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Thermochemistry of some mono-substituted iodine fluorides and a comparison of gas and solid phase structures

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Abstract

The heat of formation of iodine trifluoride, obtained from an ab initio calculation of its heat of dismutation to mono- and penta-fluorides, was close to their average value. The mean bond dissociation energies of these iodine fluorides is almost invariant. The reduction couples between penta and trifluoro, or tri and mono-fluoro compounds, were employed to calculate formation heats of phenyl and trifluoromethyl iodine fluorides via similar isodesmic reactions. The substituted derivatives were stronger oxidants than the unsubstituted iodine fluorides as quantified by their redox couples. Similarly the corresponding chloro-fluorides were stronger oxidants than the iodo-fluorides. Heats of formation of other iodine fluoride derivatives can be obtained by additivity methods. Recent X-ray structures, when compared with calculated gas-phase structures, showed a lesser tilt of axial I–F bonds to the vertical in the solids probably due to intermolecular association. Rotational barriers around C–I bonds were small enough to permit almost free rotation at ambient temperatures.

Keywords: Thermochemistry; Iodine fluorides; Reduction couples; Ab initio calculations

1. Introduction

The relative fluorinating ability of isoelectronic E_3AF_2 compounds, where E represents a bonded or non-bonded electron pair and A a main group V–VIII element, was estimated from the reduction couples ($\Delta_f H^\circ E_3AF_2 - \Delta_f H^\circ E_3A$) and shown to be related to the position of A in the periodic table increasing from Group V to VIII and decreasing as Groups were descended [1]. It followed that phenyl iodonium difluorides would be comparatively mild selective fluorinating agents. It was expected that these compounds would act as electrophilic reagents under Friedel Craft conditions via $PhIF^+$. However Motherwell and co-workers have selectively fluorinated steroids with *p*-(*t*-butyl)phenyl iodine difluoride via radical mechanisms initially generating $Bu_tC_6H_4IF_2^-$ by catalytic electron transfer from 'paraquat' [2]. Before alternative mechanisms can be examined the enthalpies and free energies of simple and substituted iodine fluorides are needed, as well as their geometries for assessing possible transition states. The former can be derived from ab initio calculations on isodesmic reactions.

2. Heats of formation of simple iodine fluorides

2.1. All heats are given in kcal mol^{-1} units

2.1.1. Iodine monofluoride

A virtual form can be generated from N-iodo amines and fluoride ions or by precipitating silver iodide from silver fluoride and di-iodine in methyl cyanide. In solution these species add electrophilically to alkenes producing trans iodofluorides. However free iodine monofluoride is only a transient species. It was formed in a flow system from atomic fluorine and iodine monochloride for spectral examination at extremely low pressures of 0.5–1 mTorr [3]. A review of spectroscopic transitions of binary interhalogens included energy levels for IF [4]. The fluorescent decay dynamics of ro-vibronic states induced by laser illumination enabled the onset of the pre-dissociation of IF to be captured and with suitable corrections to obtain a D_o° value for $IF \rightarrow I + F$ of 63.84. This increases to 64.70 for D_{298}° from which $\Delta_f H^\circ IF = -20.2 \pm 0.1$.

The usual quoted value of -22.9 was selected from older work with higher D_o° values [5].

2.1.2. Iodine pentafluoride

This heat can be determined by conventional calorimetry. The heats of hydrolysis under acid [6] and alkaline [7]

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conditions, together with ancillary heats, lead to values for $\Delta_fH^\circ(IF_5)$ which agree within 0.2. The direct fluorination of iodine by fluorine bomb calorimetry should be more accurate since ancillary heats should not be required. However variable amounts of IF_7, formed with IF_5, require analysis. Also $\Delta_fH^\circ(IF_7)$ is dependent on that of IF_5 being determined from equilibrium measurements on $IF_7 \rightleftarrows IF_5 + F_2$ at 450–550°C. The bomb value differs by 0.7 from the hydrolysis results [8]. The accepted value for $\Delta_fH^\circ(IF_5)g$ is −200.8.

2.1.3. Iodine trifluoride

This is another unstable species decomposing above −30°C. Since thermodynamic data is unavailable an electronic structure calculation is the only route to a heat of formation. Semi empirical methods are too inaccurate as illustrated for halogen fluorides in Table 1 especially using the AM1 method with hypervalent molecules.

Ab initio calculations are limited because few basis sets contain parameters for iodine. Only relatively simple sets such as STOnG and 3-21G are available which restricts calculation of heats to isodesmic reactions with conservation of bond type to cancel correlation errors. The total energies (E) obtained with the STO 3G basis set in the Hyperchem programme, and heat corrections from 0 to 298 K using the Gamess or Gaussian programmes are collected in Appendix A.

The reaction heat ΔH_r for the gaseous isodesmic reaction $IF_5 + IF = 2IF_3$ in which the number of I–F bonds is unchanged i.e., $\Delta H_r = \Delta E + \Delta(zpe) + \Delta(H_{298} - H_o)$ was −0.6. This together with the above experimental heats for IF_5 and IF leads to $\Delta_fH^\circ(IF_3) = -110.8$. (Heat corrections for these isodesmic reactions were usually less than 1. Consequently calculated corrections can be 10% in error without changing heats of formation by more than 0.1). Finch and co-workers estimated $\Delta_fH^\circ(IF_3)$ between −111.4 and −125.7 [7]. However an upper limit can be fixed by considering its rapid disproportionation to IF_5 and I_2 and not to IF_5 and IF at room temperatures. Using the −110.8 figure the calculated $\Delta H_r = -9.7$ for $IF_3 = 0.2I_2 + 0.6IF_5$ together with a negative entropy change $\Delta S = -11.2$ cal K^{-1}, corresponding to the decrease of 0.2 moles, yields $\Delta G = -6.3$. Thus for ΔG to be negative $\Delta_fH^\circ(IF_3)$ must be less than −117.0. Similarly for $IF_3 = 0.5IF + 0.5IF_5$ not to occur the upper limit is −112.4. The mean I–F bond energies only decrease marginally with oxidation state unlike the corresponding Cl–F and Br–F bond energies which diminish considerably between mono and pentavalent states.

Table 1
Standard heats of formation by semi-empirical calculations compared with experimental values (kcal mol^{-1})

Compound	AM1	PM3	Experimental
ClF	−10.5	−21.7	−12.1
ClF_3	+20.2	−22.1	−38.0
ClF_5	+90.5	−54.0	−54.0
BrF	−7.2	−21.3	−14.0
BrF_3	+21.5	−47.1	−61.1
BrF_5	+81.2	−75.8	−102.5
IF	−9.5	−8.0	−20.2
IF_3	–	−64.8	–
IF_5	+67.1	−202.9	−200.8

It follows that the reduction couples IF_3/IF and IF_5/IF_3, expressed as the enthalpy difference in the couples, are almost equal. These couples were employed to calculate isodesmic heats and then formation heats of phenyl and trifluoromethyl substituted iodine fluorides. A heat for $C_6H_5ClF_2$ was also calculated to see how far non-isodesmic reactions involving changes of I–F to Cl–F bonds would affect substituted iodine fluoride heats. The results are summarized in Table 2 using the data in Appendix A. The non-isodesmic reactions yield formation heats quite close to isodesmic heats, the differences decreasing with increasing exothermicity (i.e., from −2.6 to 1.4). Fluorination of the precursor iodides increases stability as shown in Table 3.

The reduction couples collected in Table 4 using the above data show that substituted iodine or chlorine fluorides are

Table 2
Heats of formation of mono-substituted iodine and chlorine fluorides derived from isodesmic reaction heats (ΔH_r) using the STO 3G basis set (kcal mol^{-1})

Reaction	ΔH_r	Δ_fH°
$PhClF_2 + ClF = PhCl + ClF_3$	−24.0	10.5 $PhClF_2$
$PhClF_4 + PhCl = {}_2PhClF_2$	−17.3	25.9 $PhClF_4$
$PhClF_2 + ClF_3 = PhClF_4 + ClF$	42.1	26.7 $PhClF_4$
$PhI + IF_3 = PhIF_2 + IF$	20.1	−31.2 $PhIF_2$
$PhI + IF_5 = PhIF_2 + IF_3$	−19.3	−31.3 $PhIF_2$
$PhI + ClF_3 = PhIF_2 + ClF$	−47.4[a]	−33.9 $PhIF_2$
$PhI + PhClF_2 = PhCl + PhIF_2$	−71.3[a]	−33.8 $PhIF_2$
$PhIF_4 + PhI = 2PhIF_2$	4.7	−106.7 $PhIF_4$
$PhI + IF_5 = PhIF_4 + IF$	33.6	−107.6 $PhIF_4$
$PhIF_2 + IF_3 = PhIF_4 + IF$	14.3	−107.6 $PhIF_4$
$PhIF_2 + PhClF_2 = PhIF_4 + PhCl$	−76.0[a]	−109.2 $PhIF_4$
$PhIF_2 + CF_3I = PhI + CF_3IF_2$	−4.03	−215.2 CF_3IF_2
$CF_3I + IF_3 = CF_3IF_2 + IF$	15.9	−215.2 CF_3IF_2
$CF_3I + IF_5 = CF_3IF_2 + IF_3$	15.3	−215.2 CF_3IF_2
$CF_3I + ClF_3 = CF_3IF_2 + ClF$	−50.5[a]	−216.8 CF_3IF_2
$CF_3I + CF_3IF_4 = 2CF_3IF_2$	1.8	−291.7 CF_3IF_4
$CF_3IF_2 + IF_3 = CF_3IF_4 + IF$	−13.8	−292.0 CF_3IF_4
$CF_3I + IF_5 = CF_3IF_4 + IF$	29.4	−291.7 CF_3IF_4
$CF_3IF_2 + ClF_3 = CF_3IF_4 + ClF$	−52.1[a]	−293.2 CF_3IF_4

[a] Non-isodesmic reactions.

Table 3
Mean stabilization per fluorine addition to iodides (kcal mol^{-1})

Iodide (Δ_fH°)	Iodo-fluoride (Δ_fH°)	Δ	Δ/F
PhI (39.4)	$PhIF_2$ (−31.3)	−70.7	−35.4
PhI (39.4)	$PhIF_4$ (−107.3)	−146.7	−36.7
CF_3I (−140.5)	CF_3IF_2 (−215.2)	−74.7	−37.4
CF_3I (−140.5)	CF_3IF_4 (−291.7)	−151.2	−37.8
		Mean	−36.8 ± 0.8

Table 4
Reduction couples of iodo and chloro-fluorides for loss of difluorine based on enthalpy values (kcal mol^{-1})

Unsubstituted couples		Substituted couples			
IF_5/IF_3	−90	$PhIF_4/PhIF_2$	−76	CF_3IF_4/CF_3IF_2	−77
IF_3/IF	−91.1	$PhIF_2/PhI$	−71	CF_3IF_2/CF_3I	−75
ClF_5/ClF_3	−16	$PhClF_4/PhClF_2$	+15	–	
ClF_3/ClF	−27	$PhClF_2/PhCl$	−2	–	

more powerful oxidants than unsubstituted compounds. Also that chloro-fluorides are more powerful oxidants than corresponding iodo-fluorides.

These figures suggest that it may be possible to assist fluorination of iodides by catalytic amounts of chlorides since formation of any chloro-fluoride has the potential to oxidise the iodide to an iodo-fluoride.

3. Additivity methods for estimating other heats

The almost constant difference Δ/F in Table 3, in line with the almost invariant mean dissociation energies in Table 5, enables heats of formation of the substituted iodine fluorides to be approximated by subtracting $37n$ ($n=2$ or 4) from heats of precursor iodides. Conversions between heats of perfluoro and perhydro-carbon derivatives should be derivable from the data in Table 6 instead of employing full ab initio calculations.

For the trifluoromethyl compounds, except for X = F or OH, the mean difference is 146.0 ± 2.5. The discrepancy with F or OH is probably due to a change in polarity of the C–X bond. Less electronegative atoms or groups will tend to $CF_3^{\delta-}X^{\delta+}$ versus a constant $CH_3^{\delta+}X^{\delta-}$ polarity. An estimate for $\Delta_fH°(CH_3IF_2)$ would be −69 since the IF_2 group would have a mean electronegativity below that for F or OH. For phenyl derivatives the figures are less clear cut because the C_6H_5–X polarities are also variable. Since the IF_2 and IF_4 groups are more electronegative than I the average of the higher Δ's 201.9 ± 3.8 is chosen to predict $\Delta_fH°(C_6F_5IF_2)$ −233 and $\Delta_fH°(C_6F_5IF_4)$ −309.

Table 5
Mean bond dissociation energies of iodine fluorides (kcal mol^{-1})

	$\Delta_fH°$	Derived	Previous values	
		D(I–F)	Stein [9]	Finch [6]
IF	−20.2	64.7	67	64.8
IF_3	−110.8	64.4	~65	64.5–69.3
IF_5	−200.8	64.2	64	64.3
	Mean	64.4 ± 0.2		

Table 6
Experimental heats of formation of corresponding perfluoro and perhydro compounds [10] (kcal mol^{-1})

X	$\Delta_fH°CF_3X$	$\Delta_fH°CH_3X$	Δ	$\Delta_fH°C_6F_5X$	$\Delta_fH°C_6H_5X$	Δ
F	−223.1	−53.9[a]	169.2	−228.4	−27.7	200.7
Cl	−168.6	−19.6	149.0	−193.4	12.4	205.8
Br	−156.6	−8.5	148.1	−170.2	25.2	195.4
I	−140.5	−34.8	144.0	−131.1	39.4	170.5
OH	−217.7	−48.1	169.6	−228.7	−23.6	205.7
CF_3	−321.2	−178.2	143	−303.4	−143.2	160.2

[a] Estimated value [11].

4. Comparison of gas and solid phase structures

4.1. All bond lengths are in Ångstrom units (10^{-10} m)

Two items of interest are firstly the effect of lone pairs on the inclination of I–F bonds away from the vertical and secondly the relative orientations of IF_2 and IF_4 groups to the rest of the molecule. A structure for p-$MeC_6H_4IF_2$, partially reported in a thesis [12], is too inaccurate to be considered reliable probably due to decomposition in the X-ray beam. For example I–F distances in two distinct units vary from 1.558(23) to 2.144(19) compared to the covalent radii sum of 2.00; the ring is far from coplanar and the I–F bonds are inclined on average 71° from the ring 'plane'. The structure of $PhICl_2$ was more precise [13] with C–I = 2.017 compared to the covalent radii sum of 2.10, the ring coplanar within 0.7° and the I–Cl bonds collinear at 86° to the ring plane. The lone pair effect was not evident.

Recent structures carried out at low temperature show the effect of lone pairs making the I–F's non-collinear and tilted away from the vertical [14,15]. Some of the data is collected in Table 7 to compare with values calculated with the STO 3G basis set. The calculated I–F tilt is about 5° more than in the X-ray structures. Part of the difference may be due to the small basis set, the rest can be caused by intermolecular attractions between the positive iodine on one molecule with neigh-

Table 7
Comparison of X-ray and STO 3G calculated structures (Bond lengths in Å units)

		Mean I–F	C–I–F°	Mulliken charge on I
(C)	CF_3IF_2	1.991	75.9, 72.4	0.75
(X)	CF_3IF_4	1.915	81.2, 83.1	
(C)	CF_3IF_4	1.930	76.3, 77.8	1.62
(X)	$C_6F_5IF_2$	1.953 2.026	–	
(C)	$C_6H_5IF_2$	1.994	76.1	0.81
(X)	$C_6F_5IF_4$	1.928 1.911	84.3	
(C)	$C_6H_5IF_4$	1.927	79.7	1.68
(X)	IF_5	1.877 1.866	81.9	
(C)	IF_5	1.920 1.912	76.6	1.78

(X) X-ray data
(C) Calculated STO 3G

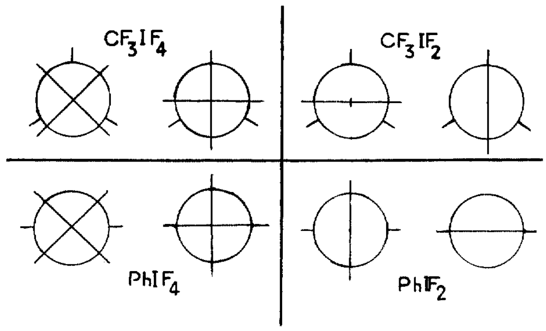

Fig. 1. Minimum and maximum energy conformations in Newman projections looking down the I–C bonds.

bouring negative fluorines. In $C_6F_5IF_4$ there is a zig-zag chain of intermolecular contacts joining each iodine to two fluorines; in CF_3IF_4 each iodine has contacts with three neighbouring fluorines.

Another indication of intermolecular interaction is in the different I–F lengths in $C_6F_5IF_2$ indicating a small polarization towards $C_6F_5IF^+F^-$ compared with the equal lengths calculated for $C_6H_5IF_2$.

The conformations of IF_2 and IF_4 groups relative to the rest of the molecules should be governed by minimization of repulsions between lone pairs on fluorines or between these and the distribution of Π-electrons in rings. Minimum and maximum energy conformations expected are shown in Newman diagrams (Fig. 1) projected, down I–C bonds.

The IF bonds in IF_4 compounds are at less than the 90° shown in the idealized projections because of the I–F tilt caused by lone pair repulsions.

In the X-ray structure of CF_3IF_4 carried out at −101°C the IF_4 portion is fixed much more precisely than the rest of the molecule. The C–F distances average 1.27(2), with large thermal ellipsoids on fluorines, are much too short compared to C–F's of 1.332 and 1.333 in CF_3I and CF_3H. The estimated standard deviations (esd) are much less on the I–F's [mean 1.915(6)]. It should be noted that e.s.d's while mathematically correct underestimate real errors [16]. The X-ray confirmation is turned by 10° from the ideal minimum in Fig. 1. giving angles of 55.5° and 35.1° in place of 45° and 45° equidistant from the C–F bond. Whether this is entirely due to intermolecular forces or uncertainties in the structure is difficult to decide.

The STO 3G energies cannot distinguish between the minimum and maximum conformations for CF_3IF_4 in Fig. 1. However there is a preference of 0.9 for the minimum using Huzinaga's 21 split valence basis set. A more direct conformation is provided by a molecular mechanics calculation starting from the X-ray orientation; a 10° rotation of a C–F bond reaches a minimum and a 55° rotation the maximum with an energy difference of 0.4. At room temperatures such low energy barriers would allow almost free rotation around the C–I bond.

The X-ray structure of $C_6F_5IF_4$ at −123°C agrees with the minimum conformation. In solution the large $^4J_{FF}$ coupling constant between fluorines on iodine and the ring was considered to show free rotation about the C–I bond presumably at ambient temperatures [4].

Appendix A

Total energies (E) and heat corrections calculated with the STO 3G basis set (kcal mol^{-1})

Compound	−E	Z.p.e.	$(H_o° - H_{298}°)$
IF	4362, 761.95	0.963	2.14
IF_3	4485, 638.75	3.730	3.56
IF_5	4608, 514.74	6.938	4.28
PhI	4443, 927.19	58.92	4.45
$PhIF_2$	4560, 783.51	61.43	4.58
$PhIF_4$	4689, 646.76	64.57	6.35
CF_3I	4509, 319.75	8.83	3.50
CF_3IF_2	4632, 179.72	11.28	4.25
CF_3IF_4	4755, 042.44	14.09	5.69
ClF	346, 719.29	1.12	2.13
ClF_3	469, 530.05	4.44	3.26
PhCl	427, 896.08	50.68	4.45
$PhClF_2$	550, 682.02	52.76	5.98
$PhClF_4$	673, 458.22	64.33	6.38

The calculated frequencies were scaled by a factor of 0.900 to obtain heat corrections.

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