rather extended set ( $\text{H}_f^{\text{O}}\text{Te}(\text{OH})_6$  -307,  $\text{TeF}_6$  -334). The telluric acid is destabilized relative to the fluoride which could reflect the distortion in the regular octahedral coordination [7]. The enthalpy difference corresponds to about 2 Kcal for each of the 12 hydrogen bonds to the eight neighbouring molecules.

In the first short period, where the coordination number is three for oxygenated species, the only comparisons are of nitryl and nitrosyl fluorides with the corresponding acids.



<sup>a</sup> Mean of cis and trans forms.

Carbonyl fluoride can be compared with carbonic acid, even though the latter does not exist in the gas phase, by summing the component oxide heats. That this is legitimate is shown by similarly estimating the heat of thionyl fluoride.



It might be expected that extensive comparisons could be made between fluoro and hydroxo compounds of carbon. However, the paucity of thermochemical data is illustrated by the complete collection (Table 2) gleaned from the standard sources [8].

The figures can also be interpreted in terms of hydrogen-bonding influences in the different phases. The heat of formation of hexafluorobenzene which cannot hydrogen bond, is identical within experimental error to that of perfluoro-phenol. The latter would not be expected to hydrogen-bond appreciably in the gas phase. In the corresponding hydrogen substituted aromatics, fluorobenzene is likely to bond more strongly than phenol in the gas phase in a similar manner to which  $\text{HF}(\text{g})$  is more associated than  $\text{H}_2\text{O}(\text{g})$ . In the liquid state the situation is reversed. Thus the mean of the gas and liquid phase

TABLE 2

Heats of formation of corresponding hydroxo and fluoro organic substances ( $-\Delta H_f^\circ$  in Kcal mol<sup>-1</sup>)

Substance	Gas (g)	Liquid (l)	Solid	(g+l)/2
C <sub>6</sub> F <sub>5</sub> OH	228.8		244.9	
C <sub>6</sub> F <sub>6</sub>	228.5	237.0		
C <sub>6</sub> H <sub>5</sub> OH	23.0	39.5		31.3
C <sub>6</sub> H <sub>5</sub> F	27.8	36.0		31.9
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	30.0		47.6	
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> F	35.3	44.7		
p-HOC <sub>6</sub> H <sub>4</sub> OH	63.4	87.1		75.2
p-FC <sub>6</sub> H <sub>4</sub> F	70.3	78.9		74.6
o-HOC <sub>6</sub> H <sub>4</sub> COOH	118.3		141	
o-FC <sub>6</sub> H <sub>4</sub> COOH			135.7	
m-FC <sub>6</sub> H <sub>4</sub> COOH			139.1	
p-FC <sub>6</sub> H <sub>4</sub> COOH	118.2		140.0	
n-C <sub>3</sub> H <sub>7</sub> OH	61.2	72.5		
n-C <sub>3</sub> H <sub>7</sub> F	69.4			
CH <sub>2</sub> (OH) <sub>2</sub>	-98			
CH <sub>2</sub> F <sub>2</sub>	-106.8			
CH <sub>3</sub> COOH	103.3	115.8		109.5
CH <sub>3</sub> COF	106.4	112.4		109.4
CH <sub>2</sub> OHCOOH			158.1	
CH <sub>2</sub> FCOOH			161.0	
CH <sub>2</sub> OHCH <sub>2</sub> OH		108.7		
CH <sub>2</sub> FCH <sub>2</sub> OH		111.3		

enthalpies tend to converge within the pairs as is also illustrated with the other two available pairs. The difference between HF(g) and H<sub>2</sub>O(g) (8.5) is most closely approached in the alkyl fluoride pairs (8.2 and 8.8) and least with the acetyl pair, because of the relative stability of acetic acid dimers in the vapour.

Measurements of the heats of combustion of acyl and perfluoroacyl fluorides in comparison with their acids would be a useful contribution especially since the enthalpy differences between fluorides and acids can be linked by aqueous solution calorimetry.

The approximate equality between enthalpies of hydroxo and fluoro compounds cannot be expected to hold when the pairs are not iso-structural. Thus fluorides of Groups I, II and III have larger enthalpies than the corresponding hydroxides. The hydroxo-compounds of Group IV, V and VI tend to occur in condensed anions whereas the fluorides are either discrete octahedra, or apex joined ones. Again it is not possible to make direct comparisons. Nevertheless as Group VI is approached crude approximations to the heats of formation of solid fluorides are obtained by simply adding heats of formations of oxides and water (e.g.  $\text{VF}_5 \equiv \frac{1}{2}\text{V}_2\text{O}_5 + 2\frac{1}{2}\text{H}_2\text{O}$ ). In general the estimates set lower limits. Some examples are collected in Table 3.

As an example of how the idea of isoelectronic heats can be applied consider the heats of formation of alkali fluoroiodates(V) and the corresponding oxyfluorides determined by Finch and his coworkers [9].

IOF <sub>3</sub>	-132.6;	KIF <sub>6</sub>	-356.5;	RbIF <sub>6</sub>	-352.1
IO <sub>2</sub> F	-58.9;	KIO <sub>2</sub> F <sub>2</sub>	-209.5;	RbIO <sub>2</sub> F <sub>2</sub>	-209.2

If F is considered approximately equivalent to OH thermochemically then the enthalpy difference between IOF<sub>3</sub> and IO<sub>2</sub>F should be numerically equal to the enthalpy of H<sub>2</sub>O(s), and that between the salts of IF<sub>6</sub><sup>-</sup> and IO<sub>2</sub>F<sub>2</sub><sup>-</sup> as twice this value i.e. 70 and 2 x 70 respectively compared with the actual differences of 73.7, 2 x 73.5 and 2 x 71.5 Kcal.mol<sup>-1</sup>. The alkali salts of the tetrafluoroiodate(V) can be predicted to have enthalpies close to 270 Kcal.mol<sup>-1</sup> and a similar pattern should be obtained with the enthalpies of the recently isolated fluorobromate(V) salts KBrO<sub>2</sub>F<sub>2</sub> and KBrOF<sub>4</sub> [10].

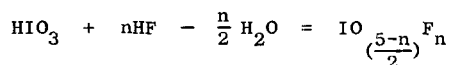
TABLE 3

Heats of formation of fluorides compared with estimate from oxide sum in parentheses

BF <sub>3</sub>	276 (258);	CF <sub>4</sub>	223 (210)
	SiF <sub>4</sub>	391 (357);	PF <sub>5</sub> <sup>*</sup> 381 (373); SF <sub>6</sub> 297 (310)
	GeF <sub>4</sub>	284 (279);	AsF <sub>5</sub> 300 (285); SeF <sub>6</sub> <sup>*</sup> 273 (260)
	SnF <sub>4</sub>	272 (279);	SbF <sub>5</sub> 322 (292); TeF <sub>6</sub> 334 (307)
TlF <sub>3</sub>	142 (146);	PbF <sub>4</sub>	222 (206)
	TiF <sub>4</sub>	394 (366);	VF <sub>5</sub> 355 (360); CrO <sub>2</sub> F <sub>2</sub> 204 (208)
		NbF <sub>5</sub>	433 (403); MoF <sub>6</sub> 380 (387)
		UF <sub>6</sub>	523 (503); WF <sub>6</sub> 418 (420)

\* Values are for the solid state except for PF<sub>5</sub> and SeF<sub>6</sub> for which liquid state values are given.

It is possible to generate the heats of formation of iodine pentafluoride and iodine oxyfluorides from that of iodic acid by assuming that thermo-neutral reactions occur in the solid state according to



	Enthalpies of solids/Kcal mol <sup>-1</sup>	
	Calc.	Experimental
IO <sub>2</sub> F	-59.2	-58.9
IOF <sub>3</sub>	-136.5	-132.6
IF <sub>5</sub>	-213.8	-213.5

The isoelectronic pair O<sub>2</sub>IF and O<sub>2</sub>I(OH) have enthalpies of -58.9 and -55.4 respectively.



The reverse process of estimating the heat of formation of a hydroxo-compound from a fluoride is given as another example. When the heat of formation of  $TiI_4$  was determined from the exothermic solution of  $TiI_4$  and  $TiCl_4$  in  $FeCl_3/HCl$  solutions [11] the results were only explicable if the titanium species formed in solution from  $TiI_4$  differed from those produced from  $TiCl_4$  i.e. different proportions of a series  $TiCl_{(6-n)}(OH)_n$ . An estimate of the thermal effect of replacing a Cl by OH was required. An upper limit to the increased stability of the complex after this displacement was taken as  $\frac{1}{4} H_f^O(TiF_4) - H_f^O(TiCl_4)$  which is  $50 \text{ Kcal.mol}^{-1}$ . This corresponded in a 3M HCl solution to an average presence of half a hydroxide group more in the species formed from  $TiI_4$  than from  $TiCl_4$ . In terms of single species this would be equivalent to the replacement of a quarter mole of  $TiCl_4(OH)_2$  by  $TiCl_2(OH)_4$  a change too small to be detected in normal Raman spectra but easily detected calorimetrically.

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