



Figure 1.—Dependence of rate upon $[H^+]$, illustrated by a plot of k' vs. $[H^+]$, each on a logarithmic scale. The line shown is that corresponding to a least-squares fit of the data to eq 6.

cobalt(II) species which are converted to the final products rapidly compared to these three processes. The distinction intended between reactions 9 and 10 is the question of whether the role H^+ plays in the mechanism of decomposition is the same as it plays in stabilizing $Co(CN)_5^{3-}$ in solutions of relatively high hydrogen ion concentration. The kinetic data cannot distinguish the alternatives.

The rate equation associated with this mechanism is

$$-\frac{d \ln [Co(CN)_5^{3-}]}{dt} = k' = \frac{k_1K + (k_2K + k_3)[H^+]}{K + [H^+]} \quad (11)$$

Comparing this expression to eq 6, it is apparent that the empirical parameters are $a = k_1K$, $b = k_2K + k_3$, and $c = K$. The rate parameter b represents the composite contributions of reactions 9 and 10; these cannot be further sorted out from the information available since the transition states along either path have the same composition.

The simplest interpretation of the kinetic data and of the lack of dependence upon $[CN^-]$ is that loss of the first cyanide comprises the rate-determining step. Subsequent reactions in which cyanide is presumably replaced by water in a stepwise fashion must occur relatively rapidly. An alternative proposal is that one or more cyanide ions be lost rapidly and, in effect, irreversibly owing to the high hydrogen ion concentration. We cannot rule out this eventuality, although it was rendered less likely by our failure to detect changes in absorption intensity in $Co(CN)_5^{3-}$ (in CN^- solution) compared to the species present at the start of a decomposition run at low $[H^+]$.

The question concerning the stage at which the spin change accompanying reaction 1 occurs cannot be answered. It is interesting to note, however, that the abnormally low rate of cobalt(II) substitution (*cf.* the rate¹⁹ of $Co_{aq}^{2+} - H_2O$ exchange, $k_{ex} = 10^6 M^{-1} sec^{-1}$) undoubtedly originates in the low-spin $t_{2g}^6 e_g^1$ configuration of the Co(II) complex.

(19) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

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The Mass Spectrum of Methyldifluorosilyltetracarbonylcobalt^{1a}

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The existence of methyldifluorosilyltetracarbonylcobalt, $CH_3SiF_2Co(CO)_4$, was mentioned recently in a brief publication.² This compound was prepared by allowing $CH_3SiH_2Co(CO)_4$ to react with excess PF_5 . The products of this reaction— $CH_3SiF_2Co(CO)_4$, CH_3SiF_2H , $HCo(CO)_3(PF_3)$, $HCo(CO)_2(PF_3)_2$, and $HCo(CO)(PF_3)_3$ —were separated by vacuum distillation and vapor-phase chromatography. The detailed information concerning the preparation and separation will be reported elsewhere.³ The purpose of this report is to furnish the mass spectral data for $CH_3SiF_2Co(CO)_4$, from which the heat of formation of $CH_3SiF_2Co(CO)_4$ and the $CH_3F_2Si-Co(CO)_4$ bond dissociation energy have been derived.

Experimental Section

The mass spectral data reported here were obtained on a modified⁴ Bendix Model 12-107 time-of-flight (TOF) mass spectrometer. The TOF mass spectrometer was employed in this study because its relatively cool ion source ($35 \pm 5^\circ$) reduced the possibility of thermal decomposition of the compound and also permitted fragmentation patterns and appearance potential data to be obtained rapidly.⁴ A fresh sample of $CH_3SiF_2Co(CO)_4$ was introduced into the mass spectrometer for each measurement. Winters and Kiser have reported⁵ that some metal carbonyls decompose in the mass spectrometer causing a contamination problem; thus, as a precautionary measure, the ion source and electron multiplier were disassembled and cleaned every 4 hr throughout this investigation. In these cleaning procedures we were unable to detect any evidence for the thermal decomposition of $CH_3SiF_2Co(CO)_4$ in our mass spectrometer. The intense ion currents for the Co^+ and CO^+ ions suggest that some decomposition may have taken place; however, it was impossible to substantiate this suspicion by inspection of the ion source and electron multiplier components. Measurements taken before and after the cleaning procedure agreed within the limits quoted.

Results and Discussion

The monoisotopic fragmentation pattern of $CH_3SiF_2Co(CO)_4$, corrected for residual background in the mass spectrometer, is shown in Table I. Ions of minor abundance (<0.05) are not reported. These very

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(2) A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1941 (1967).

(3) S. K. Gondal, A. G. MacDiarmid, M. V. McDowell, and F. E. Saalfeld, to be submitted for publication.

(4) F. E. Saalfeld and M. V. McDowell, *Inorg. Chem.*, **6**, 96 (1967).

(5) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 1618 (1965).

TABLE I
 SUMMARY OF MASS SPECTRAL RESULTS

Ion	% $I/\Sigma I_i^a$	Neutral product	Appearance potential, ^b eV	ΔH_f° (ion), kcal/ mol
$\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4^+$	1.4	...	9.0 ± 0.1	-228
$\text{SiF}_2\text{Co}(\text{CO})_4^+$	0.6	$\text{CH}_3\cdot$	13.8 ± 0.2	-151
$\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_3^+$	2.7	CO	10.0 ± 0.1	-178
$\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_2^+$	1.2	2CO	10.7 ± 0.3	-136
$\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})^+$	4.8	3CO	12.9 ± 0.2	-60
$\text{CH}_3\text{SiF}_2\text{Co}^+$	12.3	4CO	14.5 ± 0.4	4
SiF_2Co^+	1.5
$\text{Co}(\text{CO})_2^+$	4.0	$\text{CH}_3\text{SiF}_2\cdot + 2\text{CO}$	14.7 ± 0.3	138 ^c
$\text{Co}(\text{CO})^+$	8.0	$\text{CH}_3\text{SiF}_2\cdot + 3\text{CO}$	16.4 ± 0.4	203 ^c
$\text{CH}_3\text{SiF}_2^+$	3.3	$\cdot\text{Co}(\text{CO})_4$	17.0 ± 0.4	88
CH_3Co^+	5.4	$\cdot\text{SiF}_2\cdot + 4\text{CO}$	16.6 ± 0.3	192
SiF_2^+	0.8
Co^+	11.4	$\text{CH}_3\text{SiF}_2\cdot + 4\text{CO}$	19.5 ± 0.3	287 ^d
$\text{Co}(\text{CO})_2^{2+}$	0.6
SiF^+	5.1
$\text{Co}(\text{CO})_2^+$	4.8
Si^+	5.4
CO^+	25.2
CH_3^+	1.3

^a Ionizing voltage, 70 eV; ionizing current, 0.125 μA ; instrument operated in the pulsed mode, with the ion lens on; reduced to monoisotopic spectrum. ^b Average of seven independent measurements determined by Warren's method of extrapolated differences: J. W. Warren, *Nature*, **165**, 810 (1950). Calibrating gases: Ar ($I = 15.8$ V), Kr ($I = 14.0$ V), and Xe ($I = 12.1$ V). Error is the standard deviation of the mean. ^c Reference 4. ^d F. H. Field and J. L. Franklin, "Electron Impact Phenomena and Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957.

small ion currents included ion species which had lost an oxygen atom from one of the CO ligands or a fluorine atom from the CH_3SiF_2 moiety. The ion current observed at m/e 28 could be due to CO^+ or Si^+ , or both. Our mass spectrometer does not have sufficient resolution to differentiate between these ions; however, analysis of the contribution of Si, C, and O isotopes showed this peak (m/e 28) to consist of 5 parts of CO^+ to 1 part of Si^+ . Another salient feature of the spectrum is the rearrangement ion, CH_3CO^+ . The clastogram⁶ of $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ suggests that this ion is produced by a methyl shift⁷ from the $\text{CH}_3\text{SiF}_2\text{Co}^+$ ion. Silicon difluoride, SiF_2 , presumably the neutral species eliminated, is a stable radical⁸ and hence could constitute a driving force for this reaction. We conclude that the ion current at m/e 87 is CoCO^+ rather than CoSi^+ because the ion current intensity at m/e 88 is 1.1% of the intensity at m/e 87, in agreement with the expected abundance for a ^{13}C isotope.

Doubly charged ions at m/e 57.5, $\text{Co}(\text{CO})_2^{2+}$, and m/e 43.5, $\text{Co}(\text{CO})^{2+}$, are observed in the mass spectrum of $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$. These are also present in the spectra of other metallic carbonyls⁹ and in the spectrum of $\text{HCo}(\text{CO})_4$ ¹⁰ but have not been observed in the spectrum of $\text{Co}_2(\text{CO})_8$ ⁴ or the phosphorus trifluoride derivatives of $\text{HCo}(\text{CO})_4$.¹⁰

The appearance potential, postulated neutral products, and heats of formation for $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ and its positive ions are shown in Table I. The relationship

(6) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 191.

(7) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 2711 (1967).

(8) T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1966).

(9) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **70**, 1680 (1966).

(10) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **90**, 3684 (1968).

between the appearance potentials and the heats of formation and bond energies, as well as the errors associated with these measurements, have been discussed by Field and Franklin.¹¹ It has been assumed that no excess kinetic energy is contained in the measured appearance potentials; thus, the heats of formation of the positive ions and the value of the $\text{CH}_3\text{F}_2\text{Si}-\text{Co}(\text{CO})_4$ bond dissociation energy should be taken as upper limits, while the heat of formation reported for $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ must be viewed as a lower limit. Ancillary values used in the thermochemical calculations were (in kcal/mol): $\Delta H_f^\circ(\text{SiF}_2) = -139$,⁸ $\Delta H_f^\circ(\text{Co}^+) = 287$,¹² $\Delta H_f^\circ(\text{CO}) = -26.4$,¹² $\Delta H_f^\circ(\text{Co}(\text{CO})_4) = -132$,⁵ $\Delta H_f^\circ(\text{CH}_3) = 33$,¹² $\Delta H_f^\circ(\text{Co}(\text{CO})_2^+) = 138$,⁵ $\Delta H_f^\circ(\text{Co}(\text{CO})^+) = 203$,⁵ and $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2) = -178$ (estimated). The heat of formation of CH_3SiF_2 was estimated from the heats of formation of SiF_2 ⁸ and CH_3 ,¹² the $\text{H}_3\text{C}-\text{Si}$ bond energy (BE) of $(\text{CH}_3)_4\text{Si}$ (72 kcal/mol),¹³ and the relation¹⁴ $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2) = \Delta H_f^\circ(\text{SiF}_2) + \Delta H_f^\circ(\text{CH}_3) - \text{BE}(\text{H}_3\text{C}-\text{Si})$. Using the ancillary data just presented and the appearance potentials for the ions $\text{Co}(\text{CO})_2^+$, $\text{Co}(\text{CO})^+$, and Co^+ , formed *via* the processes indicated in Table I, $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4)$ calculated for the three processes is -432, -432, and -447 kcal/mol, respectively. The average of these results, -437 ± 12 kcal/mol, is taken as the heat of formation of $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$, where the error represents the error in the measured appearance potential and an estimate of the error in the heat of formation of the positive ion used in the $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4)$ calculations.

The difference between the calculated heat of formation of $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ (-437 ± 12 kcal/mol) and the sum of the heats of formation of $\text{Co}(\text{CO})_4$ (-132 kcal/mol)⁵ and of CH_3SiF_2 (-178 kcal/mol) can be ascribed to the dissociation energy of the $\text{CH}_3\text{F}_2\text{Si}-\text{Co}(\text{CO})_4$ bond.

The value of 127 ± 15 kcal/mol for the $\text{CH}_3\text{SiF}_2-\text{Co}(\text{CO})_4$ bond energy appears to be rather high in view of other values reported for other metal-silicon and metal-carbon bonds. It should be pointed out, however, that the bond being ruptured in this instance is one which is believed² to contain considerable ($d \rightarrow d$) π bonding between the silicon and cobalt. Thus, the energy reported may not be unreasonable; however, it should be emphasized that bond energies determined by mass spectrometric techniques must be viewed as upper limits to the true energy.

The calculated dissociation energy, 127 ± 15 kcal/mol, can be used to compute the ionization potential (I) of CH_3SiF_2 from the equation¹¹

$$\text{AP} = I(\text{CH}_3\text{SiF}_2) + D(\text{CH}_3\text{F}_2\text{Si}-\text{Co}(\text{CO})_4)$$

(11) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957.

(12) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(13) T. L. Cottrell, "The Strengths of Chemical Bond," 2nd ed, Butterworth and Co. Ltd., London, 1953, p 275.

(14) J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953).

where AP is the appearance potential (14.5 eV) of the $\text{CH}_3\text{SiF}_2^+$ ion cited in Table I. The ionization potential of CH_3SiF_2 thus calculated is 265 kcal/mol or 11.5 eV.

It would be desirable to compare the values reported here with values determined by other methods. Unfortunately, there is no literature available for such a comparison. However, $I(\text{CH}_3\text{SiF}_2)$ can be independently estimated and since $I(\text{CH}_3\text{SiF}_2)$ reported above depends on the values reported for the other quantities, such a comparison can serve as a check on the $\text{CH}_3\text{SiF}_2\text{-Co}(\text{CO})_4$ bond energy and on the estimation of $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2)$.

The ionization potential of $(\text{CH}_3)_3\text{Si}$ is 6.94 eV¹⁵ and the ionization potential of F_3Si is 13.3 eV.¹⁶ Thus, the ionization potential is reduced an average of 2.12 eV for every fluorine atom replaced by a methyl group and the ionization potential of CH_3SiF_2 is estimated to be 11.18 eV. This value is in reasonable agreement with the value of 11.5 eV reported for $I(\text{CH}_3\text{SiF}_2)$ above. While this substituent effect extrapolation may be somewhat tenuous, it appears legitimate in view of the paucity of data available for this type of compound. This agreement is gratifying and furnishes some support of the values reported for $\Delta H_f^\circ(\text{CH}_3\text{SiF}_2)$ and $D(\text{CH}_3\text{SiF}_2\text{-Co}(\text{CO})_4)$. However, as stated previously, there is no assurance that the measured appearance potentials did not contain excess energy or that $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ did not thermally decompose in the ion source, and the data reported must be considered in light of these possible errors. Nevertheless, until the thermodynamic values of $\text{CH}_3\text{SiF}_2\text{Co}(\text{CO})_4$ can be measured by another method, e.g., calorimetry, the values cited here are the best acceptable estimates now available.

(15) G. G. Hess, F. W. Lampe, and A. C. Yergey, *Ann. N. Y. Acad. Sci.*, **136**, 106 (1966).

(16) J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract O-173.

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Stoichiometry and Kinetics of the Reduction of the Chloroerythrochromium(III) Ion by Chromium(II)

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The binuclear chromium(III) complex $(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}^{4+}$, commonly known as the chloroerythro ion, contains two chemically different chromium atoms, either of which, in principle, could accept an electron from a one-electron reducing agent. If a one-electron reduction occurred *via* a bridged activated complex, attack by the reducing agent would be expected to

occur at the chloride ion, which is an effective bridging group, so that the incoming electron would reach the tetraammine chromium first. It should be noted, however, that the two chromium atoms of the complex are connected by means of a hydroxo bridge, and the hydroxide ion is at least as effective an electron mediator as is the chloride ion.¹ Thus the introduction of an electron onto the tetraammine chromium atom would generate a moiety having some the characteristics of an inner-sphere activated complex for electron transfer, namely, two metal centers capable of exchanging an electron and linked by a bridging group. It might then be possible for an electron to pass through the chromium atom of the tetraammine fragment and reduce the chromium atom of the pentaammine fragment.

The one-electron reducing agent which we have chosen to treat with the chloroerythro ion is the aquochromium(II) ion, the reaction being the chromium(II)-catalyzed loss of ammonia from the binuclear complex in acidic aqueous solutions.

Experimental Section

Chloroerythrochromium(III) chloride, $[\text{Cr}(\text{NH}_3)_5(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}]\text{Cl}_4$, was prepared according to the method of Linhard and Weigel.² The perchlorate salt of the dimer, $[\text{Cr}(\text{NH}_3)_5(\text{OH})\text{Cr}(\text{NH}_3)_4\text{Cl}](\text{ClO}_4)_4$, was prepared by stirring the solid chloride salt together with slightly less than the stoichiometric amount of solid AgClO_4 in dilute HClO_4 , filtering the solution to remove AgCl , and precipitating the complex from the cold filtrate with 70% HClO_4 . The perchlorate salt was recrystallized several times from dilute perchloric acid. Since the solid perchlorate salt decomposes rather quickly, it was prepared on the same day it was to be used. *Anal.* Calcd for $[(\text{NH}_3)_5\text{Cr}_2(\text{OH})\text{Cl}](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$: N, 16.55; Cr, 13.65. Found: N, 16.39; Cr, 13.51 (N/Cr = 4.50).

Chromium(II) perchlorate solutions were prepared by the dissolution of weighed samples of 99.99% pure chromium metal (United Mineral and Chemical Corp.) in 1 M HClO_4 . The chromium(II) solutions were prepared, stored, and otherwise handled under an atmosphere of nitrogen gas, which had been freed of oxygen by passage through chromium(II) perchlorate solutions. The chromium(II) solution was dispensed by means of a microburet connected to the storage flask and fitted with a hypodermic needle. The chromium(II) content of the solution was determined by reaction with excess standard iodate solution followed by back-titration of the iodate (as I_2) with standard sodium thiosulfate.³ Total chromium was determined volumetrically⁴ as dichromate after oxidation with alkaline peroxide.

The reaction vessel for kinetic measurements was a quartz spectrophotometric cell onto which a small side compartment had been sealed. A solution containing the desired amounts of the chloroerythro perchlorate, sodium perchlorate, and perchloric acid was placed in the main part of the cell, and both compartments of the cell were sealed with rubber serum caps. The cell was deaerated with a stream of prepurified nitrogen and filled with nitrogen at about 5 psi above atmospheric pressure; then the desired amount of chromium(II) perchlorate solution was injected into the side compartment. The contents of the cell were brought to a chosen temperature by immersion of the cell in a water bath. The cell was inverted, shaken vigorously to mix the contents, and placed immediately in the thermostated cell compartment ($\pm 0.1^\circ$) of a Cary Model 15 spectrophotometer. The recording of absorbance *vs.* time was begun less than

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(2) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **299**, 15 (1959).

(3) H. W. Stone, *Anal. Chem.*, **20**, 747 (1948).

(4) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., Ltd., London, 1961, p 311.