

Anomalous Properties of Fluorine

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Abstract: Evidence is presented to show that the interaction of a fluorine atom with an external electron, as in the formation of an ionic or covalent bond, is accompanied by an anomalous destabilization energy of about 26 kcal/mole. It is suggested that this is the reason for the unusually low dissociation energy of the fluorine molecule.

Fluorine exhibits a number of anomalous properties, both as an atom and as a molecule. In Table I are listed the ionization potentials and the electron affinities of the halogen atoms. The ionization potentials show the anticipated monotonic increase in going from iodine to fluorine. The electron affinities of iodine, bromine, and chlorine also increase gradually, as expected; in fact, for these three elements there is an excellent linear correlation between ionization potential and electron affinity, shown in Figure 1. The electron affinity of fluorine deviates very markedly from the general trend, however—it is *less* than that of chlorine. A measure of the extent of this deviation can be obtained by extrapolating the relationship in Figure 1 to the ionization potential of fluorine. It corresponds to an electron affinity of 4.59 eV, which is 1.14 eV (26.3 kcal/mole) greater than the true value. Thus, the electron affinity of fluorine is 26.3 kcal/mole less than would be predicted on the basis of the trend among the other halogen atoms.

(kcal/mole), as determined by extrapolation, are 25 for LiF, 26 for NaF, 28 for KF, 25 for RbF, and 31 for CsF. In view of the uncertainties of some of the experimental bond energies, the consistency of these results (with the exception of CsF) and their agreement with the deviation observed in the case of the electron affinity are most gratifying.

Thus the alkali halides, which are generally considered to be essentially ionic in character, do show the expected feature: the bond energies of the fluorides are consistently lower, by about 26 kcal/mole, than would be predicted from the trends among the other halides. A rather unexpected result is obtained, however, when the investigation is extended to covalently bound fluorine. In Figure 3, the dissociation energies of the hydrogen halides and of the C-X bonds (X = halogen) in the methyl halides are plotted against the reciprocals of their bond lengths.² Again linear correlations are obtained, from which the fluorine-containing molecules again deviate: HF by 27 kcal/mole, CH₃F by 23 kcal/mole.

Table I. Some Properties of the Halogens

Halogen	Atomic ionization potential, ^a eV	Atomic electron affinity, ^b eV	Atomic radius, ^c Å	Bond length of molecule, R _e , ^d Å	Dissociation energy of molecule, D _e , ^{d,e} kcal/mole
F	17.418	3.448	0.5741	1.43	37
Cl	12.96	3.613	0.9748	1.988	57.88
Br	11.811	3.363	1.117	2.284	45.92
I	10.448	3.063	1.324	2.666	35.86

^a C. M. Sitterly, Atomic Energy Levels Program, National Bureau of Standards, Washington, D. C. ^b B. L. Moiseiwitsch, *Advan. Atom. Mol. Phys.*, **1**, 61 (1965). ^c The atomic radius is taken to be the average radial distance from the nucleus of the outermost p electrons. These values were computed for the atoms from Hartree-Fock atomic wave functions by C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966). ^d T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth & Co., Ltd., London, 1958. ^e G. Herzberg, "Molecular Structure and Molecular Spectra. I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Princeton, N. J., 1950.

Apparently, then, the formation of the fluoride ion includes an unusual destabilizing effect of some sort, with which is associated an energy of about 26 kcal/mole. It is to be expected that this effect will manifest itself in various situations involving this ion. For example, there should be observed a corresponding lowering of the bond energies of the diatomic alkali fluorides. Figure 2 shows that the experimentally measured dissociation energies of the gaseous halides of each alkali metal vary linearly with the reciprocals of the bond lengths—with the consistent exception of the fluoride.¹ In each case, the dissociation energy of the fluoride is anomalously low. The magnitudes of the deviations

(1) The dissociation energies were taken from L. Brewer and E. Brackett, *Chem. Rev.*, **61**, 425 (1961); the bond lengths are from R. K. Ritchie and H. Lew, *Can. J. Phys.*, **42**, 43 (1964), and S. E. Veazy and W. Gordy, *Phys. Rev.*, **138A**, 1306 (1965).

Thus the destabilizing effect is of essentially the same magnitude in species in which fluorine is, in terms of the conventional models, "sharing" an electron as in those cases in which it has "gained" an electron. The distinction between "ionic" and "covalent" bonds can indeed be a vague one!

Finally, it is particularly interesting to consider the case of the fluorine molecule. The dissociation energy of F₂ is very low, relative to the trend among the other halogen molecules. This can be seen from the experi-

(2) The dissociation energies of the hydrogen halides are from P. G. Wilkinson, *Astrophys. J.*, **138**, 778 (1963); those of the methyl halides were taken from J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). All bond lengths are from "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement, Special Publication No. 18, The Chemical Society, London, 1965. Unfortunately, the dissociation energies available for the methyl halides are rather uncertain; the estimated errors are 1-3 kcal.

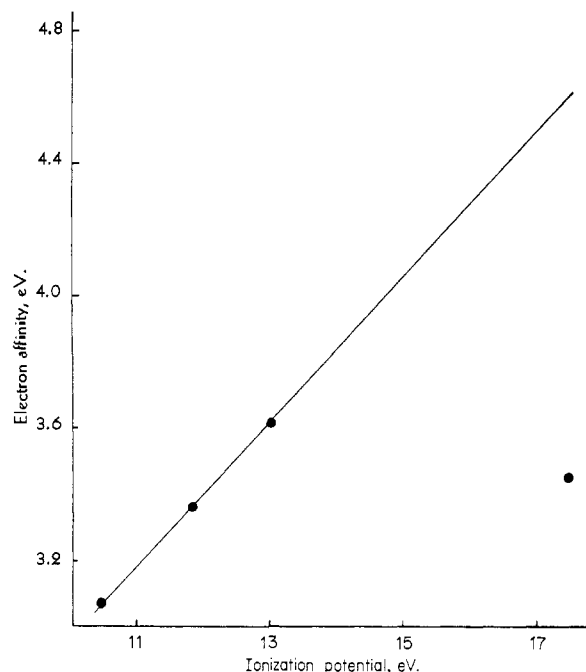


Figure 1. The relationship between the electron affinities and the ionization potentials of the halogen atoms.

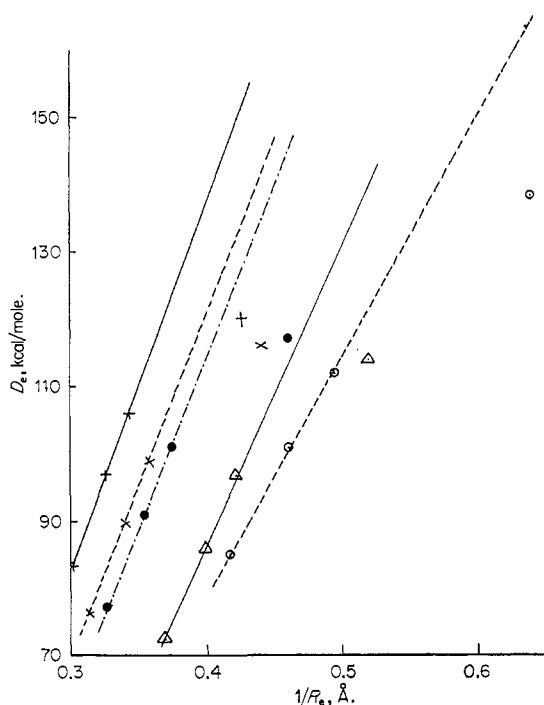


Figure 2. The relationships between the dissociation energies, D_e , and the reciprocals of the bond lengths, $1/R_e$, of the gaseous alkali halides: \circ , lithium halides; Δ , sodium halides; \bullet , potassium halides; \times , rubidium halides; $+$, cesium halides.

mental data presented in Table I. Several explanations or interpretations of this anomaly have been proposed;³⁻⁸ the most widely accepted at present seems to

(3) R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 884 (1955).

(4) M. G. Brown, *Trans. Faraday Soc.*, **55**, 9 (1959).

(5) K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

(6) K. S. Pitzer, *Advan. Chem. Phys.*, **2**, 59 (1959).

(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 142.

(8) G. L. Caldow and C. A. Coulson, *Trans. Faraday Soc.*, **58**, 633 (1962).

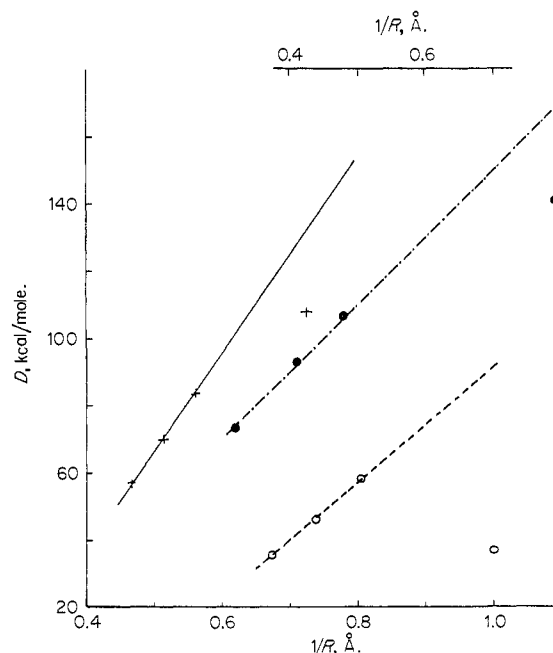


Figure 3. The relationships between the dissociation energies and the reciprocals of the bond lengths of the hydrogen halides, the methyl halides, and the halogen molecules: \bullet , plot of D_e vs. $1/R_e$ for the hydrogen halides; $+$, plot of D_0 vs. $1/R_0$ for the C-X bonds of the methyl halides; \circ , plot of D_e vs. $1/R_e$ for the halogen molecules (upper horizontal axis).

be that it is due to repulsion between the unshared outer-shell electrons on one fluorine atom and those on the other.

Figure 3 shows that the linear D vs. $1/R$ relationship which has prevailed throughout this work holds true also for I_2 , Br_2 , and Cl_2 , while F_2 falls short by 54 kcal/mole. Thus, again showing consistency, the deviation in the case of this molecule containing two fluorine atoms is twice that observed for a single atom.

If F_2 fit the linear relationship shown in Figure 3, its dissociation energy would be 91 kcal/mole, instead of its actual 37 kcal/mole. It has been pointed out by Sanderson that extrapolations in terms of a variety of other properties, such as melting points, critical temperatures, and polarizabilities, would also indicate a dissociation energy in the neighborhood of 90 kcal/mole for F_2 .⁹ This supports the validity of the procedure followed in this work, which has involved extrapolations in terms of $1/R$.

Further support can be found in the work of Caldow and Coulson, who computed the Coulomb energies of the halogen molecules.⁸ The Coulomb energy can be interpreted as the energy of the classical electrostatic interaction of two atoms whose electronic charge distributions interpenetrate without undergoing distortion.¹⁰ It is the sum of three terms: one represents the repulsion between the electrons on one atom and those on the other, a second term arises from the attraction between each nucleus and the electrons on the other atom, and the third represents the repulsion between the nuclei. In their calculations, Caldow and Coulson considered only the valence shells of the atoms, and used mutually orthogonal Slater atomic orbitals to represent

(9) R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960, p 226.

(10) S. Fraga and R. S. Mulliken, *Rev. Mod. Phys.*, **32**, 254 (1960).

the distributions of the electrons. They found that the Coulomb energies of the halogen molecules are negative, and therefore contribute to the stabilization of the molecules; the values calculated were -30.2 kcal/mole for I_2 , -37.6 for Br_2 , -42.8 for Cl_2 , and -10.3 for F_2 . The Coulomb energy for F_2 is clearly very small compared to the others, and it was concluded that "the source of the anomaly [in the dissociation energy of F_2] does indeed lie here."⁸

This conclusion can now be put on a more quantitative basis, and also given a somewhat different interpretation. If the calculated Coulomb energies are plotted against $1/R$, the usual extrapolation leads to a value of 62.5 kcal/mole for F_2 ; the deviation is therefore $62.5 - 10.3 = 52$ kcal/mole, which is essentially the same as that observed in the dissociation energy of the fluorine molecule (54 kcal/mole). This strongly supports the idea that the anomaly in the Coulomb energy is responsible for the deviation in the dissociation energy.

It is suggested, however, that the accepted interpretation of this anomaly, as arising from the unusually strong repulsion of the unshared outer-shell electrons on one fluorine atom for those on the other, should be reexamined. It has been shown in this work that a destabilizing effect of essentially the same magnitude, per fluorine atom, as that found in F_2 occurs in a number of other diatomic species, in which the fluorine atom is associated with various other atoms. Such an effect also occurs in the formation of the *free* fluoride ion, in the absence of any second atom.

It does not seem justifiable, therefore, to attribute this destabilization to an interaction associated with a specific molecule or bond. It appears rather that the anomaly involves the fluorine atom, in whatever circumstances, and its interaction with an external electron which enters its outer shell. This external electron may be provided, for example, by an alkali metal atom, in forming an "ionic" bond, or it may be provided by a nonmetal atom, as part of a "covalent" bond, or it may simply be involved in an attachment process, $F + e^- \rightarrow F^-$. In any case, it is suggested that because of the exceptionally small size of the fluorine atom (see Table I), the entering electron feels unusually large forces of attraction from the nucleus and repulsion from the electrons already associated with the atom. It appears that the magnitude of the anomaly in the repulsive forces is greater than in the attractive forces. Thus, although the attractive forces are by far the dominant ones and the electron does enter the outer shell of the fluorine atom, the energy of the interaction is less, by about 26 kcal/mole, than what it would be if there were no anomalous effects present. It is suggested, therefore, that the Coulomb energies calculated by Caldow and Coulson reflect primarily the interaction of each fluorine atom with the electron provided to the bond by the other fluorine.¹¹

(11) A very interesting treatment of bond energies has been presented by R. T. Sanderson, *J. Inorg. Nucl. Chem.*, **30**, 375 (1968), whose qualitative interpretation of the anomaly in the F_2 bond energy also de-emphasizes the role played by repulsion between the unshared electrons on one fluorine atom and those on the other.

Homogeneous Exchange of Iodine with Methyl Iodide in the Single-Pulse Shock Tube^{1,2}

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Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010. Received April 1, 1969

Abstract: The homogeneous gas-phase exchange of iodine with methyl iodide was studied in a single-pulse shock tube in the temperature range 870 – 1105 °K. Tracer quantities of the γ -ray emitter, ^{131}I , were introduced in the iodine. The observed exchange rates were consistent with the mechanism $M + I_2 \rightleftharpoons 2I + M$ and $I + CH_3I \rightleftharpoons CH_3 + I_2$ (where M is the inert carrier gas, argon), with a rate $k_1 = 10^{13.2} \exp(-17.4 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.

The gas-phase exchange of iodine with methyl iodide has not been successfully studied in the past because of complications caused by surface-catalyzed exchange. Clark, Pritchard, and Trotman-Dickenson⁴ found the exchange rate extremely sensitive to changes in the surface-volume ratio of the reaction vessel. For an unpacked vessel they found the exchange to proceed by the rate law $R = k(I_2)^{1/2}(CH_3I)$. Only a lower limit of 32 kcal for the over-all activation energy of this exchange could be inferred from this work. They proposed the

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission. Contribution No. 2509.

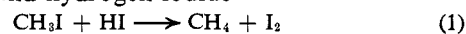
(2) Based on a Ph.D. Thesis by A. J. Kassman submitted 1969 to Iowa State University, Ames, Iowa.

(3) Pratt & Whitney Aircraft, AMRDL, Middletown, Conn.

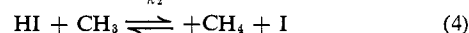
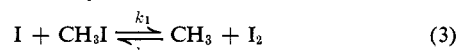
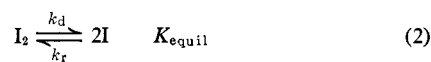
(4) D. Clark, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2633 (1954).

exchange to proceed by an SN_2 inversion of the methyl iodide by atomic iodine.

However, in a consideration of the reaction between methyl iodide and hydrogen iodide



Flowers and Benson⁵ as well as Sullivan⁶ have convincingly argued that the reaction occurs primarily *via* the radical mechanism



(5) M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, **38**, 882 (1963).

(6) J. H. Sullivan, *ibid.*, **46**, 73 (1967).