Bonding in C_1 and C_2 Fluorides

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A Farlow-type reaction involving manganese trifluoride and graphite has been used to generate the gaseous species $(CF_2)_{n=1,2,3...}$, CF_3, and C_2F_2 under equilibrium conditions. By mass spectrometric methods it has been found that $\Delta H_f{}^\circ{}_{298}$ for CF_2(g), CF_3(g), and C_2F_2(g) are -41.1 ± 2, -102.5 ± 3, and -45 ± 6 kcal mol^{-1}, respectively. These and other data show that $D^\circ{}_{298}(CF_3\text{-}F)$, -($CF_2$-F), -(CF-F), and -(C-F) are 139.4, 80.2, 123.7, and 126.0 (all $\pm$3) kcal mol^{-1}, respectively. The C≡C bond in difluoroacetylene is found to be 60 kcal weaker than that in acetylene.

Introduction

Complete bond dissociation energy data are available for very few molecules having more than three atoms. In this paper the existing data on C_1 fluorides are reviewed and new experimental data are presented which permit evaluation of $D(CF_3-F)$, $D(CF_2\text{-}F)$, D(CF-F), and D(C-F). Values for the carbon-carbon triple bond and the carbon-carbon double bond in C_2 fluorides are reported.

An accurate value for the total bond energy in CF_4 may be calculated from $\Delta H_f{}^\circ{}_{298}[CF_4(g)]$ recently reported to be -223.04 ± 0.18 kcal mol^{-1}.[1] Using the sublimation enthalpy of carbon and the dissociation energy of fluorine,[2] one finds $\Delta H^\circ{}_{\text{atom}}[CF_4(g)] = 469.4 \pm 2.3$ kcal mol^{-1}. For CF_3(g) $\Delta H_f{}^\circ{}_{298} = -94.8$ kcal mol^{-1} may be obtained by combining the ionization potential (I.P.) of CF_3, 9.25 ± 0.04 eV;[3] the appearance potential (A.P.) of $CF_3{}^+$ from CHF_3, 14.53 ± 0.05 eV,[4] with enthalpy of formation data for CHF_3(g) and H(g).[2] However, $\Delta H_f{}^\circ{}_{298} = -110.8 \pm 2.1$ kcal mol^{-1} is obtained using $D(CF_3\text{-}H) = 106.4 \pm 0.5$ kcal mol^{-1} from the kinetics of chlorinating CHF_3.[5] The possibility of excited product formation in the dissociative ionization of CHF_3 requires that 94.5 kcal be considered a lower limit to $-\Delta H_f{}^\circ[CF_3(g)]$ while the latter value should be an upper limit since it is based upon the activation energy for the reaction $Cl + CHF_3 \rightarrow HCl + CF_3$. It is apparent that an independent check on this value would be very desirable. The standard enthalpy of formation of CF_2(g) seems to be close to -41 kcal mol^{-1} at 298°K since a large number of diverse methods give values within a few kilocalories of this.[2] Evidently then $D^\circ(CF\text{-}F) + D^\circ(C\text{-}F) = 249.6 \pm 3.3$ kcal mol^{-1} at 298°K. $D^\circ{}_0$(C-F) has been reported as 114 kcal mol^{-1} (4.96 eV),[6] but it was recently found[7] that inclusion of the second anharmonicity constant in the Birge-Sponer extrapolation raised $D^\circ{}_e$ to 126.8 kcal mol^{-1} (5.50 ± 0.10 eV) and $D^\circ{}_{298}$ to 126.0 ± 2.3 kcal mol^{-1}.

If one defines the strength of the double bond in C_2F_4 as ΔH for the reaction

$$C_2F_4(g) \longrightarrow 2CF_2(g) \qquad (1)$$

then available data give 73 ± 6 kcal mol^{-1} at 298°K.[2] While the true value of ΔH_{298} for reaction 1 almost certainly lies within the limits given, an attempt to reduce the uncertainty seemed worthwhile. The situation with regard to the triple bond in FC≡CF is far less satisfactory since there are no experimental data on the stability of C_2F_2. If such were available it would be possible to calculate the "triple" bond strength in this molecule and thereby improve our understanding of the effect of fluorine substitution on the bonding ability of carbon.

Experimental Section

The apparatus, consisting of an effusion molecular beam source and a quadrupole mass spectrometer for studying the species produced in the beam source, has been described previously.[8] To improve the quality of the appearance potential measurements the energy spread in the ionizing beam was reduced by narrowing the ionizer entrance and exit slits. Also, trap current regulation of the ionizing electron beam was used instead of emission current regulation. A cylindrical effusion cell, machined from spectrographic grade graphite to have a 90° conical orifice 1.1 mm in diameter at the smaller (lower) end, was degassed by heating under vacuum before loading with 0.5 g of 99.5% MnF_3. The MnF_3 was used as received[9] without further purification. Precautions were taken to minimize contact with moisture. To help assure the attainment of equilibrium inside the cell, the quantity of sample used was such as to provide a sample surface at least 100 times larger than the orifice area while

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sample pressure at no time exceeded 10^{-5} atm within the cell.

The sample temperature was monitored with chromel–alumel thermocouples, one inserted in the cell top and another in the base. Thermocouple junction potentials, measured with a Honeywell 2732 potentiometer, were reproducible to 0.01 mV (0.25°). A third thermocouple, located in the cell base, provided an error signal to operate the beam source temperature control, maintaining the temperature of the sample cell constant within 1°. To minimize temperature errors (a) the thermocouple wires were continuous from sample to potentiometer or cold junction, (b) the wires were air-annealed at a red heat after installation, (c) the cold junctions were immersed at least 7 in. in separate distilled water–ice mixtures, and (d) the cell top was made 10 to 15° hotter than the base. Junction potentials were converted to temperature using the manufacturer's calibration[10] after these corrections were verified, ±0.05 mV, in a separate experiment. Sample temperatures were taken as an average of the top and bottom temperatures weighted by the distance of the sample from the top and bottom thermocouples.

Getter ion pumps maintained the pressure at less than 10^{-6} mm in the beam source region and considerably lower in the quadrupole region even at the highest sample temperatures.

Owing to the linear mass dispersion of the quadrupole analyzer, the determination of ion mass-to-charge ratios (*m/e*) was straightforward. Ions derived from neutral species originating in the effusion cell were identified by their abrupt disappearance upon closing the slit through which the sample vapors pass in order to reach the ionizer. Ionization efficiency curves[11] were obtained by varying the electron energy in 0.1- or 0.2-eV steps while maintaining the sample temperature and the electron beam current constant. The electron energy scale was calibrated by comparison of the observed A.P. of O_2^+, 13.06 ± 0.1 eV, with I.P. of $O_2 = 12.063 \pm 0.001$ eV.[12] Both the "initial break" method[11] and a recently described deconvolution method[13] were used to determine A.P.'s. Agreement between the two methods was within experimental error in all cases. Identification of the neutral precursor of ionic species was based upon temperature dependence studies, the A.P., and isotopic abundance in addition to the *m/e* value of the ion.

Results and Discussion

An extremely complex mass spectrum resulted when 70-V electrons were used for ionization of the sample vapors. At least 100 peaks were produced, extending to above *m/e* 400. Reducing the electron energy to 15 V still gave detectable signals for the monopositive ionic species CF, C_2F, CF_2, C_3F, C_2F_2, CF_3, C_3F_2, C_2F_3, C_3F_3, C_2F_4, C_3F_4, C_2F_5, C_3F_6, C_4F_6, C_3F_7, C_5F_7, C_4F_8, C_6F_9, C_6F_{10}, and C_7F_{10}. Since the mass analyzer would not resolve the 0.06 amu mass difference between $^{55}MnF_x$ and $^{12}C_3F_{x+1}$, the possibility of contribution by MnF_x to these species was given careful consideration. As discussed in the following text only the $x = 0$ species, *m/e* 55, was satisfactorily identified—as due to simple ionization of Mn(g) at low electron energies. Considering this plus the low intensity of the heavier ions, identification efforts were limited to the species listed in Table I. The ion with *m/e* 31, certainly CF^+, could arise from numerous fragmentation processes,[14] but not from simple ionization of CF as evidenced by the high A.P. Interpretation of the *m/e* 43 ionization efficiency curve was not attempted.

Table I: AP's and Precursors in the MnF_3—Graphite Reaction

Ion *m/e*	A.P., eV	Precursor
31	13.3 ± 0.3	?
50	11.7 ± 0.2	CF_2
55	7.4 ± 0.1	Mn
62	11.4 ± 0.5	C_2F_2
69	9.8 ± 0.2	CF_3
74	13.9 ± 0.5	?
93	12.4 ± 0.3	?
100	9.8 ± 0.3	C_2F_4
112	12.0 ± 0.2	?
150	10.8 ± 0.2	C_3F_6?

The agreement of the observed A.P. of *m/e* 50 with the I.P. reported for CF_2, 11.7 eV[15] suggests that CF_2 is the precursor of this ion at least to the first upward inflection at 14.0 ± 0.4 eV. The process beginning at 14.0 was not determined but it is not CF_2^+ from C_2F_4 since this requires 15.1 eV.[16] Additional evidence that *m/e* 50 is a C_1 species came from measurement of the relative currents of *m/e* 50 and *m/e* 51 ions. With 70-V electrons *m/e* 51 was 1.2 ± 0.2% of *m/e* 50. The expected abundance of $^{13}CF_2$ relative to $^{12}CF_2$ is 1.1%.

There is little doubt that the low energy ion current of *m/e* 55 derives from the simple ionization of Mn(g). Using the observed A.P. of O_2^+, 13.06 ± 0.1 eV, to calibrate the electron energy scale, A.P. *m/e* 55 was found to be 7.4 ± 0.1 eV, in excellent agreement with

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the spectroscopic I.P. of Mn, 7.43 eV.[17] Furthermore, an upward inflection found at 9.2 ± 0.1 eV agrees with the appearance of Mn^+ in the lowest of the closely spaced ^5D states, 1.77 to 1.86 eV above the ground state of Mn^+.[17] In its other features the observed ionization efficiency curve closely resembles that reported in an earlier study of the MnF_2–Mn reaction.[18] All parts of the m/e 55 curve were found to have a temperature dependence essentially equivalent to the heat of sublimation of α-manganese.[19] The ion current of m/e 56 was less than 0.1% of the m/e 55 current compared to about 3% expected if m/e 55 is C_3F^+ and m/e 56 is $^{13}C^{12}C_2F^+$. Whereas these findings strongly support the electron energy scale correction applied and suggest the presence of Mn(c) in the reaction mixture, reaction heats involving Mn species were not evaluated because no other Mn species could be unequivocally identified.

The I.P. of C_2F_2 has not been reported previously. The similar molecules, acetylene and propyne, have I.P. = 11.41 and 10.36 eV, respectively.[11] The observed A.P., 11.4 ± 0.5 eV, thus suggests that m/e 62 arises from simple ionization of C_2F_2, at least to the first upward break at 13.8 ± 0.3 eV. The m/e 63 ion current was found to be 2.0 ± 0.2% of the m/e 62 current compared to 2.0% expected for a C_2 species. No attempt was made to identify the higher energy process.

Although CF_3^+ is also a common fragment in fluorocarbon mass spectra the very low A.P. found here for m/e 69, 9.8 ± 0.2 eV, is convincing evidence of the presence of $CF_3(g)$. It should be noted that the electron impact I.P. of CF_3, 10.10 ± 0.05 eV,[4] differs from the photon impact I.P., 9.25 ± 0.04 eV, because of the structural difference between CF_3 and CF_3^+.[3] The presence of a 1% satellite at m/e 70 supports the identification of m/e 69 as CF_3^+. Since the A.P.'s of CF_3^+ from C_2F_4 and CF_4, the most abundant products in Farlow type reactions,[20,21] are 13.5 and 15.4 eV, respectively,[22] the thermodynamic studies were performed using 13.5-V electrons. There was evidence for the presence of both C_3 and Mn species at m/e 74, 93, and 112, but despite considerable efforts we were unable to identify the precursors of any of these ions in the threshold region. Certainly m/e 74 cannot be due to simple ionization of MnF, a process which requires only 8.7 eV, while the observed A.P. of m/e 93 is too high to reconcile with the I.P. of MnF_2, 11.5 ± 0.3 eV, but too low to be MnF_2^+ from MnF_3, a process which requires 13.7 ± 0.3 eV.[18,23] Each peak was found to have a small satellite (3%, 1%, and 1% of the main peak, respectively) at the next higher mass number. Sensitivity considerations alone indicate that ions derived from subliming MnF_2 or MnF_3 should have been undetectable in the threshold region at the temperature of the ionization efficiency studies. As a consequence, reactions involving MnF_x and C_3F_{x+1} were excluded from the thermodynamic studies. C_2F_4 is interpreted to be the precursor to $C_2F_4^+$ because the observed A.P. agrees with both previously reported values for I.P. C_2F_4, 10.12[16] and 9.3 ± 0.2 eV,[24] and is too low to be due to a fragmentation process. Again, this interpretation is substantiated by the presence of a 2% isotope peak at m/e 101. Lastly, the low A.P. of $C_3F_6^+$ at m/e 150 indicates the ion is not a fragment and by its similarity to the I.P.'s of olefins and acetylenic molecules supports the conclusion that C_3F_6 is the precursor.

After having determined the precursors to the various ions formed by low-energy electron impact ionization, the ion currents for CF_2^+, CF_3^+, $C_2F_2^+$, and $C_2F_4^+$ were measured at each of a series of temperature ranging from 874 to 944°K in run 1 and from 867 to 963°K in run 2 using 13.5-V electrons to assure that the only parent ion currents were measured. From these data equilibrium constants for the equilibria

$$2CF_2(g) \longrightarrow C_2F_4(g) \tag{2}$$

$$3C_2F_4(g) \longrightarrow 4CF_3(g) + 2C(s) \tag{3}$$

and

$$2C(s) + C_2F_4(g) \longrightarrow 2C_2F_2(g) \tag{4}$$

were found using the $P = kI^+T$,[25] which relates the partial pressure of a species in the effusion cell to the absolute temperature of the sample and the measured positive ion current through the proportionality constant k. In order to do this it was first necessary to evaluate k for each species in the equilibria. A calibration experiment was performed wherein cadmium was vaporized from the same effusion cell and the total Cd^+ current produced at a known temperature was measured from which k_{Cd} was calculated using the vapor

Table II: Values of $k = P/I^+T$ for C–F Species, Atm A^{-1} °K^{-1}

Ion	Run 1	Run 2
$C_2F_2^+$	4.81	5.47
$C_2F_4^+$	0.816	0.927
CF_2^+	5.27	5.99
CF_3^+	0.679	0.772

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Table III: Equilibrium Constant Equation Parameters and Reaction Enthalpies with Standard Deviations

Reaction	Run	A, kcal mol^{-1} °K^{-1}	B, cal °K^{-1} mol^{-1}	$\Delta H°_{298}$, kcal mol^{-1} Second law	$\Delta H°_{298}$, kcal mol^{-1} Third law
2	1	66.98 ± 0.7	−36.50 ± 0.8	−68.2 ± 0.4	−72.6
	2	67.72 ± 3	−36.99 ± 3	−69.0 ± 3	−72.9
3	1	−50.23 ± 4	16.87 ± 4	52.7 ± 4	66.9
	2	−54.70 ± 4	24.05 ± 4	57.1 ± 4	64.8
4	1	−75.43 ± 4	31.55 ± 6	74.9 ± 5	79.9
	2	−57.08 ± 4	11.49 ± 4	56.5 ± 4	79.6

pressure of cadmium.[26] It is easily shown that, in the presence of mass discrimination *in the mass analyzer*

$$\frac{k_j}{k_i} = \frac{G_i\sigma(E)_i A_i \tau_i}{G_j\sigma(E)_j A_j \tau_j} \tag{5}$$

where multiplier gains G convert detector output (electrons) to the equivalent positive ion input, $\sigma(E)$ is the relative cross section for ionization by electrons of energy E, A is the isotopic abundance, and τ is the ion transmission efficiency, *i.e.*, the discrimination of the quadrupole analyzer. Gains were experimentally determined except for the low intensity $C_2F_2^+$ ion which was estimated with little loss in accuracy.[27] $\sigma(E)$ values were calculated by making the usual assumptions that $\sigma(E) \propto (\sigma_{\max})(E - \text{A.P.})$, where Mann's $\sigma_{\max}$ values were used,[28] and that molecular cross sections are sums of atomic cross sections. The latter assumption holds well for hydrocarbons[29] and might therefore apply to fluorocarbons. The τ values were found as follows. Prior to this experiment the 70-eV fragmentation patterns of a large number of organic substances were obtained and compared to published[14] spectra obtained with relatively nondiscriminating analyzers. From these data a τ *vs.* mass curve was synthesized which indicated $\tau \propto (m/e)^{-1.1}$, the factor used here to get relative τ values. The resulting k values, summarized in Table II, are within 25% of a second set calculated using the measured Mn^+ current and assuming unit activity α-manganese to be present as a product of the reaction.[30] Cross section and other uncertainties remain, however, to cause as much as a factor of 2 uncertainty in these quantities. The derived equilibrium constants and reaction enthalpies found using JANAF thermodynamic functions are reported in the form

$$R \ln K_p = (A/T) + B$$

in Table III. A second-law heat of reaction at the median temperature, $\Delta H°_{913}$, was calculated from A of each equation and converted to $\Delta H°_{298}$ using available data.[2] Such second-law values are independent of pressure calibrations but suffer from rather large random deviations, presented in Table III as standard deviations from the least-squares line. In addition, cumulative systematic errors, chiefly a ±4° temperature uncertainty, contribute another ±1 kcal mol^{-1}. A single third-law $\Delta H°_{298}$ was found for each equation through the use of free-energy functions.[2] A factor of 2 uncertainty in each pressure leads to an uncertainty of about 1 kcal per such term in the equilibrium constant.

The data in Table III and supplementary information from the JANAF tables are used in the following discussion. The dissociation enthalpy, *i.e.*, the strength of the double bond, in C_2F_4 at 298°K is 68.6 ± 3 kcal mol^{-1} by the second law and 72.8 ± 2 kcal mol^{-1} by the third law. The third-law value should be more reliable in this case because the molecular parameters are rather well known. The value is in sharp contrast with $D(CH_2{=}CH_2)$, 160 kcal mol^{-1}. The $\Delta H_f°_{298}[CF_2(g)]$ is -41.1 ± 2 kcal mol^{-1}, in very close agreement with previous values. Average second- and third-law results for $\Delta H_f°_{298}[CF_3(g)]$ are -102.5 ± 3 and -99.8 ± 3 kcal mol^{-1}, respectively. Since the free-energy functions for CF_3 are based on estimated properties, the second-law value is preferred. The stepwise removal of fluorine atoms from $CF_4(g)$ therefore requires 139.4, 80.2, 123.7, and 126.0 kcal mol^{-1} at 298°K, all ± about 3 kcal mol^{-1}. The significant points in these data are the near equivalence of the p electrons and the large (60 kcal) expenditure of energy required, presumably as promotion energy, to add a fluorine to CF_2. Data for other fluorides[31,32] also show that direct involvement of the s electrons in bonding is energetically costly, *e.g.*, $D(AlF_2\text{–}F) = 156$, $D(AlF\text{–}F) = 106$, $D(Al\text{–}F) = 159$, $D(BF_2\text{–}F) = 181$, $D(BF\text{–}F) = 123$, and $D(B\text{–}F) = 159$ kcal mol^{-1}. For $C_2F_2(g)$ $\Delta H_f°_{298} = -44.6 \pm 6$ and -37.6 ± 4 kcal mol^{-1} are the respective average second- and third-law results. Although these agree within experimental error, it must be noted that the electronic states of C_2F_2

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are unknown and only the ν_3 vibrational frequency has been measured.[33] The second-law $\Delta H_f{}^\circ{}_{298}[C_2F_2(g)]$, -45 ± 6 kcal mol^{-1}, plus $\Delta H_f{}^\circ{}_{298}[CF(g)]$ found from $D^\circ{}_{298}$ give 171 kcal for $D(CF{\equiv}CF)$ which is about 60 kcal *weaker* than the triple bond in acetylene. While the reason for this effect is not obvious, it is apparent that the fluorine is charge-withdrawing, not charge-donating as is sometimes postulated, in the CF_2 and CF molecules.

Acknowledgments. This work has been supported by the Research Corporation and the National Science Foundation.

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Catalytic Polarographic Current of a Metal Complex.[1] VI. Correlation of the Nickel(II)–*o*-Phenylenediamine Prewave Height with the Surface Concentration of the Ligand[2]

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The surface concentration, Γ, of *o*-phenylenediamine on mercury has been determined by differential capacitance measurements as a function of both the ligand volume concentration and the electrode potential in several different electrolyte systems. The Γ values obtained at relatively high bulk ligand concentrations (10^{-3}–10^{-1} *M*) have been extrapolated to the concentration range (2×10^{-5}–4×10^{-4} *M*) employed in previous polarographic measurements of the nickel(II)-*o*-phenylenediamine prewave. The rate of attainment of near-equilibrium surface coverage at these low bulk concentrations has been examined through a study of the dependence of the prewave height on the time of current measurement. The experimental results are in accord with those predicted by a simplified mathematical treatment based on a surface-controlled catalytic mechanism assuming fast adsorption when the ligand concentration is in excess of 10^{-4} *M* in 0.1 *M* electrolytes. The dependence of the prewave height on the ligand surface concentration is also correctly predicted by the theoretical treatment. A previously reported examination of the effect of the electrode double layer on the prewave height had indicated that the electroactive species possessed a charge of +1 rather than the charge of +2 expected for a complex formed by Ni(II) and an uncharged ligand. In this study it was found that correction for differing ψ^0 potentials in 0.1 and 0.5 *M* potassium chloride also indicated that an effective charge of +1 is involved in the rate-determining step.

It was shown in a previous paper[2d] that the structure of the electrode double layer has a pronounced effect on the height of the polarographic prewave obtained with Ni(II) in the presence of *o*-phenylenediamine. The results of that study were qualitatively consistent with a previous suggestion that the prewave reaction mechanism involves a rate-limiting chemical reaction between the hexaaquonickel ion and the adsorbed ligand which is cyclically regenerated by reduction of the electroactive adsorbed complex.[2a,b] The simplified mathematical treatment of the reaction mechanism presented on that basis, however, incorporated unsubstantiated assumptions concerning the adsorption behavior of the ligand and produced an unexpected result with respect to the charge of the electroactive species.

This paper presents the results of the determination of the surface concentration of the ligand on mercury as a function of volume concentration and electrode potential in several electrolytes. The theoretical dependence of the prewave height on the ligand surface concentration is further examined using these experimental values.

Experimental Section

The methods used in making the polarographic measurements generally followed routine procedures and have been described in a previous paper.[2d] Surface concentrations of *o*-phenylenediamine were calculated from differential capacitance measurements. The impedance bridge and polarizing circuits used in making

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[1] This research was supported in part by grants from the National Science Foundation (NSF GP-4620 and GP-6425) and the U. S. Army Office of Research, Durham, N. C. (No. DA-31-124-ARO-D-284).

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