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IF BOND STRENGTH IN IIP, CUP, and HIP

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IF BOND STRENGTH IN IIF, C1IF, AND HIF

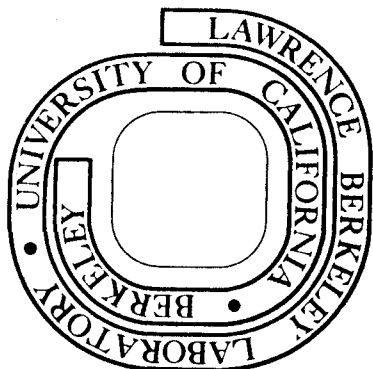
James J. Valentini, M. J. Coggiola, and Y. T. Lee

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Abstract for Communication to the Editor,  
Journal of the American Chemical Society

IF Bond Strength in IIF, ClIF, and HIF

James J. Valentini, M. J. Coggiola, and Y. T. Lee

The trihalogens IIF and ClIF and the pseudo-trihalogen HIF have been produced by an endoergic, bimolecular reaction between  $F_2$  and  $I_2$ ,  $ICl$ , or  $HI$  in a crossed molecular beam experiment. From the energy dependence of the reaction cross section lower bounds on the I-F bond strength in IIF, ClIF, and HIF are established as 33, 31, and 19 kcal/mole respectively. These values are about 1/2 to 1/3 of the dissociation energy of the diatomic molecule IF.

IF BOND STRENGTH IN IIF, ClIF, AND HIF

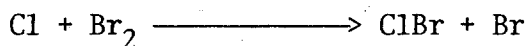
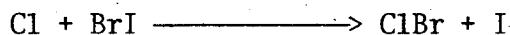
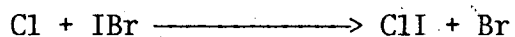
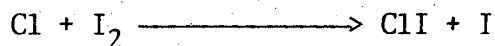
Sir:

There has long been speculation regarding the existence of triatomic halogen molecules.<sup>1</sup> These molecules have often been postulated as intermediates in photochemical reactions.<sup>2-4</sup> From the temperature dependence of the recombination rate of I atoms in the presence of I<sub>2</sub> the stability of I<sub>3</sub> has been estimated to be about 5 kcal/mole.<sup>4</sup> However, no triatomic halogen radical species has been detected in the gas phase, although Cl<sub>3</sub> has been identified from its infrared spectrum in a matrix isolation experiment.<sup>5</sup>

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<sub>2</sub> and I<sub>2</sub>, ICl, or HI in a crossed molecular beam experiment. Figure 1 shows the threshold behavior of the formation of I<sub>2</sub>F, ClIF, and HIF products as the relative kinetic energy between F<sub>2</sub> and I<sub>2</sub>, ICl, or HI is varied. From the observed threshold and the dissociation energy of F<sub>2</sub> (36.7 kcal/mole)<sup>6</sup> lower bounds on the I-F bond strength in I<sub>2</sub>F, ClIF, and HIF can be established as 33, 31, and 19 kcal/mole respectively. These bond energies are comparable to the IF bond strength of 25 kcal/mole in the recently observed CH<sub>3</sub>IF<sup>7</sup>, and are approximately 1/2 to 1/3 of the IF dissociation energy of 66.4 kcal/mole.<sup>8</sup> Figure 2 shows a schematic diagram of the reaction energetics for one of the systems, F<sub>2</sub> + I<sub>2</sub>. Similar diagrams can be constructed for the F<sub>2</sub> + ICl and F<sub>2</sub> + HI systems.

The apparatus used here has been described previously.<sup>9</sup> 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<sub>2</sub> 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/mole to more than 30 kcal/mole.

The existence of these interhalogen compounds is not surprising in view of recent crossed molecular beam experiments involving halogen containing molecules. CH<sub>3</sub>IF has been observed in an experiment using beams of F<sub>2</sub> and CH<sub>3</sub>I.<sup>7</sup> Halogen atom-halogen molecule reactions have shown evidence of short-range attraction. Reactive scattering in systems such as:



gives product angular distributions which can be well accounted for by an osculating complex model involving triatomic halogen complexes.<sup>10-12</sup>

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/mole exoergicity) than for ClBr (10 kcal/mole 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 ( $Cl^{37}IF$ ) and  $m/e$  181 ( $Cl^{35}IF$ ) as well as  $m/e$  146 (IF), but not at  $m/e$  56 ( $Cl^{37}F$ ) or  $m/e$  54 ( $Cl^{35}F$ ). 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 twelve valence electrons this general conclusion follows from the fact that the charge distribution of the  $\pi$  orbitals is generally more concentrated at the terminal atoms than at the center of the molecule.<sup>13</sup>

Simple theoretical arguments<sup>14,15</sup> 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  $Cl_3^-$ .<sup>5,16</sup> 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.<sup>17</sup>

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 identities on the stability of these molecules.

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References and Notes

1. G.K. Rollefson and H. Eyring, *J. Amer. Chem. Soc.*, 54, 170 (1932).
2. M.I. Christie, A.J. Harrison, R.G.W. Norrish, and G. Porter, *Proc. Roy. Soc. (London)*, A231, 446 (1955).
3. P.F. Ashmore, F.S. Dainton, and T.M. Sugden, Eds., Photochemistry and Reaction Kinetics (Cambridge University Press, London, 1967), pp. 75, 81, 103, 115.
4. D.L. Bunker and N. Davidson, *J. Amer. Chem. Soc.*, 80, 5090 (1958).
5. L.Y. Nelson and G.C. Pimentel, *J. Chem. Phys.*, 47, 3671 (1967).
6. J. Berkowitz and A.C. Wahl in Adv. in Fluorine Chemistry (ed., J.C. Tatlow, R.D. Peacock, and H.H. Hyman, CRC Press) 7, 147 (1973).
7. J.M. Farrar and Y.T. Lee, *J. Amer. Chem. Soc.*, 96, 7570 (1974).
8. J.A. Coxon, *Chem. Phys. Lett.*, 33, 136 (1975).
9. Y.T. Lee, J.D. McDonald, P.R. LeBreton, and D.R. Herschbach, *Rev. Sci. Instrum.*, 40, 1402 (1969).
10. Y.T. Lee, J.D. McDonald, P.R. LeBreton, and D.R. Herschbach, *J. Chem. Phys.*, 49, 2447 (1968).
11. Y.T. Lee, P.R. LeBreton, J.D. McDonald, and D.R. Herschbach, *J. Chem. Phys.*, 51, 455 (1969).
12. P.R. LeBreton, Ph.D. dissertation, Harvard University, Cambridge, Massachusetts, 1970.
13. S.D. Peyerimhoff and R.J. Buenker, *J. Chem. Phys.*, 49, 2473 (1968).
14. G.C. Pimentel, *J. Chem. Phys.*, 19, 446 (1951).
15. A.D. Walsh, *J. Chem. Soc.*, 1953, 2266.
16. J.C. Evans and G.Y-S. Lo, *J. Chem. Phys.*, 44, 3638 (1966).

17. W. B. Person, G.R. Anderson, J.N. Fordemwalt, H. Stammreich,  
and R. Forneris, *J. Chem. Phys.*, 35, 908 (1961).
18. National Science Foundation Predoctoral Fellow

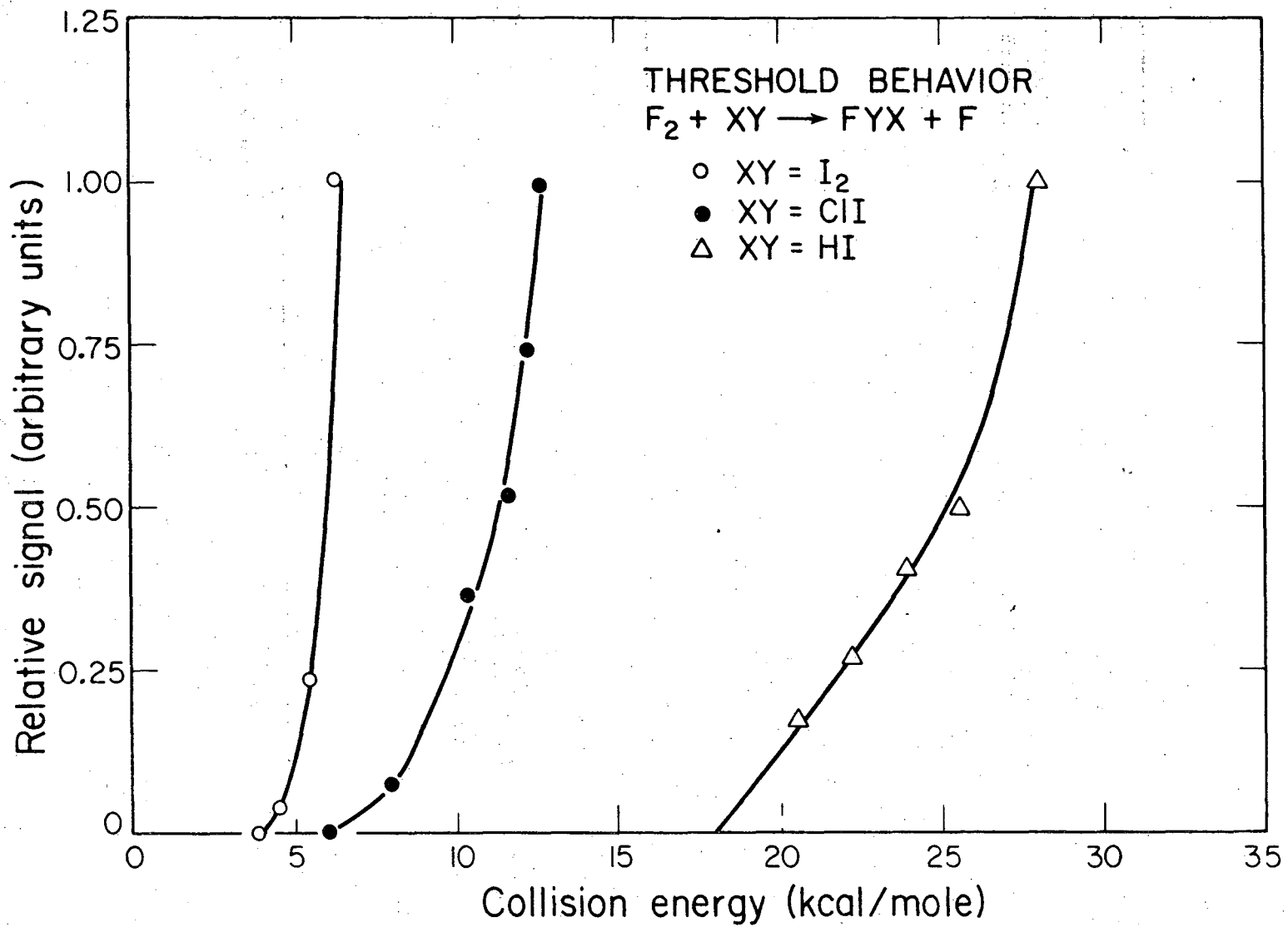
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Figure Captions

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

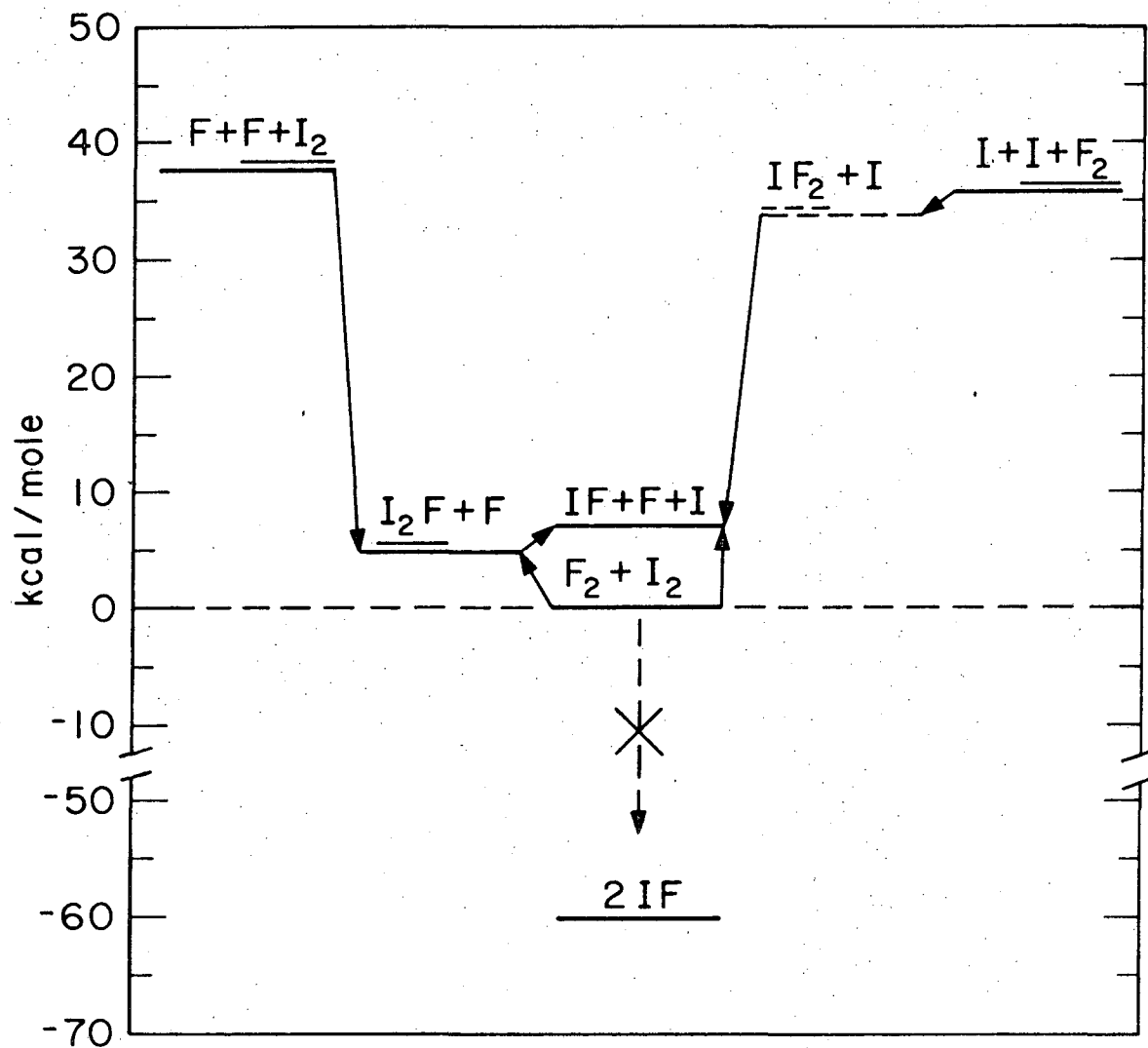
Figure 2. Schematic diagram of the reaction energetics for  $F_2 + I_2$ .



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Fig. 1

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Fig. 2

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