

Destabilization of fluoro imino and fluoro oxy compounds

Kevin Sudlow, Alfred A. Woolf *

Faculty of Applied Sciences, University of the West of England, Bristol BS16 1QY, UK

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Abstract

The stability enhancement when a C–H bond is replaced by a C–F bond vanishes when N–H is converted to N–F and is reversed in the O–H to O–F bond change in conformity with the greater fluorinating ability and lesser selectivity of *O*-fluoro reagents compared with the newer *N*-fluoro reagents. The enthalpy of the simplest such compound, monofluoramine, is estimated as -11.5 ± 0.6 kcal mol⁻¹ by interpolation of experimental values and from ab initio calculations. It is near to that of hydroxylamine (-12.0 kcal mol⁻¹) or ammonia (-11.0 kcal mol⁻¹). Strong electron-withdrawing groups further destabilize R₂NF compounds relative to R₂NH. More highly fluorinated *N*-fluoro compounds are also destabilized relative to their hydroxy analogues and this can be related to differences in the number of lone pair repulsions. A similar treatment of the destabilization of HOF and FOF relative to HOOH and HOOOH allows a value of $\Delta H_f^\circ(\text{H}_2\text{O}_3) = -16.7$ kcal mol⁻¹ to be approximated in between previous estimates and this is supported by an ab initio calculation which gives -17.2 kcal mol⁻¹.

Keywords: Fluoro imino compounds; Fluoro oxy compounds; Fluorination; Destabilization

1. Introduction

The fluorinating ability of some *N*-fluoro-pyridinium salts has been ordered in a recent communication [1]. In a continuation of this work with neutral X₂NF reagents we were surprised to find they were less stable than the corresponding imino compounds according to enthalpies calculated semi-empirically. This is in sharp contrast to the increased stability when a C–H bond is replaced by C–F as shown by the Benson increments used to estimate enthalpies, i.e. C(H)(C)₃ = -1.90 vs. C(F)C₃ = -48.5 or C(H)₂(C)₂ = -4.93 vs. C(F)(H)(C)₂ = -49.0 kcal mol⁻¹ [2].

Since the fluorinating ability of X₂NF reagents will be assisted by $\Delta H_f^\circ(\text{X}_2\text{NH})$ being more negative (more stable) than $\Delta H_f^\circ(\text{X}_2\text{NF})$, we have examined the conversion with the smallest possible reagent, H₂NF, because this is amenable to ab initio calculation when taken together with established experimental enthalpy values.

The effect of replacing fluorine in monofluoramine by a hydroxy group has also been considered in view of a previous prediction that it would be nearly athermal [3]. An extension to fluorine replacement by OH in fluoro oxy compounds is included because a recent

synthesis of hydrogen sesquioxide (H₂O₃) makes the latter more available for study [4].

2. Results and discussion

Bond dissociation energies are in the order O–H > C–F > C–H > N–H > N–F > O–F with N–F < N–H and O–F ≪ O–H [5]. However, *perfluoro* nitrogen compounds are more stable than the hydro compounds, irrespective of the oxidation state of nitrogen in the former, by an average of 7.9 ± 0.6 kcal mol⁻¹ per fluorine (Table 1). Hence any destabilization must occur in partly fluorinated compounds. (The units kcal mol⁻¹ are omitted for brevity in all heat values hereafter).

Table 1
Enthalpy differences per fluorine between N–H and N–F compounds for different nitrogen oxidation states [5]

Fluoro compound	Oxidation state of N	$\Delta H_f^\circ(\text{NH}) - \Delta H_f^\circ(\text{NF})$ per fluorine
N ₂ F ₂	I	9.0 *
N ₂ F ₄	II	7.7 [6]
NF ₃	III	6.9 [7,8]
NF ₄ ⁺	V	8.1 [10]
		Mean 7.9 ± 0.6

* Corresponding author.

* Based on an average value for *cis*- and *trans*-N₂F₂.

2.1. Calculations on the $\text{NH}_3\text{-}_n\text{F}_n$ series

The PM3 or AM1 modified MNDO parameters were used for semi-empirical calculations, the MOPAC 93 program for fundamental frequencies and the GAMESS or GAUSSIAN 92 program for ab initio energies.

2.1.1. Interpolation of experimental values

No vibrational spectra or thermodynamic energies have been reported for monofluoramine, no doubt because of its reactivity. These have to be found by interpolation or calculation. Some semi-empirical enthalpies are collected in Table 2.

Fig. 1 shows the unreliability of the AM1 values because when plotted they cross the experimental values. The PM3 values appear consistently on one side. Both sets lie on smooth curves and justify an interpolation for $\Delta H_f^\circ(\text{FNH}_2)$ on the experimental curve. This can be assisted by straightening the curve using the function e^x as abscissa where x is the mass ratio of the fluorinated amines relative to ammonia. An interpolated $\Delta H_f^\circ(\text{FNH}_2) = -12.0$ is obtained. (It is also possible to bracket a value of -12.5 ± 2.5 using bond dissociation energies.)

2.1.2. Ab initio calculations of reaction heats

Lengthy correlation calculations are generally avoided by choosing reactions which minimize any change in the number of bonds and their environment. Deriving a single enthalpy from a reaction heat is also dependent on the accuracy of the remaining experimental enthalpies. Pople and co-workers [11,12] calculated heats of hydrogenation for molecules containing two first row

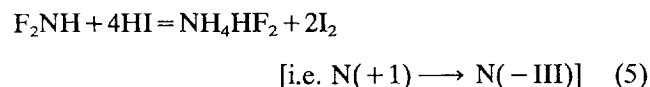
elements using the 4-31G basis set. They estimated $\Delta H_f^\circ(\text{FNH}_2) = -6.6$ and $\Delta H_f^\circ(\text{F}_2\text{NH}) = -7.8$ from the reaction heats for



after applying rather arbitrary corrections and using the enthalpy $\Delta H_f^\circ(\text{HF}) = -64.9$ available at the time. Adjustments to older fluoride values have been tabulated [13] and a recalculation yields values of -8.8 and -12.9 , respectively. However neither reaction was isodesmic. Now that experimental enthalpies are available for NF_3 and F_2NH , it is possible to construct true homodesmotic reactions to calculate $\Delta H_f^\circ(\text{FNH}_2)$ from



Reaction (4) is preferred because the NF_3 enthalpy has been determined three times by fluorine bomb calorimetry as -31.75 ± 0.2 , -31.44 ± 0.3 and -32.3 ± 1.2 . A mean value of -31.6 ± 0.3 is adopted [7-9]. The FNH_2 value of -15.6 ± 1.5 is much less certain having been determined by oxidation of aqueous potassium iodide after making allowance for a variable amount of a secondary reaction [14]



The other uncertainty in the procedure is the calculation of heat corrections involving large zero-point energies (zpe) and lesser enthalpy changes. Because the fundamental frequencies for FNH_2 are unavailable, its zpe was interpolated. This is justified by comparison with values calculated via the MOPAC program as shown in Fig. 2. The $(H_{298}^\circ - H_0^\circ)$ corrections were either available [15] or derived with minor error (< 0.05) from MOPAC frequencies. Ab initio energies and heat corrections are collected below in Table 4.

Table 2
Experimental versus calculated enthalpies in the $\text{NH}_3\text{-NF}_3$ series

	AM1	PM3	Experimental
NH_3	-7.3	-3.1	-11.0 ± 0.05
NH_2F	-12.8	-4.6	-
NHF_2	-23.9	-11.5	-15.6 ± 1.5
NF_3	-40.0	-24.4	-31.6 ± 0.3

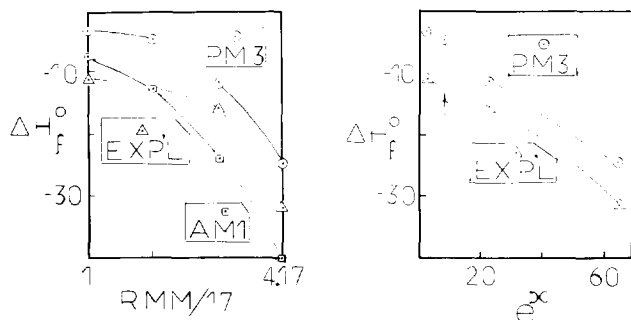


Fig. 1. Experimental and semi-empirical enthalpies in the $\text{NH}_3\text{-}_n\text{F}_n$ series as functions of relative mass.

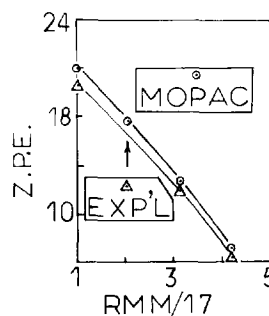


Fig. 2. Experimental and calculated zero point energies (zpe) in the $\text{NH}_3\text{-}_n\text{F}_n$ series as a function of relative mass.

From reactions (3) and (4), $\Delta H_f^\circ(\text{FNH}_2)$ values of -10.9 and -10.4 were obtained indicating that the experimental $\Delta H_f^\circ(\text{F}_2\text{NH})$ value is correct within the assigned error limit. Hence a value of $\Delta H_f^\circ(\text{FNH}_2) = -11.5 \pm 0.6$ is proposed taking into account the previous interpolation of experimental values. The difference $[\Delta H_f^\circ(\text{FNH}_2) - \Delta H_f^\circ(\text{F}_2\text{NH})]$ calculated from Eqs. (1) and (2) of 4.1 agrees with the difference calculated from Eq. (4) and the experimental value of $\Delta H_f^\circ(\text{F}_2\text{NH})$. Thus, monofluoramine is only 0.5 ± 0.6 more stable than ammonia, in comparison with the average 7.9 ± 0.6 for the pairs listed in Table 1 for fully fluorinated species. In this sense also the monofluoro compound is a destabilized species.

2.1.3. Some empirical calculations

The effect of alkylation and perfluoralkylation has been examined semi-empirically using the PM3 parameters and the results obtained are listed in Table 3.

The amine values are in reasonable agreement with experimental values: that for $(\text{CH}_3)_2\text{NH}$ being -6.6 and a $(\text{CF}_3)_2\text{NH}$ value of -322.0 can be estimated with Benson increments [2]. While the individual values may be in error, the differences should be reliable enough to show that substituting FNH_2 with electron-withdrawing groups destabilizes *N*-fluoro compounds relative to the amines as found earlier for $\text{C}_6\text{H}_5\text{SO}_2$ or $\text{C}_6\text{F}_5\text{SO}_2$ substituents.

2.2. Exchange of fluorine with the hydroxyl group

Anhydrous hydroxylamine resembles NH_2F in being unstable especially in the vapour phase despite extensive association (Trouton constant $27.5 \text{ cal K}^{-1} \text{ mol}^{-1}$). However an enthalpy value $\Delta H_f^\circ(\text{NH}_2\text{OH}_s) = -27.3$ has been determined for the solid, which together with the heats of fusion and vaporization yields $\Delta H_f^\circ(\text{NH}_2\text{OH}_g) = -12.0$ [16], which is very close to our estimates for $\Delta H_f^\circ(\text{NH}_2\text{F})$. An ab initio calculation on the reaction



produced a value of -10.0 .

The proximity of enthalpies for organofluorine compounds and corresponding hydroxo compounds, called isoelectronic heats, has been commented on previously [17,18]. The failure of this correspondence with most

Table 3

Heats of formation of R_2NF and R_2NH compounds calculated semi-empirically (PM3 parameters)

	ΔH_f°		ΔH_f°
$(\text{CH}_3)_2\text{NH}$	-8.00	$(\text{CF}_3)_2\text{NH}$	-324.60
$(\text{CH}_3)_2\text{NF}$	-9.57	$(\text{CF}_3)_2\text{NF}$	-319.25
Difference	1.57		-5.35

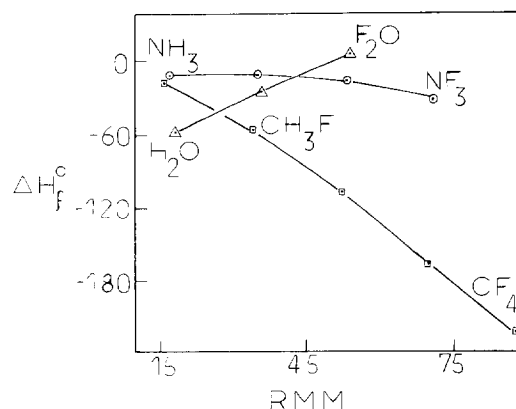


Fig. 3. Heats of formation in the XH_n/XF_n series with $\text{X} = \text{O}, \text{N}$ and C .

fluoro nitrogen compounds has been correlated with differences in lone-pair repulsions found in N-OH and N-F compounds. The destabilizations described previously [3] followed an approximately linear relation. There is only a difference of one lone-pair repulsion between FNH_2 and HONH_2 which should minimize their enthalpy difference, whereas for the $\text{F}_2\text{NH}/(\text{OH})_2\text{NH}$ couple, with a difference of seven lone-pair repulsions, the expected destabilization would be about 10.

A related treatment can be applied to hypofluorites with oxygen as the central atom. Hydrogen sesquioxide (H_2O_3), which behaves as an electrophilic oxidant like hypofluorites, was identified as a transient species by Giguère and Herman [19] and its enthalpy estimated as -15.7 by group additivity [20]. More recently, a bond dissociation estimate $D(\text{HO-OOH})$ of 31.7 ± 1.5 together with $\Delta H_f^\circ(\text{OH}) = 9.3$ and $\Delta H_f^\circ(\text{O}_2\text{H}) = 3$ leads to $\Delta H_f^\circ(\text{H}_2\text{O}_3) = -19.4 \pm 1.5$ [21].

Another estimate can be made using the following enthalpies which show vertical destabilization



The destabilizations in the upper two rows are in the ratio 41.8:25.3 or 1.65. This corresponds approximately with lone-pair repulsion differences of 6:4. The ratio of lone-pair repulsion differences between the second and third rows is 15:8 which would lead to a destabilization of H_2O_3 over H_2O_2 of $(23.5 + 5.9) \times 8/15$ and an approximate $\Delta H_f^\circ(\text{H}_2\text{O}_3)$ of -16.9 in between the two previous estimates. Ab initio heats of reactions (8) and (9), i.e.



lead to $\Delta H_f^\circ(\text{H}_2\text{O}_3) = -17.2$ and -17.9 , respectively. The former value is preferred being derived from an

Table 4

	Total energies ^a ab initio 4-31G	Zero point ^b energies	$H_{298}^{\circ} - H_0^{\circ}$ ^c
NH ₃	-56.10452	20.63	2.388
NH ₂ F	-154.75160	16.5	2.581
NHF ₂	-253.40759	11.84	2.490
NF ₃	-352.07606	6.44	2.827
NH ₂ OH	-130.78729	23.87	2.677
H ₂ O	-75.90841	12.88	2.367
H ₂ O ₂	-150.55257	15.79	2.594
H ₂ O ₃	-255.20512	17.4	3.372
HF	-99.88720	5.92	2.055
H ₂	-1.12676	6.28	2.024

^a 1 Hartree unit=627.51 kcal.

^b zpe = 1.4296 $\sum_i v_i$; frequencies in cm⁻¹ units, zpe in kcal.

^c $H_{298}^{\circ} - H_0^{\circ} = 2.369 + \sum_i 0.592[x/(e^x - 1)]$ where $x = v_i/207.223$ for non-linear molecules (and 0.296 less for linear ones) [15].

isodesmic reaction. The average -17.6 ± 0.4 is just within the range of Francisco and Williams' estimate of -19.4 ± 1.5 .

An extension to estimate H₂O₄ via its relationship with F₂O₂ is not possible because the latter no longer has the same O–F or O–O bonds found in the other molecules (O–O = 121.7, O–F = 157.5 in F₂O₂; O–O 147.5 in H₂O₂ and 142.6 in H₂O₃; O–F 144.2 in HOF and 140.8 pm in F₂O). Indeed F₂O₂ is slightly more stable than F₂O as determined by its heat of decomposition to the elements [22].

Liebman and co-workers have carried out a broad survey of enthalpy differences $1/n[\Delta H_f^{\circ}(H_{p-n}YF_n) - \Delta H_f^{\circ}(H_{p-n}Y(OH)_n)]$ where Y = B, C, N, O, Al, Si, P and S using semi-empirical AM1 values [23]. They reach the same conclusions concerning destabilization when fluorine is replaced by hydroxyl in N–F and O–F compounds as reported here. However, calculated AM1 values can be capricious in that the direction of errors is unpredictable as illustrated in Fig. 1. Supporting evidence from group additivity schemes and ab initio calculations, as well as direct experimental values is desirable to reliably correlate enthalpy differences with the electronegativity of Y [23].

In conclusion, the destabilization of N–H and O–H compounds relative to C–H on fluorination is well illustrated in Fig. 3 and its relevance to fluorination energetics is apparent from the equations where the

change of linkages to C, N and O are all exothermic, i.e.



The values used to calculate reaction heats throughout are listed in Table 4.

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