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A COMPARISON OF ENTHALPIES OF TETRAFLUOROAMMONIUM SALTS AND OTHER FLUORO-NITROGEN SPECIES

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SUMMARY

It is shown that enthalpies of nitrogen fluorides and oxo fluorides deviate markedly from enthalpies of corresponding hydroxo compounds, whereas there is good agreement (circa 2%) between carbon mono, di and trifluoro compounds and their hydroxo analogues. The extent of deviation correlates with the extra number of lone pair repulsions of fluoro over oxo compounds. The enthalpy of $NF_4^+(g)$ can be extrapolated from the other (N,F) and (N,O,F) compounds. The enthalpies of solid NF_4^+ salts are close to those of corresponding NO_2^+ salts and from this an exothermic heat of formation for $NF_4^+F^-$ is predicted.

INTRODUCTION

The determination of heats of formation for reactive fluorine compounds is difficult experimentally and liable to error. Hence any test of consistency with previously obtained values helps to reinforce confidence in the newer values. One such test with fluoro compounds is to compare their heats with those of isoelectronic and often isostructural hydroxo compounds, or, where the appropriate polyhydroxo compounds dissociate, with the sum of component oxide values [1]. In Table 1 all the available data on carbon-fluorine compounds and their hydroxo analogues are collected [2]. It can be seen that the values agree within 2-3%. The errors just perceptibly increase with fluorine substitution. In general the gaseous fluorides are slightly more stable than the corresponding hydroxo compounds, and vice versa for liquid or solid fluorides, in line with the differences found between the simplest pair,

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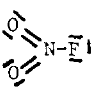
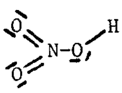
HF and HOH, which were ascribed to differences in hydrogen bonding association [1]. We do not expect the same accuracy in matching heat data as obtained by various methods of group additivity [3]. Rather, we employ the approximation in the spirit implied in the use of Raoult's 'Law'. It is never obeyed exactly but ideal values serve as a reference from which deviations can be rationalized in terms of specific interactions [4] and hence trends can be assessed.

Recent thermochemistry of tetrafluoroammonium salts [5,6] can be examined in the same way. In Table 2 the known enthalpies of nitrogen fluorides and oxo fluorides are compared with hydroxo analogues. Values for NF_2H and N_2F_4 have been omitted because it seems unlikely that enthalpies for the unknown compounds $NH(OH)_2$ and $N_2(OH)_4$ can be equated with those of ($HNO + H_2O$) and ($2NO + 2H_2O$) respectively. The hydroxo compounds are expected to be less stable just as hyponitrous acid is less stable than $N_2O + H_2O$ into which it decomposes.

For nitrosyl and nitryl fluorides the magnitudes of the differences from the hydroxo analogues are consistent with those encountered with mono-fluoro carbon compounds. However, the gaseous fluorides are less, rather than more, stable than the hydroxides. The magnitudes of the differences are similar to those found for the pairs ClO_3F - ClO_3OH, SO_2F_2 - $SO_2(OH)_2$ and OPF_3 - $OP(OH)_3$ [1]. The differences found with the N(III) and N(V) trifluorides are an order of magnitude larger than with any carbon compound apart from CF_4, and can no longer be ascribed to hydrogen bonding differences alone. It seems reasonable to suggest that the destabilizing effect results mainly from increasing lone pair repulsions with the increase in the number of fluorines. In Table 3 we correlate the deviations (A-B) with the differences in the number of lone pair-lone pair interactions in the fluoro-compound and hydroxo analogue. For example, we compare the lone pair counts



F-O 2(3x2) at 220 pm
O-O 2x2 at 219 pm



O-O(H) 2(2x2) at 221 pm
O-O(2x2) at 219 pm

and take the net difference of four lone pair repulsions as a rough measure of destabilization of the fluoro-compound. This type of crude counting of interactions can be related to enthalpies, as shown by the barriers to rotation in H_3C-CH_3, H_3C-NH_2 and H_3C-OH which are

TABLE 1

Comparison of heats of formation of carbon-fluorine compounds and hydroxo analogues ($-\Delta H_f^o$/kJ mol^{-1})

≥C-F compounds				Difference (%)
$nC_3H_7F(l)$	293	$nC_3H_7OH(l)$	303	-3.2
CH_3COF	456[a]	CH_3COOH	458[a]	-0.4
$HOCH_2CH_2F(l)$	466	$HOCH_2CH_2OH(l)$	474	-1.7
C_6H_5F	133[a]	C_6H_5OH	131[a]	1.9
$pFC_6H_4F(s)$	372	$pHOC_6H_4OH(s)$	365	2.0
			Mean:	$\|1.8\|$
$>CF_2$ compounds				
$OCF_2(g)$	640	$CO_2(g)+H_2O(g)$	635	0.7
$Cl_2CF_2(g)$	477	$Cl_2CO(g)+H_2O(g)$	460	3.6
$CFCl{=}CF_2(g)$	573	$2CO(g)+HCl(g)+H_2O(g)$	555	-3.1
$CF_2Cl{=}CF_2Cl(l)$	924	$ClOCCOCl(l)+2H_2O(l)$	932	0.7
			Mean:	$\|2.0\|$
$-CF_3$ compounds				
$HCF_3(l)$	716[c]	$HCOOH(l)+H_2O(l)$	711	0.7
$FOCF_3(g)$	775	$H_2O_2(g)+H_2O(g)+CO_2(g)$	771	0.5
$HOOCCF_3$	1054[b]	$HOOCCOOH+H_2O$	1047[b]	0.6
$CH_3CF_3(l)$	765[c]	$CH_3COOH(l)+H_2O(l)$	770	-0.7
$CH_2{=}CHCF_3(g)$	614	$CH_2{=}CHCOOH(g)+H_2O(g)$	588[c]	4.2
$HOCH_2CF_3(s)$	969[d]	$HOCH_2COOH(s)+H_2O(s)$	953	1.7
$C_6H_5CF_3(l)$	637	$C_6H_5COOH(l)+H_2O(l)$	653[d]	2.6
$HOCH_2CH_2CF_3(s)$	1003[d]	$HOOCCH(OH)CH_3(s)$[e]$+H_2O(s)$	986	1.7
$mHOOCC_6H_4CF_3(s)$	1070	$HOOCC_6H_4COOH(s)+H_2O(s)$	1095	-2.3
$F_3CCF_3(s)$	1375[c,d]	$HOOCCOOH(s)+2H_2O(s)$	1413	2.8
$CF_4(g)$	934	$OCF_2(g)+H_2O(g)$	882	5.7
			Mean:	$\|2.2\|$

[a] Mean heat of gas and liquid phases.

[b] Mean heat of gas and solid phases.

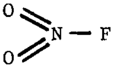
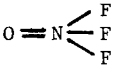
[c] Includes an estimated heat of vapourization based on Trouton's rule.

[d] Includes an estimated heat of fusion [7].

[e] $-(\Delta H_f^o)HOCH_2CH_2COOH$ is assumed equal to that of its isomer.

TABLE 2

Comparison of heats of formation of nitrogen-fluorine compounds and hydroxo analogues ($-\Delta H^o_f(g)$/kJ mol^{-1}).

	A		B	A-B
	66.3	HNO_2	78.0[a]	11.7
	108.8	HNO_3	134.3	25.5
$F-N=N-F$	-70.8[a]	$H_2N_2O_2$	20.5[b]	91.3
	131.5	$NOF + H_2O$	308.1	176.5
	163.2	$NO_2F + H_2O$	350.6	187.4

[a] Mean of cis and trans isomers.

[b] An estimate of the heat of aqueous solution of $H_2N_2O_2(g)$ as the mean of values for $HNO_2(g)$ and $N_2H_5OH(g)$ is included in this figure (41.4 and 46.4 kJ mol^{-1} respectively).

TABLE 4

Standard heats of formation of nitronium compared with potassium and tetrafluoroammonium salts with common anions ($-\Delta H_f{}^o$/kJ mol^{-1}).

	$NO_2{}^+$	K^+	$\Delta(NO_2{}^+-K^+)$		$NF_4{}^+$
SO_3F^-	-682	-1161[11]	479	Mean 474	-
ClO_4^-	-432	36[11]	468		-
BF_4^-	$\boxed{-1417}$	-1891[12]			-1410[6]
SbF_6^-	$\boxed{-1669}$	-2143[13]			-1669[6]

The boxed values are estimates assuming that the mean $\Delta(NO_2{}^+-K^+)$ value for the oxo-anion salts holds for the complex fluorides. Salts of the first three anions are often isostructural.

TABLE 3

Correlation of lone pair repulsions (l.p.) with destabilization of nitrogen-fluorine compounds

	Differences			Distances in pm		
	l.p. - l.p. count	in l.p. - l.p. counts	in enthalpies /kJ	Bonding N - F	Bonding N - O	Non-bonding
NOF	11 >	3	12	151.2	113.6	218(O,F)
HNO_2	8			143	118	216(O,OH)
NO_2F	16 >	4	25	146.7	118	220(O,F); 219(O,O)
HNO_3	12			140	121	219(O,O); 221(O,OH)
N_2F_2	22 >	9	91	140.9	---	220(N,F); 217(F,F)
$H_2N_2O_2$	13			unknown		
NF_3	36 >	25	177	137	---	213(F,F)
$NOF(+H_2O)$	11					
NOF_3	45 >	29	187	143.1	115.8	221(O,F); 221(F,F)
$NO_2F(+H_2O)$	16					

approximately in the ratios 3/2/1, as expected from peripheral bond-bond repulsions (9/6/3) [8]. Lone pair repulsions from fluorine have been invoked previously to rationalize the anomalously low dissociation energy of difluorine, and the reactivity of fluoro-aromatics and olefins [9]. The data in Table 3 show a remarkable constancy in non-bonding distances 219.2 ± 1.4 pm for ten distances (compare ref [21]), apart from the short (F,F) distance in NF_3, and show agreement between the sequence of destabilization energies and lone pair counts.

We can extrapolate this line of reasoning. At one end it is possible to predict that the heat of formation of NH_2F will be close to that of hydroxylamine since the difference in lone pair counts is only one, and at the other end that the heats of formation of NF_4^+ salts will approach that of corresponding NO_2^+ salts. The NF_4^+ cation is isoelectronic with $N(OH)_4^+$ which can be taken as equivalent to $NO_2^+ + 2H_2O$ for enthalpy calculations (the equilibrium between nitronium ions and nitracidium ions also indicates only a small heat change for $H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$).

The NF_4^+ is then destabilized by the six (F,F) edge repulsions less the (O,O) repulsions in NO_2^+. This predicted destabilization can now be compared with experiment results. $\Delta H_f^o NF_4(g)$ has been calculated, from Born-Haber cycles on NF_4^+ and K^+ salts with a common anion as 784 ± 30 kJ mol^{-1}, or from a single cycle on $NF_4^+BF_4^-$ as 854 ± 40 kJ mol^{-1} [6]. The ionization energy of NO_2^+ has been difficult to measure. The photo-ionization values are preferred [10]. Using a mean value of 935 kJ mol^{-1} for the ionization energy, the $\Delta H_f^o(NO_2^+)$ becomes 968 kJ mol^{-1}, and hence NF_4^+ is more stable, by 116 kJ mol^{-1}, if the mean value is used. NF_4^+ is destabilized by 335 kJ mol^{-1} compared with $(NO_2^+ + 2H_2O)$ and this can be associated with the difference of 50 lp-lp repulsions between the analogues (cf Table 3). It is roughly in line with extrapolations from NF_3 and NOF_3 (ie 50/25 x 177, or 50/29 x 187, from Table 3). However, in view of the large uncertainties in the $\Delta H_f^o(NF_4^+)g$ value, a more direct comparison of enthalpies of NF_4^+ and NO_2^+ salts in the solid state is attempted. Heats of formation of nitronium tetrafluoroborate and hexafluoroantimonate, although unmeasured can be estimated, as in Table 4, by assuming a constant difference of 474 kJ mol^{-1} between nitronium and potassium salts with a common anion. This figure is closely approached by considering Born-Haber cycles with a common anion. The difference in enthalpies is then the sum of ionization energy differences and lattice energy differences. The latter, approximated using Kapustinskii's formula by 2403×(radius sum difference/radius sum product), vary little with the radii involved; eg for NO_2ClO_4 - $KClO_4$ we obtain 484 kJ mol^{-1}, and for NO_2SbF_6 - $KSbF_6$ we obtain 472 kJ mol^{-1}. It seems that NF_4^+ salts are destabilized to a greater extent than NF_4^+ in the gas phase. The discrepancy would be reduced if $\Delta H_f^o(NF_4^+)$ were more positive and hence we favour Sinke's value of the two available.

Accepting that NO_2^+ and NF_4^+ salts have about the same enthalpies, an estimate for the heat of formation of $NF_4^+F^-$ as -91 kJ mol^{-1} can be made by equating $NF_4^+ F^-$ with the unknown $NO_2^+F^-$ and estimating the latter from KF using the $\Delta(NO_2^+ - K^+)$ difference in Table 4. The previous prediction of instability carries more uncertainty [6].

The lone pair repulsion approximation could be refined, for example, by allowing for the interaction distances and assuming some inverse repulsion law ($\propto 1/r^5$), provided that the thermochemical values were accurate enough. However, the present heats of formation of NF_4^+ salts carry large uncertainties. The heats derived from D.S. calorimetry are measured at temperatures in the range 100-400°C and it is arbitrarily assumed that $[H^T-H^o]$ correction terms for solid reactants and gaseous products cancel. Corrections for change of volume of products less salt have also been neglected. These are difficult to estimate because of varying temperature and extent of decomposition. Heats derived from aqueous solution calorimetry are bedevilled by uncertainties in the actual oxidation products formed in water, and a choice between values obtained in different aqueous media had to be made. Hence an alternative method is suggested for obtaining more precise values. This involves using pure bromine trifluorine as a non-aqueous calorimetric medium [11]. It is likely that the fluorinating couple NF_4^+/NF_3 will oxidise the solvent to bromine pentafluoride in which the salts are stable [14]. A heat of reaction of about 70 kJ mol^{-1} is anticipated for the reaction $NF_4^+SbF_6^- + 2BrF_3 = NF_3\uparrow + BrF_3.SbF_{5(BrF_3)} + BrF_{5(BrF_3)}$ using data in references [6, 16, 17, 15].

It might be assumed that quantum mechanical calculations could reveal the trends in stability of nitrogen fluorides and oxo fluorides. Heats of formation cannot be calculated ab initio with sufficient accuracy and hence it is usual to calculate bond separation energies and then derive heats of multi-atom molecules from smaller molecules

TABLE 5

Comparison of dissociation energies for substituted carbon tetrafluorides ($-\Delta H^{o}$/kJ mol^{-1}).

Dissociation reaction					Dissociation energy
CF_4	→	CF_3	+	F	
933		488		-79.4	524
CF_3OF[b]	→	CF_3	+	OF	396
775		488		-109	
CF_3CF_3	→	$2CF_3$			374
1350		2 x 488			
CF_3NF_2[a]	→	CF_3	+	NF_2	239
694		488		-33	
$CF_2(OF)_2$[b]	→	CF_2	+	2OF	302 x 2
570		184		-2 x 109	
$CF_2(NF_2)_2$	→	CF_2	+	$2NF_2$	169 x 2
455		184		2 x 33	

[a] This heat is an interpolated value in the measured series $CF_{4-n}(NF_2)_n$ where n = 0, 2, 3 and 4 [22].

[b] Ref [23].

of similar bond type. The results for N,O and N,F compounds are poor; NOF and HNO_2 are calculated to be 65 kJ mol^{-1} less stable than they actually are; NHF_2 (-32 kJ mol^{-1}) is calculated as within 5 kJ mol^{-1} of NH_2F. Much better agreement is obtained for heats of C,O and C,F compounds [18]. It is now more usual to use semi-empirical calculations in which experimental data is inserted to obtain atom or bond parameters. Thus Dewar and Rzepa inserted fifty properties of twelve fluorine-containing molecules including NF_3, NOF and CNF to obtain fluorine parameters in their MNDO calculations. In spite of this careful parametization, large errors for N,F and N,O,F compounds resulted [19] (eg. errors in kJ mol^{-1} for N_2F_4, 68; N_2F_2, 77; CNF, 47; NOF, 38; NO_2F, 13; NOF_3, 259; CF_3OF, 81.)

Ganguli and McGee with a MINDO programme incorporating fifteen bond lengths and parameters for nine molecules including HNO, HNO_2, HNO_3, N_2O_3, N_2O_4, NF_3, and NOF, calculated heats of N,O,F molecules reasonably well in spite of the use of an incorrect $\Delta H_f^o(F)g$ value [20]. However, any bond-addition scheme with this number of disposable parameters could hardly be less efficient.

It can be concluded that quantum calculations which do not take account of repulsion effects when more than one N-F or N-O bond is present in the molecule will give unrealistic results. The effects are only just noticeable with molecules containing C-F bonds and satisfactory calculations are possible.

Finally, as an illustration of the extreme destabilizing effects of fluoro-nitrogen groups compared with CF_3 or OF groups, we have calculated dissociation energies of substituted carbon tetrafluorides in Table 5. In this way we avoid the arbitrary partition of atomization energies into 'transferable' bond energies. The dissociation energies to trifluoromethyl and X radicals decrease in the order X = F, OF, CF_3, NF_2.

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