

Mass Spectrometric Studies at High Temperatures.

VII. The Sublimation Pressure of Chromium(II) Fluoride and the Dissociation Energy of Chromium(I) Fluoride

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Mass spectrometric studies of CrF_2 sublimation and vaporization from a Knudsen cell have established $\text{CrF}_2(\text{g})$ as the major vapor species and $\Delta H^\circ_{298}[\text{sublimation}] = 86.8 \pm 2.0 \text{ kcal. mole}^{-1}$. When $\text{Cr}(\text{s})$ is heated with $\text{CrF}_2(\text{s})$, the lower fluoride, CrF , is produced. From equilibrium measurements the dissociation energy of $\text{CrF}(\text{g})$ has been established as $D^\circ_{298} = 4.61 \pm 0.15 \text{ e.v.}$ ($106.4 \pm 3.5 \text{ kcal. mole}^{-1}$).

I. Introduction

Because reliable Knudsen or Langmuir vaporization and sublimation rates for many transition metal halides were not available, the review of Brewer, Somayajulu, and Brackett¹ on the thermodynamic properties of the gaseous metal dihalides includes many estimated heats of sublimation. The sublimation rate of CrF_2 had not previously been determined experimentally.

The dissociation energies of the transition metal monofluorides are also poorly known. The thermochemical work on the alkaline earth fluorides^{2,3} and on MnF_4 suggests that the stabilities of transition metal monofluorides may be much greater than previously suspected, *i.e.*, in the range 4.0–7.0 e.v.

In this work the sublimation rate of CrF_2 has been measured and the vapor species identified by the Knudsen technique employing a mass spectrometer. In addition, the dissociation energy of the CrF molecule has been evaluated by utilizing the mass spectrometer to study the equilibrium $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{g})$ in a Knudsen cell.

II. Experimental

The mass spectrometer employed in this work has been described previously.² The CrF_2 powder used was commercially available reagent grade. All samples were extensively outgassed in the instrument before temperature dependence studies were begun.

III. Results and Discussion

The Sublimation and Vaporization of CrF_2 . The rates of sublimation and vaporization were measured and the vapor species identified between 1112 and 1333°K. by means of the mass spectrometric technique. The ionic species formed by electron bombardment of

the molecules effusing from the tantalum Knudsen cell were Cr^+ , CrF^+ , and CrF_2^+ with lesser amounts of TaF_4^+ . No dimers or higher polymeric species were observed although the spectrum was scanned to mass 400.

Ionization efficiency curves for Cr^+ , CrF^+ , and CrF_2^+ are presented in Figure 1. In each case the measured ion intensity was corrected for background and photoionization effects.⁵ Using as a standard the known value⁶ of 10.4 e.v. for the ionization potential for Hg, one obtains $\text{AP}(\text{Cr}^+) = 6.7$, $\text{AP}(\text{CrF}^+) = 8.4$, and $\text{AP}(\text{CrF}_2^+) = 10.1 \text{ e.v.}$, with estimated uncertainties of $\pm 0.3 \text{ e.v.}$ The appearance potential of the Cr^+ ion when compared to the known⁶ ionization potential of chromium, 6.76 e.v., indicates that, below the break at *ca.* 19 e.v., this ion is probably due to simple ionization of $\text{Cr}(\text{g})$ most likely formed by reaction of the sample with the tantalum Knudsen cell. The break in the curve is attributed to the formation of the Cr^+ ion by the dissociative ionization of $\text{CrF}_2(\text{g})$. The low-energy tail of the CrF^+ ionization efficiency curve probably is due to simple ionization of the $\text{CrF}(\text{g})$ molecule, while the break at *ca.* 14 e.v. is attributed to the onset of the process forming CrF^+ ions from $\text{CrF}_2(\text{g})$ by dissociative ionization. The CrF_2^+ ion is attributed to simple ionization of $\text{CrF}_2(\text{g})$.

The heat of sublimation of CrF_2 was determined from the experimentally observed ion currents of CrF_2^+ in the following manner. The intensity of the $^{52}\text{CrF}_2^+$ peak, using 70-v. electrons, was followed as a function of temperature between 1112 and 1165°K. By making use of the ion current–pressure relationship,⁷ $P = kI^+T$, and the integrated form of the Clausius–Clapeyron equation, one finds a value of ΔH_T which is independent of the proportionality constant k . The slope of the $\log(I^+T)$ vs. $(1/T)$ curve yielded a heat of sublimation $\Delta H^\circ_{1133} = 83.4 \pm 1.5 \text{ kcal. mole}^{-1}$, where the uncertainty given is the standard deviation of the least-squares treatment. The true uncertainty may be two or three times this figure owing to such factors as temperature gradients in the crucible. Because no heat capacity data for $\text{CrF}_2(\text{s})$ were available, the thermodynamic functions for $\text{CrF}_2(\text{s})$ were estimated from a combination of the data for $\text{MnF}_2(\text{s})$ listed by Mah,⁸ the heat capacity equations for $\text{NiF}_2(\text{s})$ presented by Glassner,⁹ and the data for $\text{Cr}(\text{s})$, $\text{Mn}(\text{s})$, and $\text{Ni}(\text{s})$

(1) L. Brewer, G. R. Somayajulu, and E. Brackett, Lawrence Radiation Laboratory Report UCRL-9840, Sept. 1961; *Chem. Rev.*, **63**, 111 (1963).

(2) G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, *J. Phys. Chem.*, **67**, 877 (1963).

(3) G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, *Nature*, **199**, 804 (1963).

(4) R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **86**, 5090 (1964).

(5) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(6) C. E. Moore, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949.

(7) W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953).

(8) A. D. Mah, U. S. Department of Interior, Bureau of Mines, Report of Investigation 5600, U. S. Government Printing Office, Washington, D. C., 1960.

presented by Stull and Sinke.¹⁰ Thermodynamic functions for $\text{CrF}_2(\text{g})$ were calculated from the parameters presented by Brewer, *et al.*,¹ who assumed the CrF_2 gaseous molecule to be linear with a Cr-F bond distance of 1.72 Å. and estimated the vibrational frequencies to be $\omega_1 = 535$, $\omega_2 = 70$, and $\omega_3 = 704 \text{ cm}^{-1}$. When corrected to 298°K., the second law heat of sublimation becomes $\Delta H^\circ_{298} = 86.2 \pm 1.5 \text{ kcal. mole}^{-1}$ which is close to the value, 85 kcal. mole⁻¹, estimated by Brewer.¹

A plot of $\log(I^+T)$ vs. $1/T$ for the CrF_2^+ ion in the temperature range 1170 to 1333°K. yielded a value for the heat of vaporization of $\Delta H^\circ_{1249} = 78.1 \pm 0.5 \text{ kcal. mole}^{-1}$. These data would indicate that the heat of fusion of $\text{CrF}_2(\text{s})$ is approximately $5.3 \pm 1.6 \text{ kcal. mole}^{-1}$. When corrected to 298°K. the second law heat becomes $86.9 \pm 0.5 \text{ kcal. mole}^{-1}$. A plot of $\log(I^+T)$ vs. $1/T$ for CrF^+ in the range 1228–1312°K., again using 70-v. electrons, yielded $\Delta H^\circ_{1273} = 77.4 \pm 1.8 \text{ kcal. mole}^{-1}$, which agrees with the value obtained for CrF_2^+ within the limits of the standard deviations and further indicates that, above the break at *ca.* 14 e.v., the major portion of the CrF^+ ions came from the dissociative ionization of $\text{CrF}_2(\text{g})$.

An alternative approach is to calculate ΔH°_{298} at each temperature from the absolute pressure and the free-energy function change for the reaction. In order to determine the instrument constant k , a weighed sample of previously degassed CrF_2 was vaporized from the crucible at a constant temperature and the intensity of the $^{52}\text{CrF}_2^+$ peak was followed as a function of time. At 1182°K. $10.1 \times 10^{-4} \text{ g.}$ effused in 150 min. By use of the Knudsen equation the pressure was calculated to be $5.96 \times 10^{-7} \text{ atm.}$ The value of k thus determined was combined with the experimentally determined values of I^+T to calculate a value of $\log P$ for each observation. These values for $\log P$ were then combined with the free-energy functions for $\text{CrF}_2(\text{s})$ and $\text{CrF}_2(\text{g})$ taken from Brewer, *et al.*,¹ to obtain third law values for the heat of sublimation. The results of the mass spectrometric runs are presented in Table I and plotted in Figure 2. The small standard deviation of $\pm 0.1 \text{ kcal. mole}^{-1}$ for the third law heat reflects the high reproducibility of the measurements, although the true uncertainty must reflect possible errors in the estimated thermodynamic functions for $\text{CrF}_2(\text{g})$. The third law heat, ΔH°_{298} , is, therefore, taken to be $86.8 \pm 2.0 \text{ kcal. mole}^{-1}$. For the second law results, the major inherent errors are those in temperature measurement as the enthalpy correction for the gas is fairly insensitive to the choice of molecular parameters. In practice, uncertainties of $\pm 3 \text{ kcal. mole}^{-1}$ are obtained in the temperature range covered by this investigation. The derived second law heat, ΔH°_{298} , may then be taken as $86 \pm 3 \text{ kcal. mole}^{-1}$.

For calculating the pressure of $\text{CrF}_2(\text{g})$ over solid CrF_2 , the following equation has been derived

$$\log P_{\text{atm}} = -\frac{(1.822 \pm 0.030) \times 10^4}{T} + 9.14 \pm 0.18$$

and for $\text{CrF}_2(\text{g})$ over $\text{CrF}_2(\text{l})$

(9) A. Glassner, Argonne National Laboratory Report ANL-5750, Jan. 1958.

(10) D. R. Stull and G. C. Sinke, *Advances in Chemistry Series*, No. 18, American Chemical Society, Washington, D. C., 1956.

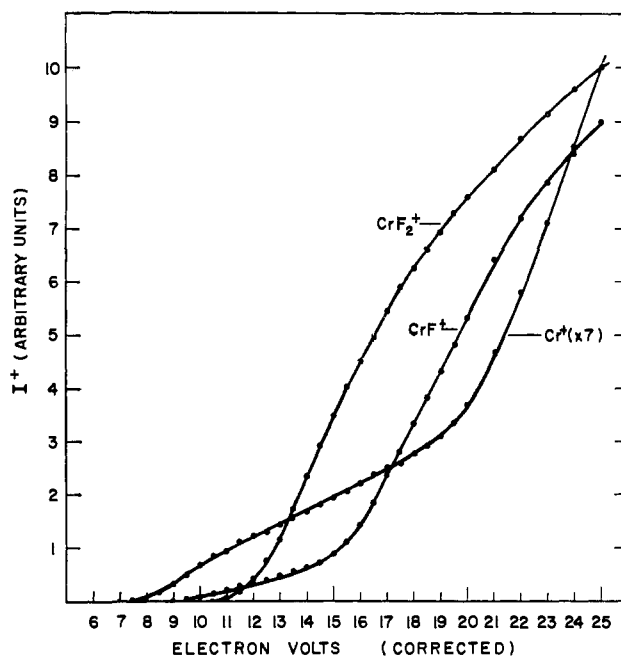


Figure 1. Ionization efficiency curves for species observed over CrF_2 .

$$\log P_{\text{atm}} = -\frac{(1.707 \pm 0.010) \times 10^4}{T} + 8.18 \pm 0.18$$

The Stability of the CrF Gaseous Molecule. In order to achieve reducing conditions and enhance the amount of $\text{CrF}(\text{g})$ present, about 200 mg. of chromium powder was added to the CrF_2 sample in the Knudsen cell. The ionic species created from the molecules effusing from the cell in the range 1259 to 1317°K. were Cr^+ , CrF^+ , and CrF_2^+ . Ionization efficiency curves are shown in Figure 3. Again, the measured ion intensities were corrected for background and photoionization effects.⁵ Using the ionization potential of Hg equal to 10.4 e.v. as a standard,⁶ one finds the appearance potentials for Cr^+ , CrF^+ , and CrF_2^+ to be 6.7, 8.3, and 10.2 e.v., respectively, with an estimated uncertainty of $\pm 0.3 \text{ e.v.}$ The appearance potential of Cr^+ again indicates that this ion is due to the ionization of $\text{Cr}(\text{g})$. Temperature dependence studies of CrF^+ established that above the break at *ca.* 14 e.v. the ion is produced by the dissociative ionization of $\text{CrF}_2(\text{g})$, whereas below 14 e.v. another process is involved which is assumed to be the simple ionization of $\text{CrF}(\text{g})$. In this system the activity of the condensed CrF_2 was less than unity, *i.e.*, the heat of formation from the condensed phase was greater than that found previously for the reaction $\text{CrF}_2(\text{l}) = \text{CrF}_2(\text{g})$.

The equilibrium constant for the homogeneous reaction $2\text{CrF}(\text{g}) = \text{CrF}_2(\text{g}) + \text{Cr}(\text{g})$ was determined at a series of temperatures using low-energy electrons. The use of electron voltages about 5 v. above the appearance potentials for the ions minimized the effects of fragmentation. The equilibrium constant K_1 for this reaction is pressure independent so that instrument geometry and sensitivity factors cancel and it was only necessary to correct the ion-current constant $K_1' = I(\text{Cr}^+)I(\text{CrF}_2^+)/[I(\text{CrF}^+)]^2$, for relative cross sections, differences in energy above the threshold, and gains.

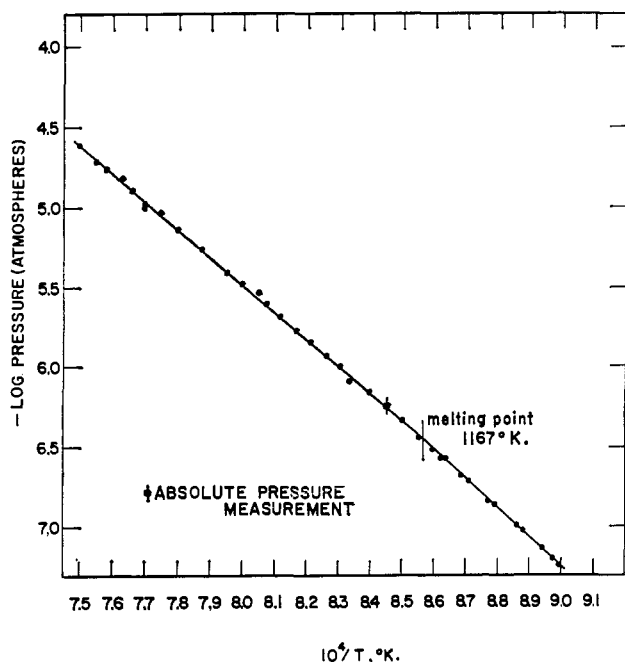


Figure 2. Vapor pressure data for CrF_2 .

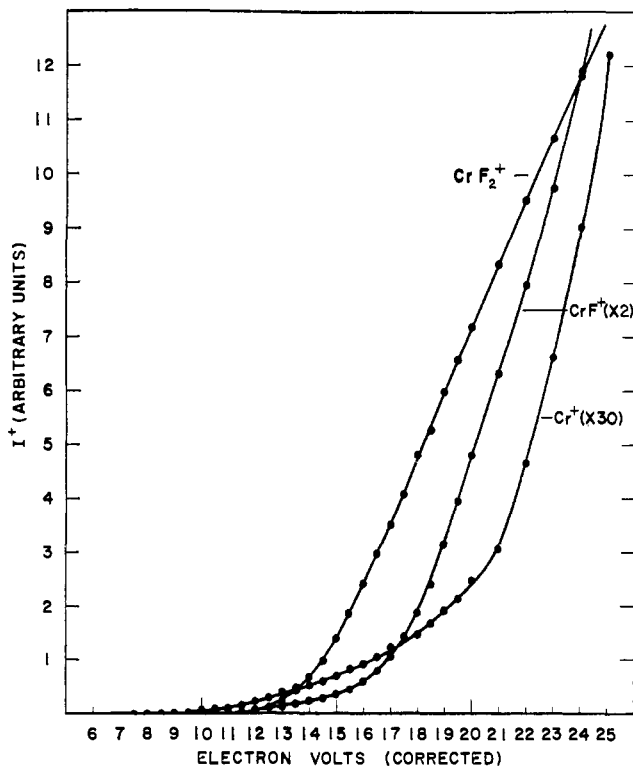


Figure 3. Ionization efficiency curves for species observed over $\text{CrF}_2\text{-Cr}$.

The tabulated cross sections of Otvos and Stevenson¹¹ and the experimental values of the gain ratios of the ions Cr^+ , CrF^+ , and CrF_2^+ were used to calculate $K_1 = 1.066 K_1'$. The values of $\log K_1$ were then used, together with the free-energy functions for $\text{CrF}_2(\text{g})$ from Brewer, *et al.*,¹ for $\text{Cr}(\text{g})$ from Stull and Sinke,¹⁰ and the free-energy functions for $\text{CrF}(\text{g})$ estimated from the

(11) J. W. Otvos and D. D. Stevenson, *J. Am. Chem. Soc.*, **78**, 546 (1956).

Table I. Mass Spectrometric Sublimation and Vaporization Data^{a,b} for CrF_2

| Temp., °K. | $I(\text{CrF}_2^+)$, arbitrary units | $-\log P_{\text{atm}}$ | $-\Delta\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$, cal. deg. ⁻¹ mole ⁻¹ | ΔH°_{298} , kcal. mole ⁻¹ |
|------------|---------------------------------------|------------------------|--|---|
| 1333 | 43.2 | 4.617 | 43.94 | 86.74 |
| 1324 | 34.3 | 4.718 | 43.98 | 86.81 |
| 1319 | 30.6 | 4.767 | 44.00 | 86.80 |
| 1311 | 27.1 | 4.820 | 44.05 | 86.67 |
| 1305 | 22.8 | 4.895 | 44.07 | 86.74 |
| 1298 | 18.9 | 4.977 | 44.11 | 86.81 |
| 1291 | 16.9 | 5.025 | 44.15 | 86.68 |
| 1282 | 12.5 | 5.156 | 44.19 | 86.89 |
| 1270 | 9.75 | 5.264 | 44.25 | 86.79 |
| 1257 | 6.95 | 5.411 | 44.31 | 86.82 |
| 1249 | 6.05 | 5.471 | 44.35 | 86.67 |
| 1242 | 5.30 | 5.529 | 44.39 | 86.55 |
| 1238 | 4.47 | 5.603 | 44.41 | 86.72 |
| 1232 | 3.78 | 5.675 | 44.44 | 86.75 |
| 1224 | 3.10 | 5.762 | 44.48 | 86.72 |
| 1217 | 2.59 | 5.840 | 44.51 | 86.69 |
| 1210 | 2.15 | 5.921 | 44.55 | 86.68 |
| 1204 | 1.83 | 5.991 | 44.58 | 86.68 |
| 1200 | 1.45 | 6.092 | 44.60 | 86.98 |
| 1191 | 1.25 | 6.156 | 44.65 | 86.73 |
| 1182 | 1.06 | 6.228 | 44.69 | 86.51 |
| 1177 | 0.872 | 6.313 | 44.71 | 86.63 |
| 1170 | 0.653 | 6.438 | 44.75 | 86.83 |
| 1299 | 17.9 | 5.000 | 44.10 | 87.01 |
| 1182 | 1.06 ^c | 6.228 | 44.69 | 86.51 |
| 1165 | 0.551 | 6.512 | 44.77 | 86.87 |
| 1160 | 0.474 | 6.587 | 44.80 | 86.93 |
| 1151 | 0.352 | 6.707 | 44.85 | 86.95 |
| 1140 | 0.255 | 6.847 | 44.90 | 86.90 |
| 1129 | 0.182 | 6.993 | 44.95 | 86.88 |
| 1115 | 0.113 | 7.200 | 45.03 | 86.95 |
| 1158 | 0.481 | 6.571 | 44.81 | 86.71 |
| 1148 | 0.322 | 6.745 | 44.86 | 86.94 |
| 1138 | 0.247 | 6.860 | 44.91 | 86.83 |
| 1126 | 0.172 | 7.017 | 44.97 | 86.79 |
| 1119 | 0.127 | 7.149 | 45.00 | 86.96 |
| 1112 | 0.102 | 7.244 | 45.04 | 86.95 |

Average = 86.79 ± 0.13

^a Last twelve points taken below melting point. ^b Second set of measurements (last six points) corrected for change in multiplier gain. ^c Absolute pressure experiment.

data for $\text{Cr}(\text{g})$ from Stull and Sinke¹⁰ and for $\text{Mn}(\text{g})$ and $\text{MnF}(\text{g})$ from Kelley¹² and Kelley and King,¹³ to calculate third law heats at 298°K. The data and results, presented in Table II, yield an average value for $\Delta H^\circ_{298} = -14.1 \pm 1.0$ kcal. mole⁻¹.

By combining the heat of sublimation (86.8 kcal. mole⁻¹) with the known¹⁴ heat of formation of $\text{CrF}_2(\text{s})$ (-181.0 kcal. mole⁻¹) together with the heat of sublimation of chromium¹⁰ (95.0 kcal. mole⁻¹) and the dissociation energy of fluorine¹⁵ (37.72 kcal. mole⁻¹), one calculates the heat of atomization of $\text{CrF}_2(\text{g})$ to be 226.9 ± 4.0 kcal. mole⁻¹, which is in good agreement with the value of 229 kcal. mole⁻¹ estimated by Brewer.¹

(12) K. K. Kelley, U. S. Department of Interior, Bureau of Mines, Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.

(13) K. K. Kelley and E. C. King, U. S. Department of Interior, Bureau of Mines, Bulletin 592, U. S. Government Printing Office, Washington, D. C., 1961.

(14) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950.

(15) J. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.*, **54**, 1592 (1958).

Table II. Equilibrium Constants and Heat for the Reaction $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{g})$

| Temp., °K. | K_1' | Log K_1 | $\Delta\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$ | |
|-----------------------------|--------|--------------|--|---|
| | | | cal. deg. ⁻¹ mole ⁻¹ | ΔH°_{298} , kcal. mole ⁻¹ |
| 1259 | 31.77 | 1.530 | 3.83 | -13.63 |
| 1286 | 46.57 | 1.696 | 3.75 | -14.80 |
| 1307 | 37.00 | 1.596 | 3.72 | -14.40 |
| 1269 | 64.78 | 1.839 | 3.82 | -15.53 |
| 1272 | 44.98 | 1.681 | 3.80 | -14.62 |
| 1290 | 43.72 | 1.668 | 3.75 | -14.68 |
| 1294 | 18.86 | 1.303 | 3.74 | -12.55 |
| 1317 | 19.19 | 1.311 | 3.70 | -12.77 |
| Average = -14.12 ± 1.04 | | | | |

By combining the heat of dissociation of $\text{CrF}_2(\text{g})$ with the heat of reaction listed in Table II, one obtains $D^\circ_{298}(\text{CrF}) = 4.61 \pm 0.15$ e.v. (106.4 ± 3.5 kcal. mole⁻¹). From this value the heat of formation of $\text{CrF}_2(\text{g})$ from the elements in their reference states at 298°K. was computed to be -94.2 kcal. mole⁻¹, in good agreement with the value of -96 kcal. mole⁻¹ estimated by Brewer.¹

It was not possible to determine the dissociation energy by measuring the heat of the heterogeneous reac-

tion $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{s})$ because, as pointed out previously, the activity of the $\text{CrF}_2(\text{s})$ in the Knudsen cell was less than unity. When Al was added to CrF_2 as a reducing agent only AlF_3 -related peaks and Cr^+ were obtained; *i.e.*, CrF was apparently reduced below the sensitivity limit of the instrument.

One may fix an upper limit on the value of $D(\text{CrF})$ in the following manner. The intensities of the ion CrF_2^+ are measured at some voltage much greater than the appearance potentials, in this experiment 70 v. The value of $I(\text{CrF}_2^+)$ must be corrected to account for that amount of $\text{CrF}_2(\text{g})$ undergoing dissociative ionization when exposed to 70-v. electrons. The intensities of the ions Cr^+ and CrF^+ are measured at some value below the breaks at *ca.* 19 and 14 e.v., respectively, and then extrapolated to 70 e.v. Calculating K_1' and K_1 for the reaction $2\text{CrF}(\text{g}) = \text{Cr}(\text{g}) + \text{CrF}_2(\text{g})$ as before, one obtains $\Delta H^\circ_{298} = -7.2 \pm 0.5$ kcal. mole⁻¹ which leads to $D^\circ_{298}(\text{CrF}) \leq 4.76 \pm 0.20$ e.v.

In a similar manner, one can set a lower limit on the value for $D(\text{CrF})$ by using the intensity of CrF_2^+ at 70 v. as above and those of Cr^+ and CrF^+ below the breaks at *ca.* 19 and 14 e.v., *i.e.*, assuming that the ionization efficiency curves level off. Calculating K_1' and K as before, one obtains $\Delta H^\circ_{298} = -18.3 \pm 1.1$ kcal. mole⁻¹ and $D^\circ_{298}(\text{CrF}) \geq 4.52 \pm 0.20$ e.v.

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Coordination Compounds with Delocalized Ground States. Bisdithioglyoxalnickel and Related Complexes^{1a,b}

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Synthesis properties and electronic structure of the first transition metal complex of the hitherto unknown ligand dithioglyoxal are reported. Bisdithioglyoxalnickel, NiS₄C₄H₄, is a monomeric, planar, diamagnetic nickel complex in which the two positive charges of the nickel atom are compensated by two electrons delocalized over the whole molecule of the complex. Its chemical properties closely resemble those of the related d⁸ metal complexes of α-dithiodiketones, M(S₂C₂R₂)₂; it possesses a low first electron excitation energy and is easily reduced to mono- and dianions. The optical spectra for the species NiS₄C₄H₄^{0,-1,-2} and of substituted derivatives are presented and interpreted on the basis of MO calculations. Satisfactory quantitative agreement with the observed transition energies was achieved using a semiempirical Hückel-type approximation. The Wolfsberg-Helmholtz method was applied as well but afforded less favorable results owing to a basic inadequacy with which the off-diagonal elements H_{ij} are computed. It follows from the available

data that the complexes of this type represent interesting examples of coordination compounds with extensive ground-state π-electron delocalization.

Introduction

The α-dithiodiketones have become some of the most interesting ligands in recent transition metal chemistry. In systems $\text{RC}(=\text{S})\text{C}(=\text{S})\text{R}$ the tendency of the sulfur atoms to form covalent bonds with metals is uniquely combined with a high electron affinity of the ligand which leads to complexes characterized by many unusual and unprecedented chemical and physical properties. Since the characterization of the first complex of this type,² we have developed several methods of synthesis for alkyl- and aryl-substituted complexes $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_z$ ($z = 2$ or 3),^{1b,3-5} while other authors have subsequently

(2) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **84**, 3221 (1962).

(3) G. N. Schrauzer and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *ibid.*, **19b**, 1080 (1964).

(4) G. N. Schrauzer and H. W. Finck, *Angew. Chem.*, **76**, 143 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 133 (1964).

(1) (a) Paper VII of the series "Chemistry of the Coordination Compounds"; (b) paper VI: G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).