lipid and then monitoring the increase in weight upon exposure to a humid atmosphere until the desired water content was obtained. For the high water content samples the appropriate quantity of water was pipetted into a vial containing the lipid. Homogenization of the low water-samples was accomplished by heating the sealed samples to above the gel-liquid crystalline transition[9] and for the high water samples (22 and 46 wt %) the lipid-water mixtures were repeatedly forced through a constriction. We believe the water contents are accurate only to ±1%, and thus the 1% difference between Figures 1b and 1c should not be taken too seriously.

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Iodine-Fluorine Bond Strength in IIF, ClIF, and HIF

Sir:

There has long been speculation regarding the existence of triatomic halogen molecules.[1] These molecules have often been postulated as intermediates in photochemical reactions.[2-4] From the temperature dependence of the recombination rate of I atoms in the presence of I_2 the stability of I_3 has been estimated to be about 5 kcal/mol.[4] However, no triatomic halogen radical species has been detected in the gas phase, although Cl_3 has been identified from its infrared spectrum in a matrix isolation experiment.[5]

We wish to report here the direct observation of the trihalogens IIF and ClIF and the pseudo-trihalogen HIF resulting from an endoergic, bimolecular reaction of F_2 and I_2, ICl, or HI in a crossed molecular beam experiment. Figure 1 shows the threshold behavior of the formation of I_2F, ClIF, and HIF products as the relative kinetic energy between F_2 and I_2, ICl, or HI is varied. From the observed threshold and the dissociation energy of F_2 (36.7 kcal/mol)[6] lower bounds on the I-F bond strength in I_2F, ClIF, and HIF can be established as 33, 31, and 26 kcal/mol, respectively. These bond energies are comparable to the IF bond strength of 25 kcal/mol in the recently observed CH_3IF,[7] and are approximately one-half to one-third of the IF dissociation energy of 66.4 kcal/mol.[8] Figure 2 shows a schematic diagram of the reaction energetics for one of the systems, $F_2 + I_2$. Similar diagrams can be constructed for the F_2 + ICl and F_2 + HI systems.

The apparatus used here has been described previously.[9] It employs two crossed supersonic beams of reactants. The products of the reaction are detected in the plane of the reactant beams by a rotatable, triply differentially pumped mass spectrometer detector utilizing electron bombardment ionization and ion counting. In these experiments a beam of pure HI or a beam of I_2 or ICl in argon carrier gas is expanded from a glass nozzle. This halogen beam is crossed with a hyperthermal beam of fluorine molecules seeded in helium (or a helium-neon mixture). This fluorine beam is produced by expansion from a resistance heated nickel nozzle. By varying the relative abundances of the fluorine and the inert carrier gases, and the temperature of the nozzle, the relative collision energy has been varied continuously from about 3 kcal/mol to more than 30 kcal/mol.

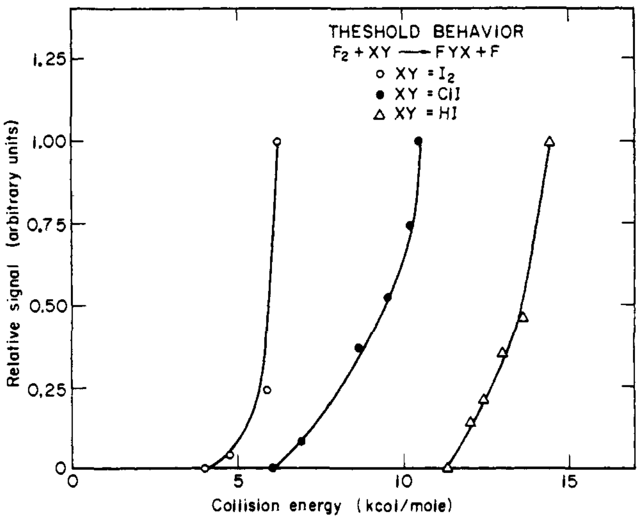

Figure 1. Energy dependence of the relative total cross sections for the reactions: (○) $F_2 + I_2$; (●) F_2 + ICl; (△) F_2 + HI.

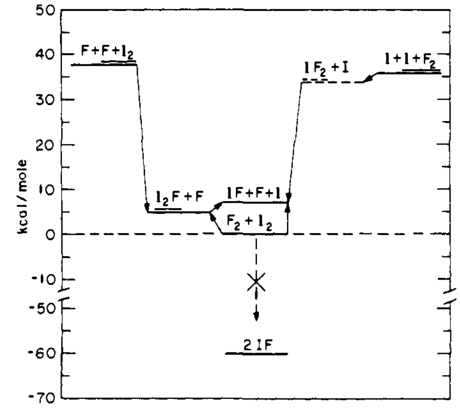

Figure 2. Schematic diagram of the reaction energetics for $F_2 + I_2$.

The existence of these interhalogen compounds is not surprising in view of recent crossed molecular beam experiments involving halogen containing molecules. CH_3IF has been observed in an experiment using beams of F_2 and CH_3I.[7] Halogen atom-halogen molecule reactions have shown evidence of short-range attraction. Reactive scattering in systems such as:

$$Cl + I_2 \rightarrow ClI + I$$

$$Cl + IBr \rightarrow ClI + Br$$

$$Cl + BrI \rightarrow ClBr + I$$

$$Cl + Br_2 \rightarrow ClBr + Br$$

$$Br + I_2 \rightarrow BrI + I$$

gives product angular distributions which can be well accounted for by an osculating complex model involving triatomic halogen complexes.[10-12] The reaction system which involved three different halogen atoms (Cl + IBr) demonstrated a preference for the geometry having the least electronegative atom in the central position, giving larger cross-section for ClI production (8 kcal/mol exoergicity) than for ClBr (10 kcal/mol exoergicity).

This same preferred geometry is evident in the present experiments. For the F_2 + ICl system prominent peaks in the mass spectrum of ClIF occurred at *m/e* 183 (^{37}ClIF) and *m/e* 181 (^{35}ClIF) as well as *m/e* 146 (IF), but not at *m/e* 56 (^{37}ClF) or *m/e* 54 (^{35}ClF). For F_2 + HI peaks from the ionization of HIF were observed at *m/e* 147 (HIF) and *m/e* 146 (IF), but not *m/e* 20 (HF). These results strongly suggest that the observed products are indeed ClIF and HIF with the F atom attached to I but not to Cl or H as IClF or IHF.

For trihalogen molecules of the type XY_2 or XYZ the most stable geometry is expected to be the one with the least electronegative atom in the central position. For all molecules with more than 12 valence electrons this general conclusion follows from the fact that the charge distribution of the π orbitals is generally more concentrated at the terminal atoms than at the center of the molecule.[13]

Simple theoretical arguments[14,15] predict the bonding in the trihalogen radicals to be similar to that in the trihalide anions. This prediction is borne out by the resemblance of Cl_3 to Cl_3^-.[5,16] These anions are linear or nearly linear and have vibrational force constants roughly one-half the value of those in the free halogens, corresponding to "half-bonds" in these anions.[17]

Additional experiments using hyperthermal molecular beams will undoubtedly be helpful in elucidating the properties and stabilities of triatomic halogen molecules. Studies of systems not involving iodine and fluorine would be especially interesting in the systematic exploration of the effect of changes in the end and central atom identifies on the stability of these molecules.

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A Quantitative Comparison of Gas- and Solution-Phase Basicities of Substituted Pyridines

Sir:

The separation of internal and external factors in the analysis of substituent effects is a longstanding problem in physical organic chemistry.[1,2] For proton transfer equilibria (eq 1) in aqueous solution, for example, the thermodynamic functions $\Delta H°$ and $T\Delta S°$ in water may be formally separated into terms arising from internal or gas-phase effects and external or solvation effects (eq 2 and 3).[3]

$$AH^+ + B \rightleftarrows A + BH^+ \quad (1)$$

$$\Delta H° = \Delta H°_{int} + \Delta H°_{ext} \quad (2)$$

$$T\Delta S° = T\Delta S°_{int} + T\Delta S°_{ext} \quad (3)$$

Analyses of the role of solvent on substituent effects for acid-base equilibria have been limited, however, by a lack of experimental data on which to base the separation of the internal and external substituent effects. Techniques for quantitative measurement of gas-phase basicities[4] provide a direct measure of internal substituent effects, and combination of these gas-phase proton affinity (PA) data with aqueous thermodynamic data allows an evaluation of solvent effects. Linear correlations of PA's and aqueous enthalpies of protonation ($\Delta H°_{prot,s}$) for alkylamines, for example, show that solvation causes a five- to sixfold attenuation of gas-phase basicity changes in solution.[4b,d] This attenuation can be interpreted in terms of electrostatic models relating the solvation energies of the ammonium ions to their charge densities.[4d] The availability of PA and $\Delta H°_{prot,s}$ values for 3- and 4-substituted pyridines now makes a quantitative analysis of the solvation terms $\Delta H°_{ext}$ possible for the important class of pyridine bases.[5-7] In addition, PA's and calorimetric heats of protonation (Table I) of 2-substituted pyridines have been measured for comparison.

The experimental PA and $\Delta H°_{prot,s}$ values for 3- and 4-substituted pyridines are summarized and correlated in Figure 1.[5-7] From the linearity of this plot (correlation coefficient = 0.996, slope = 2.59), it is clear that $\Delta H°$ is proportional to $\Delta H°_{int}$, and $\Delta H°_{int}$ is attenuated 2.6-fold in aqueous solution.[8] The proportionality of $\Delta H°_{int}$ and $\Delta H°$ and the defining equation (eq 2) also require that $\Delta H°_{ext}$ be proportional to $\Delta H°_{int}$ with a proportionality constant *h* of −0.61 for 3- and 4-substituents.

$$\Delta H°_{ext} = h\Delta H°_{int} \quad (4)$$

The heats of protonation of 2-substituted pyridines do not correlate as well with PA as for the 3- and 4-derivatives, and their slope indicates an attenuation of only 1.82 (correlation coefficient = 0.979). This smaller attenuation could be explained within the framework of Bjerrum and Kirkwood-Westheimer field effect theories[9] as a decrease in the effectiveness of solvent intervention between the charged center and the 2-substituents relative to the 3- and 4-substituents.

The free energy[3] correlations of PA and $\Delta G°_{prot,s}$ in Figure 2 are less precise than the enthalpy correlations in Fig-

Table I. Enthalpies of Protonation of Substituted Pyridines[a]

Substituent	$-\Delta H°_{prot,s}$	Substituent	$-\Delta H°_{prot,s}$
2-CN[b]	−0,91	2-CH_2CH_3	6.58
2-Cl[b]	0,25	2-$N(CH_3)_2$	7.08
2-Br[b]	0,47	4-$N(CH_3)_2$	11.73
2-OCH_3	3.88		

[a] Determined calorimetrically in aqueous perchloric acid. All values in kcal/mol. [b] Corrected for incomplete protonation, see ref 7a.