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Kinetics and mechanism of reactions of some transition metal complexes containing metal carbon bonds

William Raymond Bushey
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Kinetics and mechanism of reactions of some transition metal
complexes containing metal carbon bonds

by

William Raymond Bushey

A Dissertation Submitted to the
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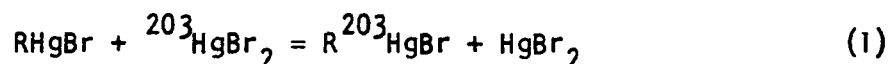
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PART I. THE MERCURY (II)-INDUCED DEMETHYLATION
OF METHYLCOBALT (III) COMPLEXES

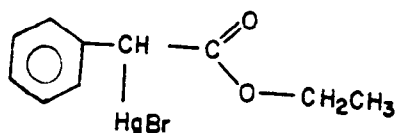
INTRODUCTION

Mercury(II) has long been known as an excellent electrophile. One of the first reported kinetic studies of the electrophilic attack on organometallics by mercury(II) was the study of the exchange reactions of an alkylmercury bromide with ^{203}Hg labelled mercuric bromide¹ as shown in eq 1.



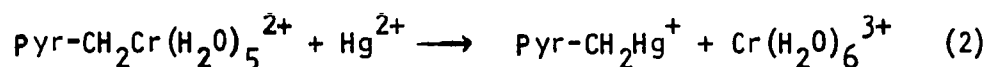
The rate law was first order in each reactant. Ingold² showed that exchange occurs with retention of configuration by using optically active alkylmercury compounds. This work established that the exchange is a bimolecular electrophilic reaction. However, experiments to determine whether the transition state is "open" (S_E2) or "closed" (S_Ei) were less conclusive.³ The rates of exchange measured for a series of compounds, HgX_2 ($X = \text{Br}^-$, I^- , OAc^- , NO_3^-) increased sharply with increasing ionic character of the Hg-X bond implying that the transition state did not contain an X ligand as a bridge, rather, reactivity was increased by the absence of an X group. Since a "closed" transition state requires a double bridge type structure with both the alkyl group and an X ligand acting as bridging ligands the evidence suggests that the reaction does not proceed via an S_Ei mechanism.

Not all mercury(II) exchange reactions occur via S_E2 mechanisms. In dimethylsulfoxide the rate of mercury exchange between ethyl α -bromomercuriphenylacetate, I, and mercuric bromide was found to be independent of the concentration of mercuric bromide.⁴ This reaction is promoted by



the substitution of electron acceptors on the benzene ring, consistent with the S_E1 mechanism since electron acceptors would be expected to stabilize the anionic intermediate. Ingold⁵ has found that optically active I racemizes at the same rate as it exchanges, confirming that configuration is lost in an S_E1 reaction. The deciding criterion as to whether an exchange will proceed via the S_E1 or S_E2 mechanism appears to be ability of the solvent to complex and stabilize the intermediate carbanion, for when I is allowed to exchange with mercuric bromide in other solvents (pyridine, dimethylformamide, aqueous dioxane, nitromethane, benzene, and aqueous ethanol) the exchange occurs via a bimolecular mechanism.⁴

In recent years other alkyl transfer reactions have been reported. The net transfer of an alkyl group from chromium(III) to mercury(II), eq 2, has been reported

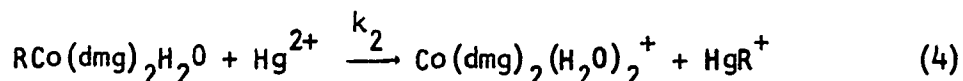


by Coombes and Johnson.⁶ There are differences between alkyl mercury exchange and the net transfer of an alkyl group from a transition metal to mercury(II) as shown in reaction 2. For the exchange reaction, ΔH° is zero (ignoring the isotope effect) and the driving force for the reaction is only the entropy of mixing. This is not true for the reaction of an organotransition metal with mercury(II). The equilibrium constant is quite large, presumably due to the formation of strong bonds between the mercury(II) ion and the alkyl group. Nevertheless one might expect to find some correlation between the two types of reaction since the transition states may be similar in structure. Such correlations have been found. For example, the reactivities of the various halo-mercury(II) complexes have been found to be similar in both the alkyl exchange reactions and dealkylation reactions. By varying the total chloride concentration and analyzing the resultant observed rate constant in terms of the known equilibria, Coombes and Johnson⁶ found the order of reactivity for the dealkylation of pyridiomethylpentaquo-chromium(III) as in reaction 2 to be $\text{Hg}^{2+} \gg \text{HgCl}^+ \gg \text{HgCl}_3^- \gg \text{HgCl}_4^{2-} \gg \text{HgCl}_2$. The rates do not follow the thermodynamic stability of mercury complexes because of a coulombic effect which causes the negatively charged mercury(II) complexes to be better electrophiles than mercuric chloride. This same type of reactivity is observed in the alkylmercury(II)-mercuric bromide exchange system.³ When lithium bromide is added to a solution containing alkylmercury(II) and mercuric bromide the rate of exchange increases, indicating increased reactivity of HgBr_3^- . Although no experiments with HgBr^+ or Hg^{2+} have been reported, the fact mentioned earlier that the exchange rate increases with increasing ionic character of the Hg-X bond

strongly suggests that such experiments would show reactivity parallel to that in the mercury(II)-alkylchromium(II) system.

Johnson⁶ has also concluded that like the exchange systems, the reaction proceeds through an "open" transition state (S_E2) since only 20% of the chromium product is $CrCl^{2+}$ when the chloride concentration is such that practically all the reaction occurs between the organochromium(III) complex and the tetrachloro- or trichloro-mercury(II) species. The 20% chlorochromium(III) product is attributed to chloride capture by a five-coordinate chromium(III) intermediate rather than to any bridged transition state.

Some studies of alkylcobalt(III) systems have been reported. Although mercury(II) preferentially removes a cyanide ligand rather than the alkyl group from pyridiomethylpentacyanocobalt(III), there are examples of other alkyl cobalt(III) complexes being dealkylated by mercury(II). Kwan and coworkers⁷ first reported the demethylation of methylaquobis(dimethylglyoximate)cobalt(III). Recently, Adin and Espenson⁸ have quantitatively studied the kinetics of a series of alkylaquobis(dimethylglyoximate)cobalt(III) complexes ($RCo(dmg)_2H_2O$). They found the mechanism could be interpreted by eq 3 and 4. The magnitudes of K and k_2 depend upon the specific alkylcobaloxime used.



Selected results of the Adin and Espenson work are summarized in Table I.

Table I
 Kinetic and Equilibrium Parameters
 for $\text{RCo(dmg)H}_2\text{O} \text{--} \text{Hg}^{2+}$ Reactions^a

R	K M^{-1}	k_2 $\text{M}^{-1}\text{sec}^{-1}$
CH_3	3.5	65.
CH_2CH_3	4.2	0.121
$\text{CH}_2\text{CH}_2\text{CH}_3$	4.3	0.092
$\text{CH}(\text{CH}_3)_2$	---	$<7 \times 10^{-6b}$
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	4.1	0.36

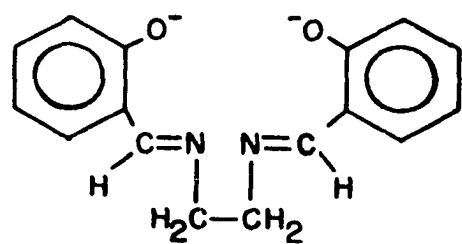
^aAqueous solutions at 25^o and 1.0 M ionic strength maintained by perchloric acid-lithium perchlorate. ^bConsiderable quantities of Hg_2^{2+} were formed.

The second order kinetics indicate that electrophilic substitution proceeds via a bimolecular mechanism. The effects of substituents at the α and β carbons of \underline{R} also support an S_E2 mechanism. The former is accompanied by marked rate effects ($Me > Et > i-Pr$), whereas the latter is nearly without effect ($Et \sim n-Pr \sim n-Bu$). This is consistent with the attack of Hg^{2+} on the same side of the α carbon as the Co atom. Such a reactivity scheme has been noted in alkylmercury(II) exchange reactions⁹ where the reaction is known to proceed by an S_E2 mechanism.

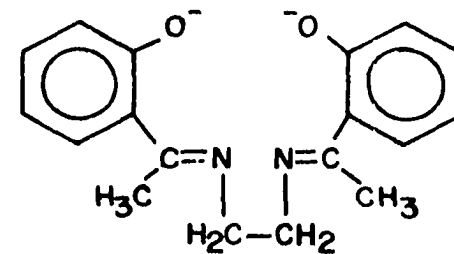
Other alkylcobalt(III) complexes which have been found to react with mercury(II) include cobalamin and cobinamides.¹⁰ However, this work cannot be compared directly with Espenson and Adinor or this present work since mercury(II) was added as the acetate which is known to be quite stable even in acid solution (β_2 for $Hg^{2+} + 2CH_3CO_2^-$ is approximately 10^8). Hence, a deactivation would be expected presuming this reaction behaves in a manner similar to other electrophilic reactions of mercury(II).

Several other alkylcobalt(III) compounds have been synthesized.¹¹ In general, these alkylcobalt(III) complexes consist of a tetradentate Schiff base occupying the equatorial positions and the alkyl group occupying one of the axial positions. The sixth ligand can be water, pyridine, ammonia, or thiocyanate.

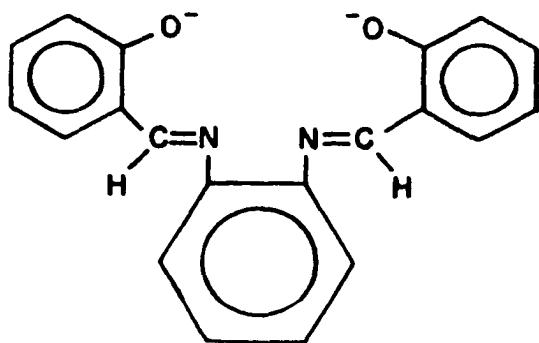
The anions of four of the many Schiff bases available are shown in Figure 1. All four can complex cobalt and form alkylcobalt(III) complexes. Since these complexes would presumably be similar in reactivity to the closely related cobaloximes and corrinoids, one would expect these



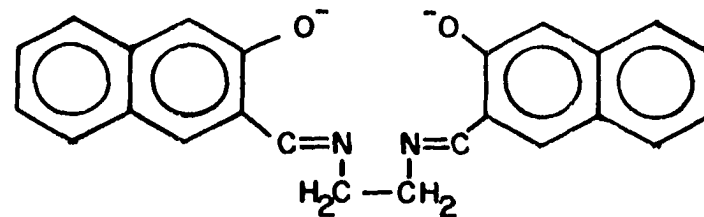
salen



dimethylsalen



saloph



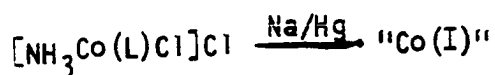
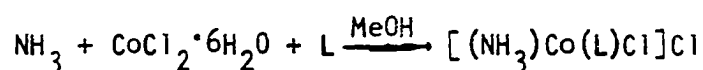
dimethylnapsalen

Figure 1.—Structures of ligands used in this study.

complexes to be dealkylated by mercury(II). The work reported here confirms this. The kinetics and mechanism of demethylation of four methylcobalt(III) complexes-- $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$, $\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}$, $\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$ and $\text{CH}_3\text{Co}(\text{dimethylnapsalen})\text{H}_2\text{O}$ have been studied. All react with mercury(II) to form methylmercury(II) and a cobalt(III) complex of the form $\text{Co}(\text{L})(\text{H}_2\text{O})_2^+$ where L is the Schiff base. Structural differences in these complexes result in different rates of demethylation. A correlation was noted between the possibility of $d\pi-p\pi$ bonding between the cobalt and the Schiff base and the complex's reactivity. This point will be discussed in detail.

EXPERIMENTAL

Materials.—In general all cobalt complexes were prepared by the reduction of the cobalt(II) complex to cobalt(I) with sodium amalgam followed by a nucleophilic attack by cobalt(I) on methyl iodide.¹¹ The synthesis is illustrated by the following set of reactions where L is the Schiff base.



The detailed procedure is given below. Abbreviations used in this section refer to ligands mentioned in the preceding section.

$\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ was prepared in the following manner. The ligand salen was prepared by refluxing 24.4g (0.2 mol) salicylaldehyde with 3.2g (0.1 mol) ethylenediamine in 100 ml of methanol. After thirty minutes the solvent was removed by evaporation and the precipitate was allowed to dry in air. After drying, 12.0g (0.05 mol) salen was added to 11.9g (0.05 mol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 ml of methanol. Five ml of concentrated ammonium hydroxide was added and the solution was refluxed for thirty minutes. The solvent was removed and the solid residue was dissolved in 100 ml of tetrahydrofuran. The solution was bubbled with nitrogen and 1% sodium amalgam was added.

After an initial induction period of approximately five minutes

(presumably due to the presence of water) the solution rapidly changed from brown to green. Then 14.2g (0.05 mol) methyl iodide was added. The green color quickly disappeared. Fifty ml of water was added, the tetrahydrofuran removed by evaporation, and the resultant reddish-brown $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ was collected by filtration, washed with ether, and dried in air.

$\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}$ and $\text{CH}_3\text{Co}(\text{dimethylnapsalen})\text{H}_2\text{O}$ were prepared in a similar manner using 27.7g (0.2 mol) o-hydroxyacetophenone and 37.2g (0.2 mol) 1-hydroxy-2-acetonaphthone respectively as starting materials in place of salicylaldehyde.

$\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$ was prepared in a similar manner to the salen complex substituting 10.8g (0.1 mol) o-phenylenediamine for ethylenediamine.

Mercury(II) perchlorate stock solutions were prepared by dissolving reagent grade mercury(II) oxide in a slight excess of perchloric acid. Solutions were analyzed by the Volhard method.¹² Lithium perchlorate was prepared by dissolving reagent grade lithium carbonate in a slight excess of 72% perchloric acid. The lithium perchlorate precipitated upon reduction of the volume and was recrystallized. Stock solutions of lithium perchlorate were analyzed by passing aliquots through a column of Dowex 50W-X8 cation resin in the H^+ form. The resin was rinsed with water and the rinsings titrated with standard sodium hydroxide.

Spectra.—All visible and ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer.

The total cobalt concentrations used to determine the molar absorptivities were obtained in two ways. In the first method,³ the cobalt

concentration was determined spectrophotometrically by measuring the absorbance of $\text{Co}(\text{NCS})_4^{2-}$ in 50% acetone solution at 623 nm where the complex has a molar absorptivity of $1842 \text{ M}^{-1} \text{ cm}^{-1}$.

The second method involves the use of emission spectroscopy. In this method, the ligands around cobalt are destroyed, the cobalt is reduced to cobalt(0) and excited by the use of an ion plasma.¹³ It is particularly convenient for water solutions of metal complexes since no sample preparation is needed. It is necessary only to have standards in the same concentration range as the unknown. The procedure for this cobalt analysis follows.

Standard solutions with cobalt concentrations of 1, 5, and 10×10^{-5} M were prepared by appropriate dilutions of a stock solution made up with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The concentrations of the stock solution were verified both by weight of the cobalt salt and spectrophotometric analysis.¹⁴ The light emission of these samples was measured at 345.35 nm from which a calibration curve was constructed. The samples were then run and the concentrations obtained from the calibration curve.

Kinetic Experiments.—The dealkylation reactions of the alkyl cobalt compounds in the present study are fast. With millimolar concentrations of mercury(II), the reactions can be followed conveniently using the stopped-flow method.

A Durrum stopped-flow spectrophotometer equipped with a D-131 Amplifier was used in all experiments. Previous experiments¹⁵ established that the effective optical pathlength was 1.92 cm. The absorbance signal was displayed on a Tektronix 564B storage oscilloscope whose time base

was calibrated with a time mark generator. The log amplifier was calibrated so that a ten volt response would correspond to one absorbance unit. With the use of an off-set control and sensitivity control any region between 0 and 2.0 absorbance units could be expanded from 1.0 absorbance unit full scale to 0.025 absorbance units full scale.

All experiments were performed at unit ionic strength, maintained with lithium perchlorate. The temperature was kept constant at 25°.

Spectrophotometric Titration.—The titration was performed in the following manner. A stock solution of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ was prepared by dissolving the solid in 1.0 M HClO_4 and filtering the undissolved solid. Six ml of this solution was poured into a 2 cm cell and the absorbance measured. Then an appropriate amount of 4.0 M mercury(II) perchlorate (0.005 to 0.05 ml) was syringed into the cell with a microsyringe, the cell shaken, and the absorbance read. For solutions where mercury(II) was the minimum reagent some decrease in absorbance was noted, due to the reaction of CH_3Hg^+ with the methyl cobalt(III). The initial absorbance reading after the addition of mercury(II) was taken to be the correct reading and used in the titration plot.

The change in volume of the cobalt solution due to the addition of mercury(II) perchlorate was negligible ($\Delta V/V \sim 0.004$).

Treatment of the Kinetic Data.—All rate runs were analyzed according to eq 5 where D_t is the absorbance at time t , D_0 is the initial absorbance

$$\ln|D_t - D_\infty| = \ln|D_0 - D_\infty| - k_{\text{obs}} t \quad (5)$$

and D_∞ is the absorbance after the reaction is complete.

The experimental rate constants, k_{obs} were fitted to eq 6 by using a non-linear least squares program.¹⁶

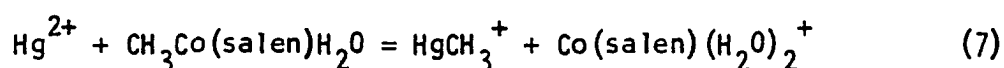
$$k_{\text{obs}} = \frac{A[\text{Hg}^{2+}]}{1 + B[\text{H}^+]} \quad (6)$$

The average relative error in k_{obs} was judged to be a constant so the data were weighted according to $1/(k_{\text{obs}})^2$ in carrying out the final analysis.

RESULTS

Spectra.—The spectrum of each of the four methylcobalt(III) complexes was measured in aqueous 1.0 M HClO₄. The calculated molar absorptivities are listed in Tables II, III, IV, and V. The maxima of each complex are listed in Table IV.

Stoichiometry.—The stoichiometry was rigorously checked for only one of the four compounds, CH₃Co(salen)H₂O and was found to follow eq 7.



The cobalt product was identified by comparing the spectrum of the product with the spectrum of an authentic sample of Co(salen)(H₂O)₂⁺ prepared by the air oxidation of Co(salen)(H₂O)₂ and subsequent acidification as described by Costa.¹¹ Methylmercury(II) could not be isolated in sufficient quantity to obtain a melting point because of the low solubility of the CH₃Co(salen)H₂O (ca. 10⁻⁴ M). However, when enough halide was added to the product solution so that the halide concentration was approximately equal to the mercury(II) concentration, the solution became opalescent indicative of formation of a precipitate. This precipitate could not have been the dihalide of mercury(II) since there is no precipitation of the dihalide until the halide to mercury(II) ratio becomes significantly larger than one.¹²

Mercury(II) was shown to react in a 1:1 ratio with CH₃Co(salen)H₂O by spectrophotometric titrimetry. Figure 2 shows the results of the titration.

As can be seen from the plot, there is a definite break when the

Table II
Spectrum of $\text{CH}_3(\text{saloph})\text{H}_2\text{O}^{\text{a}}$

λ nm	$\text{M}^{-1}\epsilon_{\text{cm}^{-1}}$	λ nm	$\text{M}^{-1}\epsilon_{\text{cm}^{-1}}$
600	221	400	563
590	219	390	600
580	222	380	635
570	227	370	662
560	232	360	719
550	236	350	863
540	244	340	1130
530	248	330	1880
520	256	320	2450
510	264	310	2670
500	275	300	2580
490	287	290	2560
480	314	280	2900
470	336	270	3210
460	363	260	3260
450	399	250	3880
440	430	240	4110
430	479	230	4200
420	522	220	3870
410	545	210	5690

^aObtained in aqueous 1.0 M HClO_4 .

Table III

Spectrum of $\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}^{\text{a}}$

λ nm	$\text{M}^{-1}\epsilon_{\text{cm}^{-1}}$	λ nm	$\text{M}^{-1}\epsilon_{\text{cm}^{-1}}$
600	106	400	2840
590	125	390	--
580	161	380	4212
570	222	370	5273
560	254	360	6110
550	363	350	7260
540	466	340	7930
530	543	330	8050
520	627	320	7780
510	682	310	7410
500	711	300	7160
490	711	290	9550
480	685	280	13800
470	659	270	28000
460	669	260	30700
450	768	250	45500
440	1020	240	41600
430	1400	230	42700
420	1860	220	50300
410	2380		

^a Obtained in aqueous 1.0 M HClO_4 .

Table IV
Spectrum of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}^{\text{a}}$

λ nm	$\text{M}^{-1}\text{cm}^{-1}$	λ nm	$\text{M}^{-1}\text{cm}^{-1}$
600	77	400	2730
590	99	390	3330
580	122	380	4300
570	210	370	5200
560	243	360	5910
550	331	350	6350
540	398	340	6410
530	486	330	6220
520	552	320	5880
510	641	310	5570
500	674	300	5540
490	696	290	8070
480	696	280	12600
470	663	270	19200
460	663	260	27600
450	740	250	32800
440	1030	240	33600
430	1460	230	35400
420	1990	220	41100
410	2350	210	41700
		200	42400

^aObtained in aqueous 1.0 M HClO_4 .

Table V

Spectrum of $\text{CH}_3\text{Co}(\text{dimethylinapsalen})\text{H}_2\text{O}^{\text{a}}$

λ nr.	$\text{M}^{-1}\text{cm}^{-1}$	λ nm	$\text{M}^{-1}\text{cm}^{-1}$
400	1820	300	3070
390	2420	290	3520
380	2740	280	4790
370	2800	270	5720
360	2600	260	9450
350	2170	250	14100
340	1820	240	14700
330	1720	230	14100
320	1890	220	13600
310	2490	210	21400

^aObtained in aqueous 1.0 M HClO_4 .

Table VI

Spectral Characteristics of Methylcobalt(III) Complexes^a

Complex	λ_{max} nm
$\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$	490, 410 (inflec), 342
$\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}$	492, 332, 265 (inflec), 239
$\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$	400 (inflec), 318, 291 (inflec), 278 (inflec), 253 (inflec), 247 (inflec), 245 (inflec)
$\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}$	365, 271 (inflec), 240

^aObtained in aqueous 1.0 M HClO_4 .

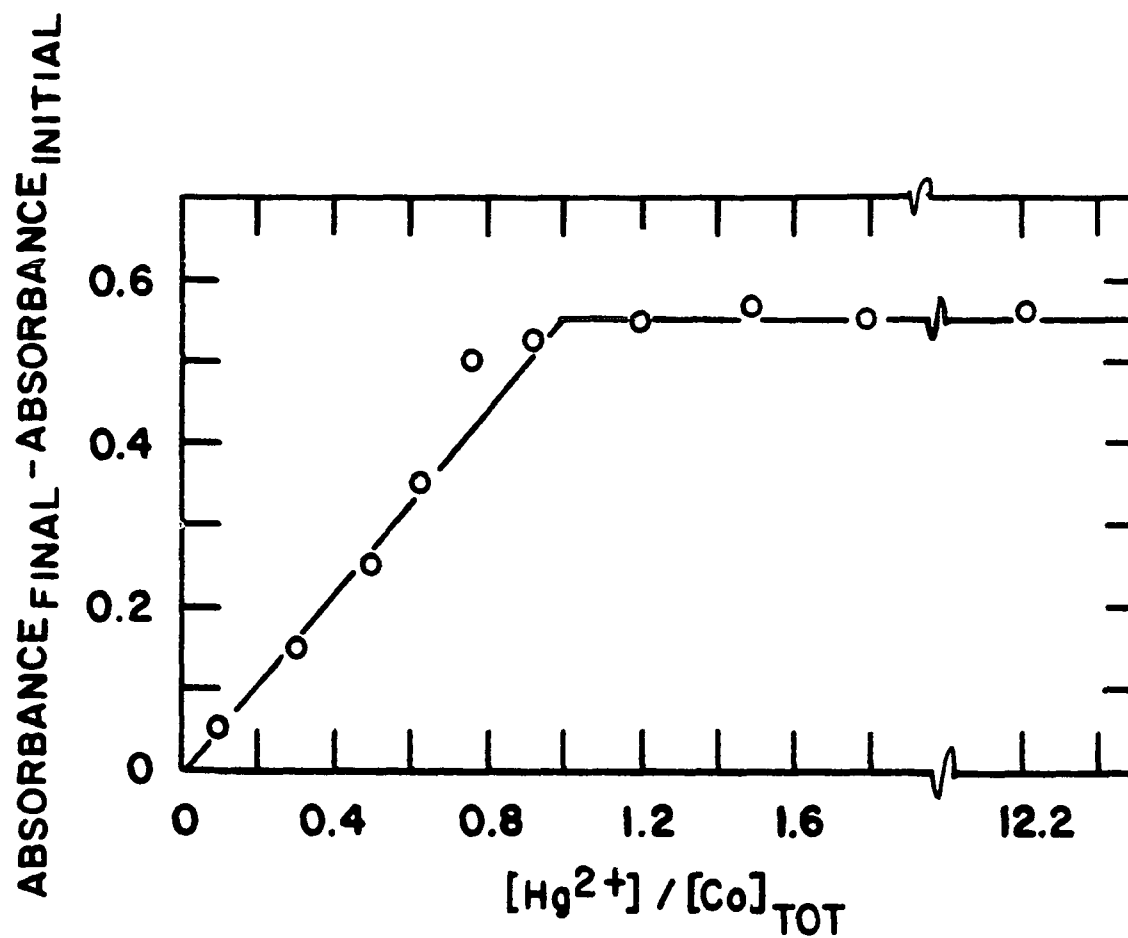


Figure 2.—Spectrophotometric titration of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ with mercury(II). Absorbances measured in a 2 cm cell at 340 nm.

ratio of complex to Hg^{2+} is 1:1. The slope of a spectrophotometric titration can be calculated from the known molar absorptivities of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ and $\text{Co}(\text{salen})(\text{H}_2\text{O})_2^+$ at 340 nm. The initial slope of Figure 1 is given by eq 8 where \underline{n} is the stoichiometric ratio of

$$\text{slope} = n\ell\Delta\epsilon[\text{Co}]_{\text{tot}} \quad (8)$$

mercury(II) to the methyl cobalt complex, ℓ is the optical pathlength, $[\text{Co}]_{\text{tot}}$ is the total concentration of cobalt, and $\Delta\epsilon$ is the difference in molar absorptivities of the two cobalt species. Using the appropriate numbers one calculates a theoretical slope of 0.564 for a 1:1 stoichiometry. The experimental slope is 0.565.

If $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ is in excess during the titration, the possibility arises of the product, CH_3Hg^+ , reacting with more cobalt(III) complex. However, the reaction was found to be quite slow in comparison to the reaction of Hg^{2+} , so that the absorbance of a solution could be obtained after all the mercury(II) had reacted and before any appreciable amount of methylmercury(II) had reacted. Nevertheless, some error is present, especially near the stoichiometric point where there is a relatively large amount of methylmercury(II) formed to react with the remaining $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$. One solution with a very large ratio of Hg^{2+} to $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ (12.2) was included in this titration to ensure that the same stoichiometry was maintained at higher reactant ratios where all of the kinetic studies were done.

Kinetics.—All four methylcobalt(III) complexes are rapidly dealkylated by mercury(II). The reactions were studied with large excesses

of both perchloric acid and mercury(II) perchlorate compared to the concentration of the methylcobalt(III). Under these conditions, the change in absorbance followed first order kinetics according to eq 9 where D_t

$$\log|D_t - D_\infty| = \log|D_0 - D_\infty| - k_{\text{obs}} t \quad (9)$$

is the absorbance at time t and D_∞ is the absorbance when the reaction has been completed. It was found that k_{obs} was independent of the wavelength at which the reaction was monitored.

Since the methylcobalt(III) complex was the minimum reagent in all experiments, the first-order change in absorbance is consistent with the rate law shown in eq 10 where $[\text{Co}]_{\text{tot}}$ is the total concentration of the

$$-\frac{d[\text{Co}]_{\text{tot}}}{dt} = k_{\text{obs}}[\text{Co}]_{\text{tot}} \quad (10)$$

methylcobalt(III) complex. The experimentally observed rate constants for each complex are listed in Tables VII, VIII, IX, and X.

The observed rate constants for each complex measured at 1.0 M HClO_4 were plotted as a function of initial mercury(II) concentration. It was assumed that the mercury(II) concentration remained constant and no correction has been made for the small percentage (generally 1-5%) which was consumed in the reaction. These plots are shown in Figures 3, 4, 5, and 6. The straight lines intersecting the origin indicate that the reaction is first order in mercury(II) as in eq 11.

$$k_{\text{obs}} = k'[\text{Hg}^{2+}] \quad (11)$$

Table VII
Pseudo-First Order Rate Constants for
the Reaction of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ with Hg^{2+}

$[\text{H}^+]$ M	$[\text{Hg}^{2+}]$ M x 10^3	$k_{\text{obs}}^{\text{a}}$ sec $^{-1}$	$k_{\text{calc}}^{\text{b}}$ sec $^{-1}$	deviation $^{\text{b}}$ %
1.00	0.100	0.119	0.141	18.5
1.00	0.200	0.266	0.283	6.4
1.00	0.711	0.989	1.01	2.1
1.00	0.711	0.989	1.01	2.1
1.00	0.711	0.990	1.01	2.1
1.00	1.42	2.04	2.01	1.5
1.00	1.42	2.06	2.01	2.4
1.00	2.10	2.95	2.97	0.7
1.00	2.28	3.33	3.23	3.0
1.00	2.83	3.69	4.00	8.4
1.00	2.83	3.88	4.00	3.1
1.00	4.00	5.63	5.65	0.4
1.00	5.00	7.20	7.07	1.8
0.875	2.28	3.96	3.65	7.6
0.750	2.28	4.59	4.23	7.8
0.625	2.28	5.45	5.00	8.3
0.500	2.28	7.05	6.12	13.2
0.375	2.28	8.15	7.90	3.1
0.250	2.28	12.0	11.1	7.5
0.125	2.28	19.4	18.8	3.1
0.0625	2.28	27.0	28.7	6.3

^a $\mu = 1.00$ M maintained with LiClO_4 ; $T = 25^\circ$; $[\text{Co}] = 10^{-5}$ M. ^bCalculated from parameters given in Table V.

Table VIII
Pseudo-First Order Rate Constants for
the Reaction of $\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$ with Hg^{2+}

$[\text{H}^+]$ M	$[\text{Hg}^{2+}]$ $\text{M} \times 10^4$	$k_{\text{obs}_1}^a$ sec ⁻¹	$k_{\text{calc}_1}^b$ sec ⁻¹	deviation %
1.00	2.00	0.856	0.892	4.2
1.00	4.00	1.65	1.78	7.9
1.00	4.00	1.82	1.78	2.2
1.00	5.00	2.55	2.23	12.5
1.00	6.00	2.57	2.67	4.9
1.00	8.00	3.88	3.57	8.0
1.00	10.00	4.49	4.46	0.7
1.00	20.00	8.99	8.92	0.8
1.00	40.00	18.4	17.8	3.3
0.800	4.55	2.51	2.44	2.8
0.700	4.55	3.02	2.72	9.9
0.625	4.00	2.53	2.61	4.7
0.600	4.55	3.09	3.07	0.6
0.500	4.55	3.66	3.53	3.6
0.375	4.00	3.67	3.80	3.5
0.300	4.55	4.82	5.00	3.7
0.138	4.00	5.60	5.75	2.7
0.094	4.00	9.24	7.74	16.2

^a $\mu = 1.00$ M maintained with LiClO_4 ; $T = 25^\circ$; $[\text{Co}] \leq 10^{-5}$ M. ^bCalculated from parameters given in Table V.

Table IX
Pseudo-First Order Rate Constants for
the Reaction of $\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}$ with Hg^{2+}

$[\text{H}^+]$ M	$[\text{Hg}^{2+}]$ M $\times 10^3$	$k_{\text{obs}_1}^{\text{a}}$ sec $^{-1}$	$k_{\text{calc}}^{\text{b}}$ sec $^{-1}$	deviation %
1.00	1.00	2.09	2.21	5.7
1.00	2.00	4.59	4.42	3.7
1.00	4.00	8.96	8.85	1.2
1.00	10.0	22.1	22.1	---
0.50	4.00	16.6	16.0	3.6
0.25	4.00	26.8	27.0	.7
0.125	4.00	39.8	40.9	2.8
0.0625	4.00	56.1	55.2	1.1

^a $\mu = 1.00$ M maintained with LiClO_4 ; $T = 25^\circ$; $[\text{Co}] \approx 10^{-4}$ M. ^bCalculated from parameters given in Table V.

Table X

Pseudo-First Order Rate Constants for
the Reaction of $\text{CH}_3\text{Co}(\text{dimethylinapsalen})\text{H}_2\text{O}$ with Hg^{2+}

$[\text{H}^+]$ M	$[\text{Hg}^{2+}]$ M $\times 10^3$	$k_{\text{obs}}^{\text{a}}$ sec $^{-1}$	$k_{\text{calc}}^{\text{b}}$ sec $^{-1}$	deviation %
1.00	0.30	0.903	0.975	8.0
1.00	0.91	3.12	2.96	5.1
1.00	1.00	3.57	3.25	6.2
1.00	1.40	3.86	4.55	17.8
1.00	1.80	6.38	5.85	8.3
1.00	2.20	6.34	7.15	12.8
1.00	2.61	8.90	8.48	4.7
0.75	0.91	3.10	2.96	4.5
0.50	0.91	3.45	2.96	14.2
0.50	4.00	12.6	13.0	3.2
0.375	0.91	3.39	2.96	12.7
0.250	0.91	2.89	2.96	2.4
0.250	1.00	3.13	3.25	3.8
0.250	4.00	12.3	13.0	5.7
0.250	6.00	17.8	19.5	9.6
0.250	8.00	20.3	26.0	28.1 ^c
0.250	10.00	24.4	32.5	33.2 ^c
0.188	0.91	2.97	2.95	0.7
0.125	0.91	2.95	2.95	0.0
0.1257	4.00	11.7	13.00	1.0
0.0625	4.00	13.0	13.00	0.0

^a $\mu = 1.00$ M maintained with LiClO_4 ; $T = 25^\circ$; $[\text{Co}] \leq 10^{-4}$ M. ^bCalculated from parameters given

in Table V. ^cWere not used to calculate average deviation.

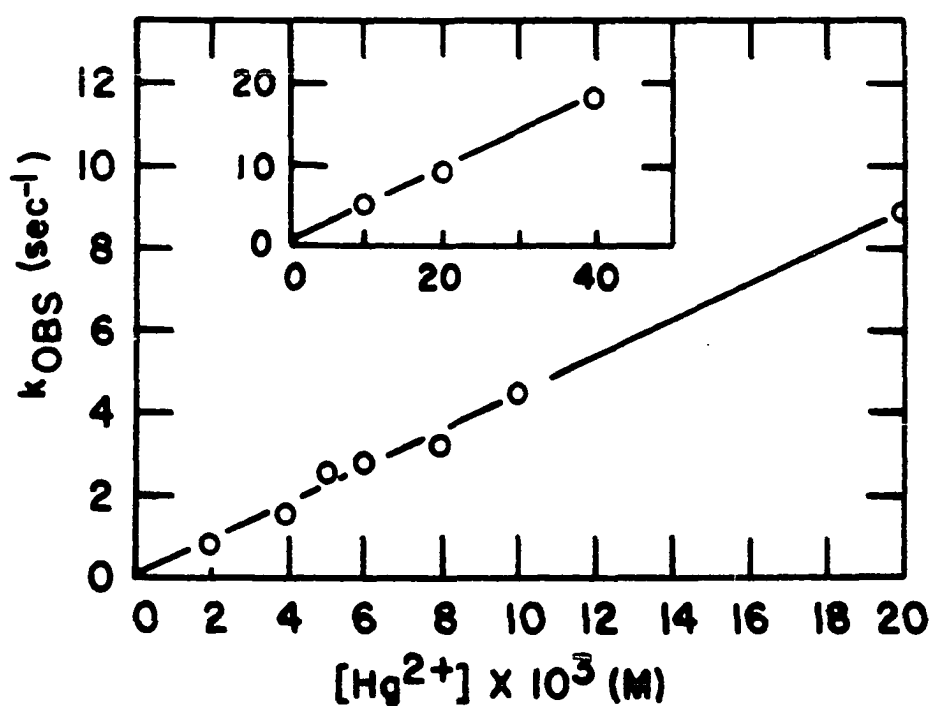


Figure 3.—The pseudo-first-order rate constant of dealkylation of $\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$ as a function of $[\text{Hg}^{2+}]$ at constant 1.0 M HClO_4 . Ionic strength is 1.0 M. $[\text{Co}] \leq 10^{-5}$ M.

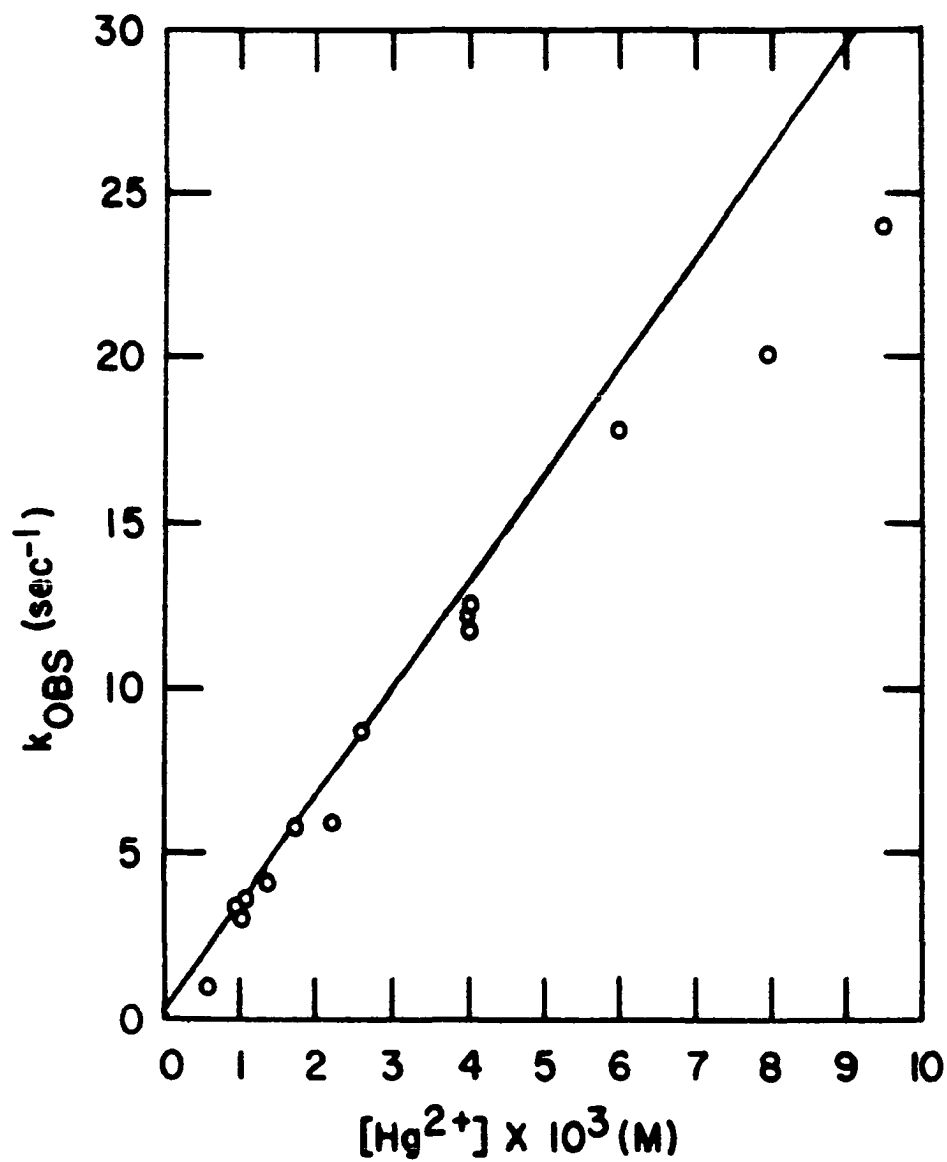


Figure 4.—The pseudo-first-order rate constant of dealkylation of $\text{CH}_3\text{Co}(\text{dimethylinapsalen})\text{H}_2\text{O}$ as a function of $[\text{Hg}^{2+}]$ at constant 1.0 M HClO_4 . Ionic strength is 1.0 M. $[\text{Co}] \leq 10^{-4}$ M.

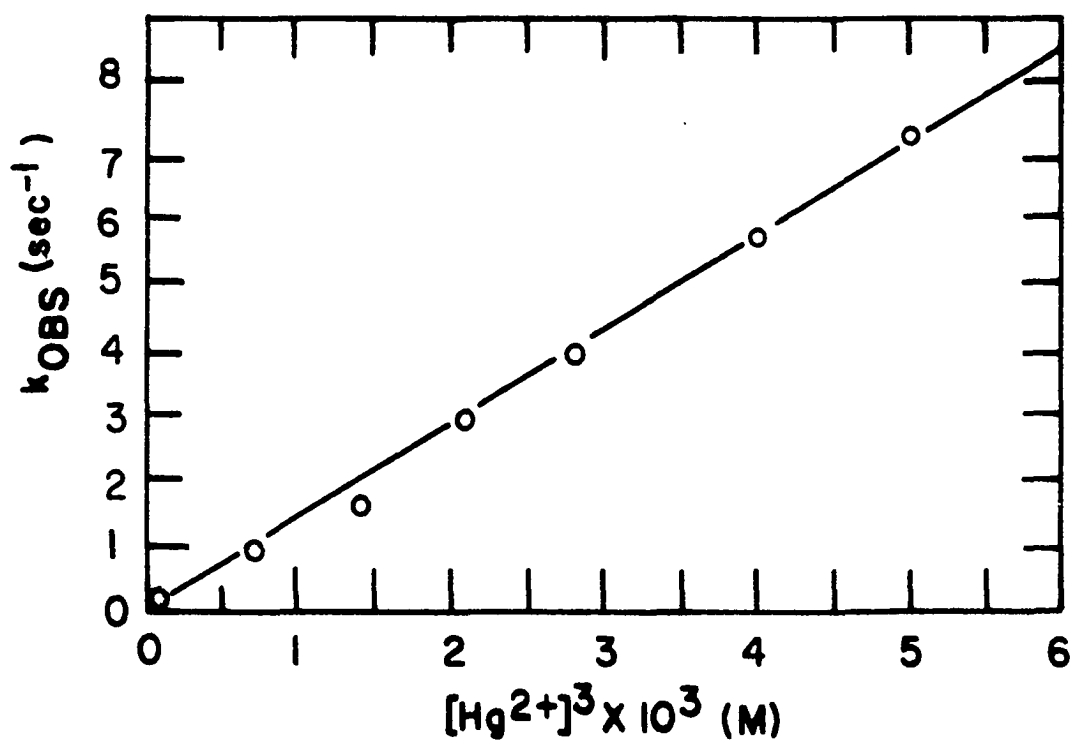


Figure 5.—The pseudo-first-order rate constant of dealkylation of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ as a function of $[\text{Hg}^{2+}]$ at constant 1.0 M HClO_4 . Ionic strength is 1.0 M. $[\text{Co}] \leq 10^{-5}$ M.

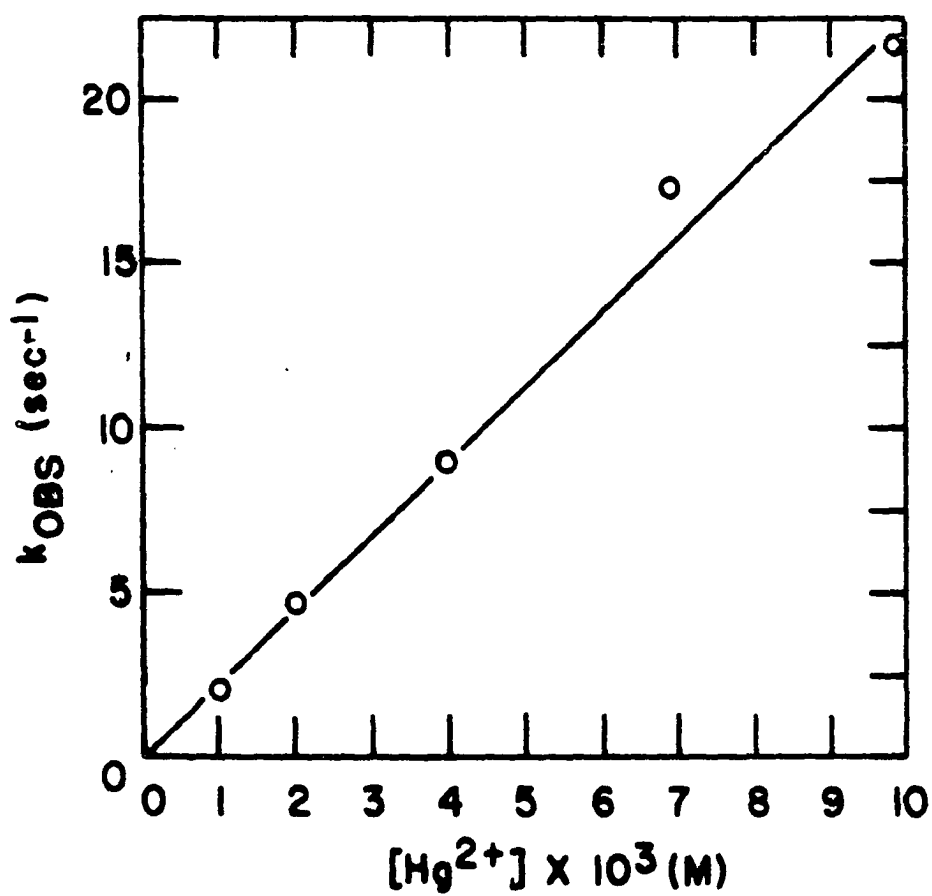
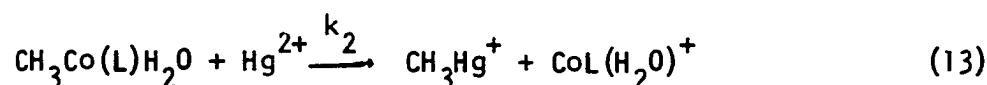
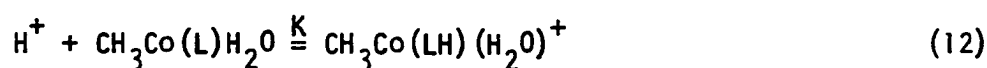


Figure 6.—The pseudo-first-order rate constant of dealkylation of $CH_3Co(dimethylsalen)H_2O$ as a function of $[Hg^{2+}]$ at constant 1.0 M $HClO_4$. Ionic strength is 1.0 M. $[Co] \leq 10^{-4}$.

Acid Dependence.—The rate of demethylation of $\text{CH}_3\text{Co}(\text{dimethylnap-salen})\text{H}_2\text{O}$ was independent of $[\text{H}^+]$ within the range studied ($0.0625 \text{ M} \leq \text{H}^+ \leq 1.0 \text{ M}$).

For the other three complexes, the rate constant, k' , proved to be an inverse function of $[\text{H}^+]$ with the order in $[\text{H}^+]$ varying from approximately minus one at high $[\text{H}^+]$ to zero at low $[\text{H}^+]$. For the sake of clarity it is useful to anticipate the results and propose a mechanism so that an appropriate plot of the data at varying $[\text{H}^+]$ can be made. If eq 12 and 13 constitute the mechanism by which these methylcobalt(III)



complexes undergo dealkylation then the rate law would be

$$-\frac{d[\text{Co}]_{\text{tot}}}{dt} = \frac{k_2[\text{Hg}^{2+}][\text{Co}]_{\text{tot}}}{1 + K[\text{H}^+]} \quad (14)$$

Therefore k' would be a function of the form

$$k' = \frac{k_{\text{obs}}}{[\text{Hg}^{2+}]} = \frac{k_2}{1 + K[\text{H}^+]} \quad (15)$$

By appropriate arithmetic manipulations eq 16 can be derived.

$$\frac{1}{k'} = \frac{[\text{Hg}^{2+}]}{k_{\text{obs}}} = \frac{1}{k_2} + \frac{K}{k_2} [\text{H}^+] \quad (16)$$

Therefore a plot of $(k')^{-1}$ vs $[H^+]$ should be a straight line with a slope of K/k_2 and intercept of $1/k_2$. Figures 7, 8, 9, and 10 show these plots for each of the methylcobalt(III) complexes. The plots give good straight lines. Naturally, if the complex is not protonated to an experimentally significant extent, the slope of the plot will be zero. Such is the case for the dimethylnapsalen complex shown in Figure 10. The experimental value is zero. Considering experimental uncertainty, the protonation constant could not be larger than ca. $0.1 M^{-1}$ without an acid dependence being detected, thereby setting the upper limit to K for this complex.

For each cobalt complex, all the data were simultaneously fit to eq 14 using a nonlinear least squares program.¹⁶ The calculated rate constants (k_{calc}) using these parameters are listed in the respective tables. The average deviations between the calculated rate constant and the experimental value are 6.1% (salen complex), 3.1% (dimethylsalen complex), 5.2% (saloph complex), and 6.3% (dimethylnapsalen complex). The values of k_2 and K determined by the least-squares computations are listed in Table XI.

Decomposition of the Reactants.—The cobalt(III) complexes decompose in acid solution, especially in light. When kinetic runs are done with a methylcobalt(III) solution which is allowed to age, the change in absorbance gradually becomes smaller indicative of decomposition of the complex. However, the observed rate constants were found not to depend on the age of the solution, implying the decomposition products do not affect the rate of demethylation.

Ionic Strength Dependence.—The rate of a reaction between a neutral molecule and a charged ion should not show a significant dependence on

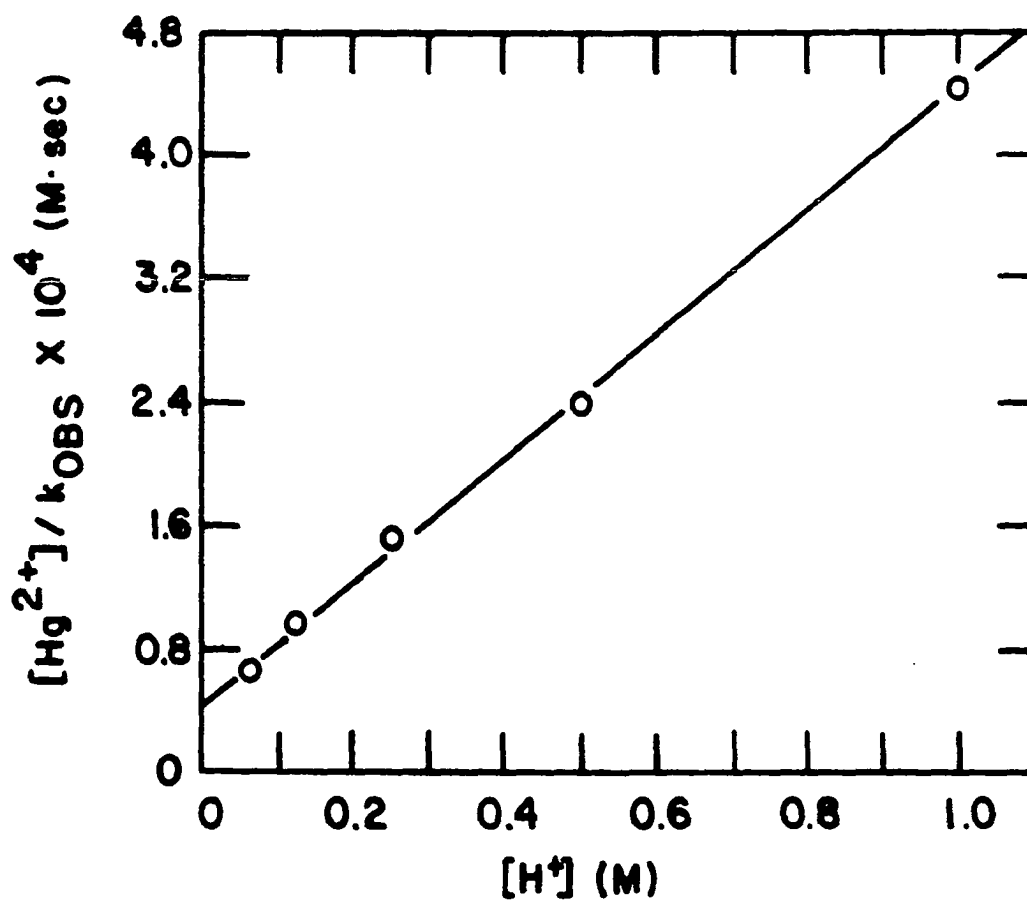


Figure 7.—Plot suggested by eq 16 for $\text{CH}_3\text{Co}(\text{dimethylsalen})\text{H}_2\text{O}$.

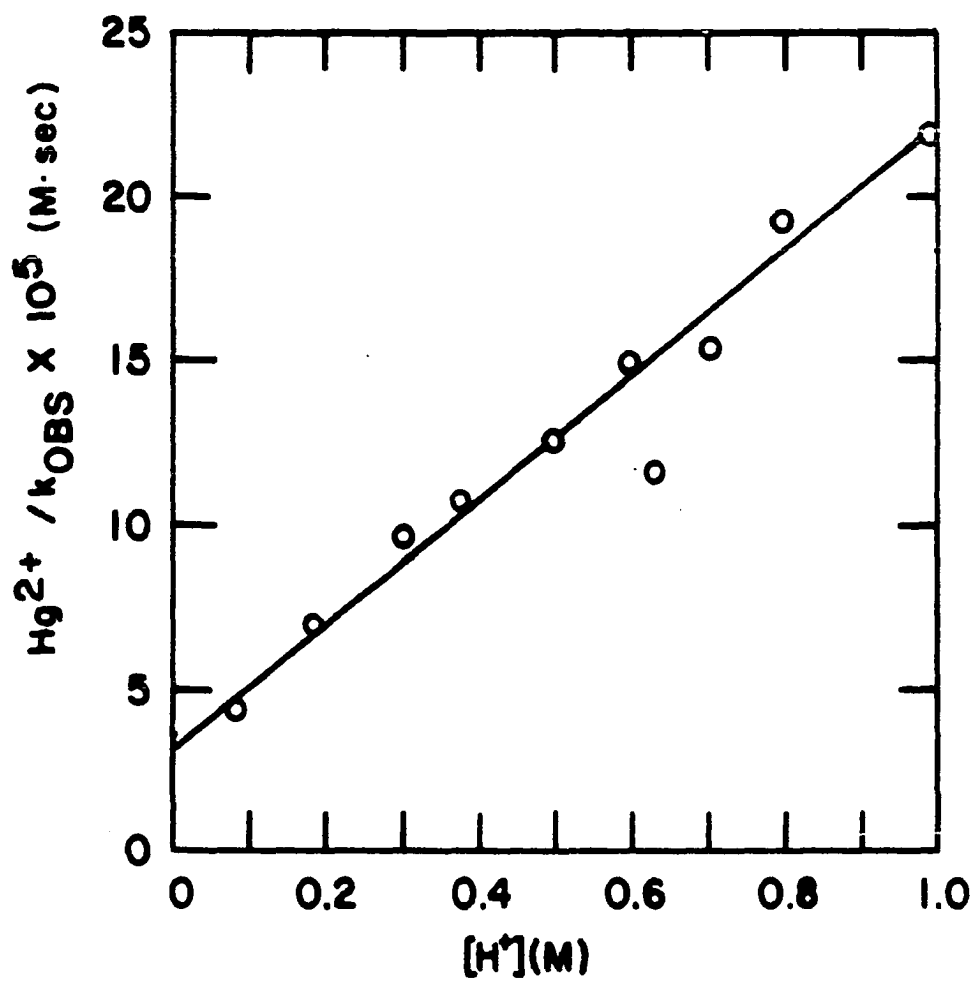


Figure 8.—Plot suggested by eq 16 for $CH_3Co(saloph)H_2O$.

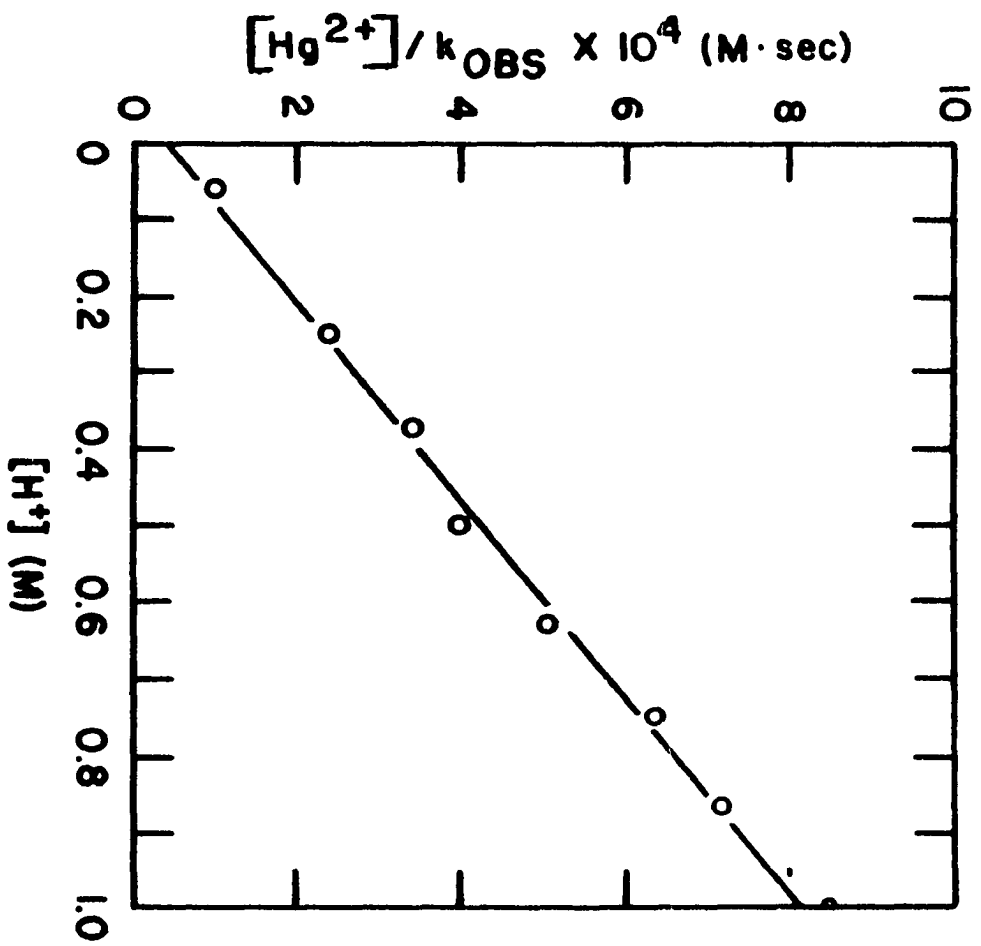


Figure 9.—Plot suggested by eq 16 for $CH_3Co(salen)H_2O$.

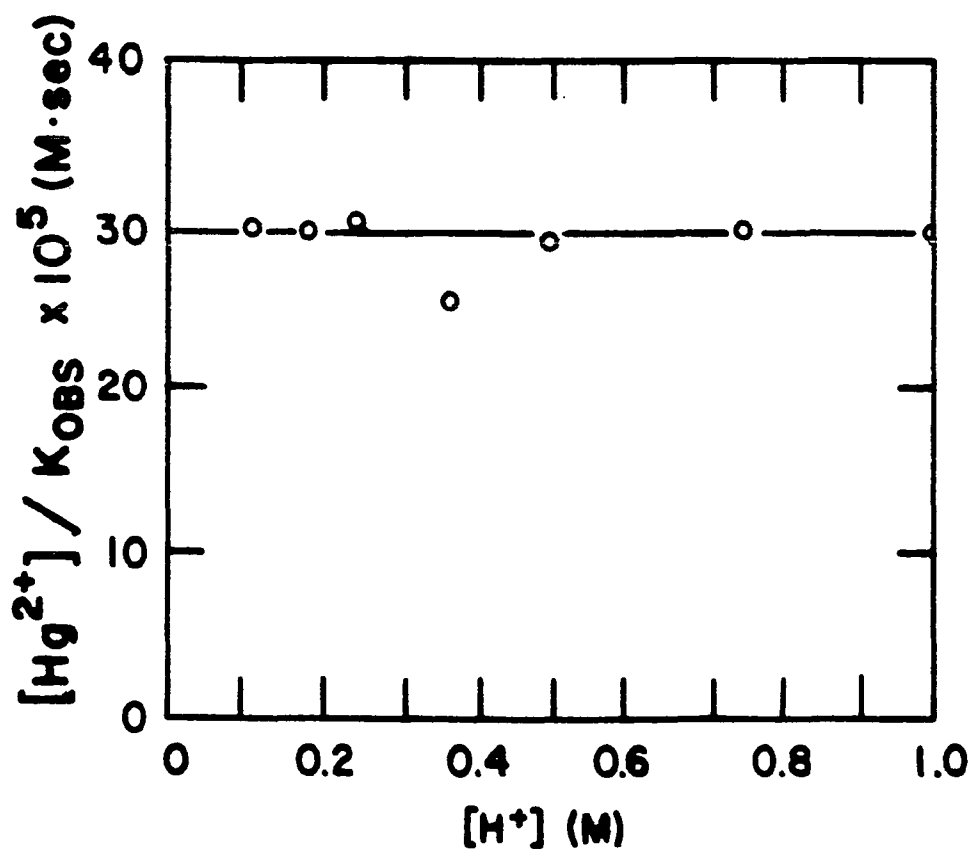


Figure 10.—Plot suggested by eq 16 for $CH_3Co(\text{dimethylnapsalen})H_2O$.

Table XI
Kinetic Parameters for the
Reaction of $\text{CH}_3\text{Co(L)H}_2\text{O}$ with Mercury(II)

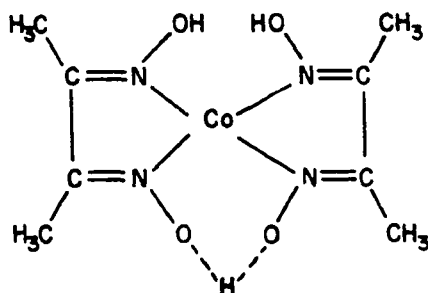
L	k_2 $\text{sec}^{-1}\text{M}^{-1}$	K_h M^{-1}	ref
salen	2.66×10^4	17.8	a
dimethylsalen	2.12×10^4	8.57	a
saloph	2.96×10^4	5.64	a
dimethylnapsalen	3.25×10^3	$<0.10^c$	a
bis(dimethylglyoxime)	62	3.5	b

^aThis work. ^bReference 8. ^cNo acid dependence observed. Estimate based on maximum possible error.

ionic strength. Since the protonation involves a neutral species no secondary salt effect is expected to arise from a variation of K with ionic strength. As additional proof of the rate law which has been formulated, the rate was measured as a function of ionic strength. Keeping $[\text{Hg}^{2+}]$ and $[\text{H}^+]$ constant at 5×10^{-4} M and 5×10^{-3} M respectively, the rate of mercury(II) dealkylation of $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ was measured at ionic strengths of 6.5×10^{-3} , 1.15×10^{-2} , and 2.15×10^{-2} M. The observed rates were found to be respectively 11.6 sec^{-1} , 11.9 sec^{-1} and 11.0 sec^{-1} , in good agreement with the predicted lack of variation with ionic strength.

DISCUSSION

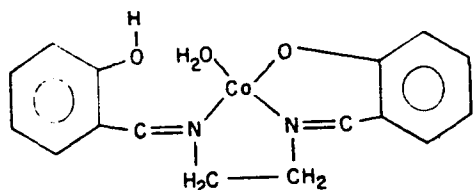
As previously noted, the kinetics are consistent with a mechanism which involves two methylcobalt(III) complexes differing in their composition by a proton. This type of behavior is also observed in the cobaloxime system.⁸ The structure of this protonated cobaloxime is believed to involve the addition of a proton to one of the oxime oxygens as shown in structure II shown below.



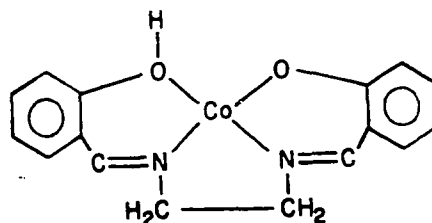
II

In the present systems, unlike cobaloxime, several different protonation sites are available. It is unlikely that the proton is sigma-bonded to an aromatic carbon atom since these atoms are very weak bases.¹⁷ Pi interactions of protons with aromatic rings are well substantiated;¹⁸ however, these also are very weak interactions. The most reasonable structures appear to involve the protonation of one of the oxygen atoms coordinated to the cobalt ion. It is not possible using the techniques available in this laboratory to distinguish unequivocally in aqueous solution whether the protonated structure is best represented by

the schematic structures III or IV shown below, since they differ only by a solvent molecule (only equatorial ligands are shown for clarity).



III



IV

However, the rapid reversible aquation of one of the coordinating atoms on the tetradentate ligand surrounding a cobalt(III) ion has no precedent. Furthermore the rigid structure of the ligand would be expected to hinder the attack of a water molecule. Hence, structure IV is favored.

The one trend in the magnitude of the protonation constant appears to be that extending the pi system by adding benzene rings decreases the basicity of the oxygen atom. Note, for example the change in K . As the equatorial ligand is changed from salen to saloph to dimethylnapsalen, there is a decrease in the magnitude of K from 17.8 M^{-1} to 5.64 M^{-1} to less than 0.1 M^{-1} . A likely explanation for this behavior could be that the molecule is stabilized by resonance. The lone pairs on the oxygen atom can be delocalized throughout the pi system. As the pi system becomes more extended, the resonance stabilization becomes greater and the electron density around the oxygen atoms is proportionately less. Since the basicity of the oxygen atoms is related to the electron density

surrounding them, any increase in delocalization will decrease the basicity and hence the protonation constant. A comparison of the pK_a 's of phenol and β -naphthol substantiate this argument. These two compounds are analogous to the salen and dimethylnapsalen complexes with respect to the aromatic ring structure. The pK_a 's for phenol and β -naphthol are 9.87 and 4.22 respectively.¹⁹ β -naphthol is more acidic than phenol, i.e. the β -naphthoxide ion is less basic than phenoxide ion, the same type of trend observed for salen and dimethylsalen.

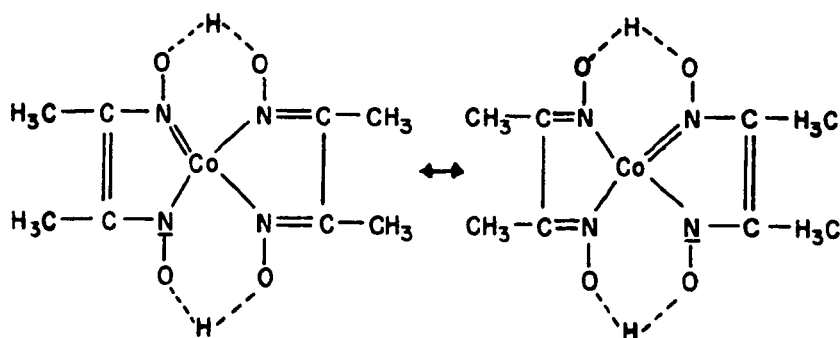
It is not clear why $CH_3Co(dimethylsalen)H_2O$ should be less basic than the corresponding salen complex. Based on previous work in organic systems the expected inductive effect would act in the opposite direction. Likewise steric arguments lack credence owing to the wide separation between the oxygen and the methyl groups. We cannot offer an explanation at this time for this apparently anomalous ordering of basicity.

Evidence presented earlier shows that all mercury(II) induced dealkylation of alkyltransition metal complexes reported in the literature occur via electrophilic attack. The products and bimolecular rate law of the reactions of mercury(II) with $CH_3Co(salen)H_2O$, $CH_3Co(dimethylsalen)H_2O$, $CH_3Co(saloph)H_2O$, and $CH_3Co(dimethylnapsalen)H_2O$ suggest that these reactions are also examples of electrophilic attack. Since all these reactions are of the same type, any explanation must explain the observed order of reactivity; $saloph > salen > dimethylsalen > dimethylnapsalen \gg cobaloxime$.

In electrophilic reactions the reactivity of a particular methylcobalt(III) complex should be related to the electron density surrounding the methyl group. This electron density on carbon would in large part be

determined by the electron distribution in the cobalt-carbon sigma bond. This sigma bond would be more or less polarized depending upon the effective charge on the cobalt atom. A high effective charge on cobalt would tend to withdraw electrons from the carbon atom; conversely, a low effective charge on the cobalt would increase the electron density around the carbon atom. Any process which would withdraw electrons from the metal atom would increase the cobalt's effective charge and thereby withdraw electrons from the carbon atom. This decrease in electron density around carbon would be reflected in a decrease in the second order rate constant for demethylation. Such a process exists in these systems.

For these low spin cobalt(III) complexes the d electrons on cobalt can be considered as occupying the t_{2g} orbitals. These orbitals have the correct symmetry to enter into $d\pi-p\pi$ bonding with the organic pi systems. For the cobaloxime system some of the resonance structures which can be visualized are illustrated below (axial groups on the cobalt



are omitted for sake of clarity). The electrons can be delocalized around the entire ring. These structures are especially favorable since the nitrogen which accepts the electron pair from cobalt would have zero formal

charge compared to a charge of +1 in the structure with no cobalt nitrogen double bonds. For salen type complexes, the oxygen cannot act as an electron acceptor; hence, the resonance structures of the type illustrated above are not possible. This decrease in resonance places more electron density on the metal which by the above argument increases the rate of electrophilic substitution. This is in perfect accord with the experimental facts; "salen type" complexes react much faster than methylcobaloxime. There are other possible resonance structures with "salen type" complexes which delocalize the electron density into the benzene ring. These can be considered less important than the four structures with electrons on the nitrogen since there would be a net negative charge on the carbon atoms unlike on the nitrogen atoms. Nevertheless within a given group of ligands where resonance structures involving nitrogen are not possible, the number of additional resonance structures involving carbon atoms should affect the electron density and, hence, the rate of demethylation. Such has been found to be the case. $\text{CH}_3\text{Co}(\text{dimethylnapsalen})\text{H}_2\text{O}$, which would be expected to be the most stabilized by resonance, is less reactive to mercury(II) attack than the salen, dimethylsalen, or saloph complexes. $\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$ does not gain any stabilization from the benzene ring attached to the two nitrogens since no simple resonance structure can place electrons donated by the cobalt into that particular benzene ring. This is reflected in a rate of demethylation relatively unchanged from the salen complex.

The spectral data also suggest a stabilization of the t_{2g} orbitals by pi bonding. The first d-d transition of the complexes increases in energy

in the order salen < dimethylsalen < saloph < dimethylnapsalen. The correlation is not exact as in the simple valence bond picture the d-d transition in the saloph complex would be expected to have the same energy as the salen and dimethylsalen transitions. Methylcobaloxime does not and would not be expected to fit in this correlation since the field surrounding the cobalt is substantially changed with the substitution of two nitrogens for the two oxygens.

A similar correlation of rate of demethylation with the chemical shift of the cobalt-bound methyl group should be observed. NMR data could not be obtained for $\text{CH}_3\text{Co}(\text{saloph})\text{H}_2\text{O}$ or $\text{CH}_3\text{Co}(\text{dimethylnapsalen})\text{H}_2\text{O}$ probably owing to their low solubility. However, we did confirm the chemical shifts reported in the literature for $\text{CH}_3\text{Co}(\text{salen})\text{DMSO}$ and $\text{CH}_3\text{Co}(\text{dmg})_2\text{DMSO}$ (DMSO = dimethylsulfoxide). The chemical shifts for the cobalt-bound methyl groups for these two complexes are 7.88 τ and 9.3 τ respectively.^{20,21} This is the opposite of what one would expect if shielding is a function of electron density. There is not necessarily a direct correspondence between the two. Theoretical treatment of chemical shift data has proved most profitable when one of several effects dominates the remainder. In the field of proton magnetic resonance this is rarely true unless the considerations are restricted to the comparison of a relatively small number of compounds of closely related structure.²² It is possible that the replacement of atoms surrounding the central cobalt atom can change the paramagnetic contribution arising from the unsymmetrical arrangement of electrons in the complex. This would result in differences in chemical shift which do not reflect the electron density around the methyl group.²³

PART II. THE REACTION OF ALKYL PENTAAQUOCHROMIUM (III)
WITH THIOCYANATE

INTRODUCTION

Ligand substitution reactions in octahedral systems as shown in eq 17 can be divided into three general categories depending upon the



mechanism. Langford and Gray²⁴ have suggested the nomenclature associative (A), dissociative (D) or interchange (I) for these mechanisms.

The associative mechanism (also known as limiting S_N2 mechanism), illustrated by eq 18, is characterized by an intermediate which contains



the metal atom with an expanded coordination number. The rate law for reaction will be first order in the metal complex, $ML_5(H_2O)$, and first order in the entering ligand, Y.

The dissociative mechanism (also known as the limiting S_N1 mechanism) is dominated by bond breaking in the rate-determining step. The mechanism shown in eq 19 is characterized by an intermediate containing the metal



atom with a reduced coordination number. The form of the rate law can vary depending upon the reactivity of the intermediate. However, in principle, it should be possible to obtain a rate law that is dependent only upon the

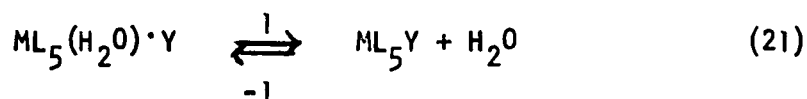
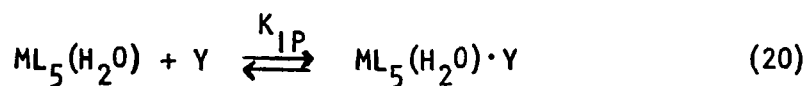
metal complex, corresponding to the first step in eq 19 being rate-determining.

The interchange mechanism consists of a concerted reaction in which the entering ligand is moving from the outer coordination sphere to the inner coordination sphere of the metal as the leaving ligand moves from the inner to the outer coordination sphere, leaving the coordination number of the central metal atom unchanged. The rate law is first-order in metal complex and first-order in entering ligand. However, the rate for an interchange mechanism is generally less sensitive to the nature of the entering group and more sensitive to the nature of the leaving group than the associative mechanism. Interchange reactions can be further categorized by the relative importance of bond-making and bond-breaking in the rate-determining step. If bond-making is important as in an A mechanism, then the mechanism is designated I_a ; if bond-breaking is important then the symbol I_d is used.

Most organic substitution reactions occur via associative interchange mechanisms. This is not true for transition metal substitution reactions. Basolo²⁵ has concluded that with very few possible exceptions ligand substitution reactions in octahedral systems occur via interchange or dissociative mechanisms. However, bond-making is important in some reactions. Langford²⁶ has shown that for acidopentaamminecobalt(III) complexes, the \log of the formation constant is a linear function of the \log of the aquation rate constant. Furthermore the slope of the line is nearly 1.0 (0.9). This linear free energy plot suggests that bond-breaking is the predominant force, i.e. the complexes react via a

dissociative interchange. Similar behavior is noted in the ligand substitution reactions of hexaaquochromium(III).²⁷ However, the correlation is not as marked and Espenson²⁸ has noted that this implies bond-making does play a significant role in the anation reactions of hexaaquochromium(III).

Since cobalt(III) ligand substitution appears to involve more bond-breaking than chromium(III), it is perhaps not surprising that until quite recently the only examples of purely dissociative mechanisms involved cobalt(III) not chromium(III). The first well-substantiated example of a D mechanism involved a kinetic study by Haim and Wilmarth²⁹ of the substitution reactions of aquopentacyanocobaltate(III). Previous attempts to obtain evidence of a dissociative mechanism had been frustrated by ion pairing. A positively charged metal complex can form ion pairs with anions in solution. To a first approximation the magnitude of the formation constant only depends upon the charges on the cation and anion. When such complexes act as intermediates in anation reactions as shown in eq 20 and 21 the observed rate constant for rate of approach to

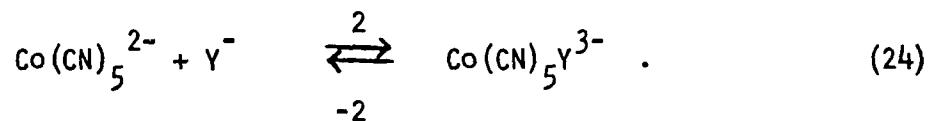
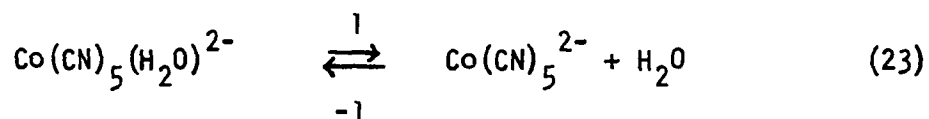


equilibrium is given by eq 22. This is also the form (as will be shown

$$k_{\text{obs}} = \frac{k_{-1} + (k_1 + k_{-1})K_{1p}[Y]}{1 + K_{1p}[Y]} \quad (22)$$

$$= \frac{A + B[Y]}{1 + C[Y]}$$

later) of a dissociative reaction. For this reason it is difficult to distinguish between a dissociative mechanism and an interchange mechanism which has significant ion pairing. This problem was eliminated by Haim and Wilmarth by employing an anionic metal complex which should not form ion pairs with entering anions. The rate of approach to equilibrium was measured as a function of the entering ligand concentration. The experimental rate had the form $\{A + B[Y^-]\}/(1 + C[Y^-])$. Since ion pairing is not expected in this system, Haim and Wilmarth concluded that the reaction occurs via a D mechanism. The proposed reaction mechanism is



The rate constant for the approach to equilibrium of this scheme, assuming steady-rate concentration in $\text{Co}(\text{CN})_5^{3-}$, is given by eq 25. In the limit

$$k_{\text{obs}} = \frac{k_1 k_2 [Y^-] + k_{-1} k_{-2}}{k_{-1} + k_2 [Y^-]} \quad (25)$$

of very high $[Y^-]$ the rate determining step should become k_1 , the rate of loss of water from aquopentacyanocobaltate(III). Good confirmation of the Haim-Wilmarth mechanism comes from the fact that k_1 is independent of the entering ligand and, furthermore, the magnitude of k_1 determined by anation experiments ($1.6 \times 10^{-3} \text{ sec}^{-1}$) is in good agreement with the water exchange measured directly using ^{18}O ($1.3 \times 10^{-3} \text{ sec}^{-1}$).

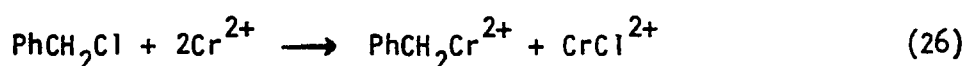
Other examples of cobalt(III) complexes which anate via a D type mechanism include sulfitopentaamminecobalt(III)³⁰, trans-aqua-sulfitotetracyanocobaltate(III)³¹, trans-aqua-sulfitobis(ethylenediamine)cobalt(III)³² and alkyl-aquo-1,3-bis(biacetylmonoximeimino)propanato-cobalt(III)³³ where alkyl = phenyl, methyl, benzyl, ethyl, or n-propyl.

In all of these examples dissociative behavior has been promoted by the addition of ligands which increase the electron density around the central metal atom via σ donation. This increase in electron density tends to weaken the metal ligand bonds--especially the trans metal-ligand bond.

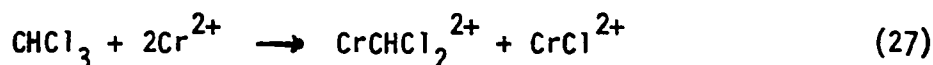
Since alkyl groups are strong donors it is not surprising that these groups have strong labilizing effects. In addition to the alkylcobalt(III) cited above, aquoalkylbis(dimethylglyoximate)cobalt(III) has also been found to be extremely labile at the coordination site trans to the alkyl group.³⁴ However, unlike previous examples this compound does not exhibit D type kinetics but follows second-order kinetics up to 0.5 M ligand

concentration. The ligands studied were SCN^- , N_3^- , Pyr, CN^- , NH_3 and OH^- .

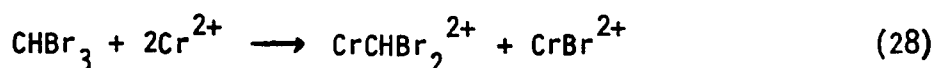
The substitution reactions of alkylchromium(III) complexes have not been investigated, perhaps because they are less stable than the alkylcobalt(III) complexes. The first reported synthesis of an alkylchromium(III) compound was by Anet.³⁵ He initially reported the preparation of benzylchromium(III) by oxidizing chromium(II) with benzyl chloride as shown in eq 26. The reaction of an organic halide with chromium(II) to



form an organochromium(III) complex is quite general and has been extended to other alkyl halides to make a variety of alkylchromium(III) complexes. Simple alkyl chlorides such as methyl chloride or methylene chloride do not react with chromous ion but chloroform is reduced in a few minutes to give $\text{Cr}(\text{CHCl}_2)^{2+}$ ³⁶ as shown in eq 27. Subsequent studies



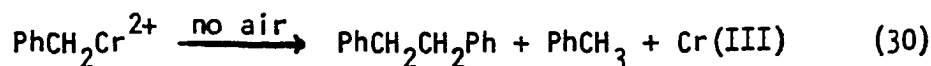
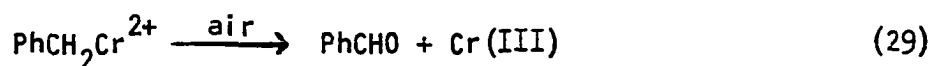
by Dodd and Johnson³⁷ have shown that the corresponding bromide (eq 28) is



more reactive. By employing this general method numerous alkyl compounds have been made including pyridiomethylchromium(III)³⁸, $\text{CrCH}_2\text{X}^{2+}$ and CrCHX_2^{2+} (X = Cl, Br, I).³⁷

The chemistry of these alkylchromium(III) complexes has not been extensively studied. Most work has been concerned with the decomposition

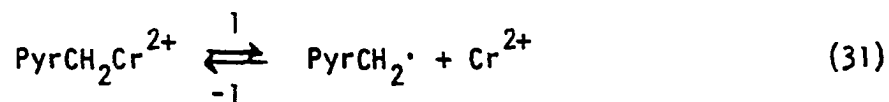
reactions. In aqueous solutions, alkylchromium(III) complexes decompose to give hexaquo chromium(III) and an organic product which depends upon the conditions of the decomposition. If oxygen is present, the organic product is generally the organic aldehyde; if oxygen is excluded the alkane or alkane dimers are the predominant products. For example Kochi³⁹ reports the following reactions of benzylchromium(III).



Similar results have been reported in other systems.^{40,41}

Kinetic studies have been reported for only two alkylchromium(III) complexes. Kochi⁴⁰ has studied the decomposition of benzylchromium(III) under anaerobic conditions employing a variety of supporting electrolytes. Coombes and Johnson⁴² have studied the decomposition of pyridiomethylchromium(III) in the presence of oxygen while Swaddle⁴³ has studied the identical complex under anaerobic conditions.

Two important observations were reported in those systems which are pertinent to this thesis. In the absence of air the decomposition of pyridiomethylchromium(III) is retarded by the addition of Cr^{2+} . This can be explained by the mechanism

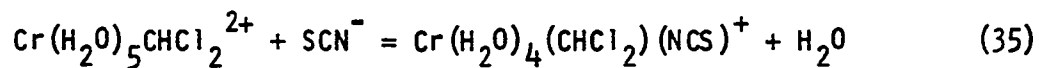
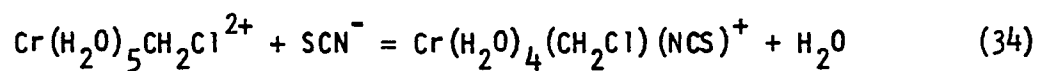


The fact that solutions of alkylchromium(III) can dissociate into Cr^{2+} and alkyl radicals is relevant to any discussion about reactions of alkylchromium(III) since Cr^{2+} could serve as an intermediate in such reactions.

The second observation led directly to the initiation of the study reported here. As previously mentioned Kochi employed a wide variety of conditions to study the decomposition of benzylchromium. One of the factors varied was the supporting electrolyte. If NaI, LiCl, LiBr or LiClO_4 were used, the rate of decomposition was essentially unchanged. However, if NaSCN were used, the rate increased three-fold. This suggested that SCN^- was interacting in some way with benzylchromium. The fact that SCN^- is a much better coordinating ligand for Cr^{3+} than I^- , Br^- or Cl^- suggested that an anation reaction was occurring but at a much higher rate than is usual for Cr(III) complexes.

Since benzylchromium(III) is so unstable toward oxidation, a more suitable alkyl complex was sought to study these reactions. Dodd and Johnson³⁷ reported that $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} were stable for days even in air. This makes these complexes ideal for observing the anation

reactions shown in eq 34 and 35. Preliminary experiments showed



unmistakably that the alkylchromium(III) was reacting with thiocyanate at a rate much faster than the normal substitution rates of Cr(III). Thus a comprehensive study of these reactions was undertaken. The results and conclusions are presented here.

EXPERIMENTAL

Reagents.—Monochloromethylchromium(III) was made using a variation of the method of Dodd and Johnson.³⁷ A typical procedure is as follows. Ten ml of ClCH_2Br was placed in a 100 ml volumetric flask and bubbled with nitrogen. Approximately 50 ml of 0.1 M Cr^{2+} (~ 0.2 M in HClO_4) was syringed into the flask and the flask stoppered. The immiscible liquids were kept well stirred with a magnetic stirring bar. The reaction appeared to be complete in one hour. At that time the unreacted ClCH_2Br was removed and the remaining solution was passed through a Dowex 50 x 8 resin ion exchange column which was in the H^+ form. On the column, the solution gave two apparent bands, a lower green one fading into a dark band, the latter containing several chromium complexes. Elution with 1 M perchloric acid separates these bands into four bands corresponding to (in the order of appearance from bottom to top) CrCl^{2+} , $\text{CrCH}_2\text{Cl}^{2+}$, Cr^{3+} , and $\text{Cr}_2(\text{OH})_2^{4+}$. The red $\text{CrCH}_2\text{Cl}^{2+}$ was collected and its concentration determined by chromate analysis.⁴⁶

A similar procedure was used to make CrCHCl_2^{2+} using chloroform as the oxidizing agent as in eq 27. However, before the product solution was placed on the ion exchange column, mercury(II) was added to destroy the small amount of $\text{CrCH}_2\text{Cl}^{2+}$ also produced, since mercury(II) reacts with $\text{CrCH}_2\text{Cl}^{2+}$ much faster than with CrCHCl_2^{2+} .³⁷ After ~ 10 min, hydrochloric acid was added to complex any remaining Hg^{2+} and the ion exchange separation was then carried out.

The identities of the alkylchromium(III) species were confirmed by comparison of the experimentally determined maxima with those reported in

the literature. The reported maxima (with the molar absorptivities in parentheses) of $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} are 262 nm ($3500 \text{ M}^{-1}\text{cm}^{-1}$), 391 (220), 517 (20) and 265 (2500), 396 (120), 514 (23) respectively.³⁷ We found the following values: $\text{CrCH}_2\text{Cl}^{2+}$ -- 265 (3600), 393 (225), 517 (23.4); CrCHCl_2^{2+} -- 266 (4290), 396 (157 ± 4), 514 (38.7 ± 1.0). The position of the maxima are in good agreement for both complexes. Although the molar absorptivities for $\text{CrCH}_2\text{Cl}^{2+}$ are in good agreement with literature values, there is a significant difference between those reported for CrCHCl_2^{2+} and the values determined in the course of this work. In this study, the molar absorptivities were independently checked by two other persons using independently prepared solutions of CrCHCl_2^{2+} .^{44, 45}

Lithium thiocyanate solutions were prepared from potassium thiocyanate and an excess of lithium perchlorate. After cooling to ice temperature, the KClO_4 was removed by filtration and the solution standardized by determining total SCN^- by the Volhard method.¹² Total $[\text{Li}^+]$ was determined by passing aliquots through a column of Dowex 50W-X8 cation resin in the H^+ form. The resin was rinsed with water and the rinsings were titrated with standard sodium hydroxide. In a typical solution $[\text{Li}^+] = 2.499 \text{ M}$; $[\text{SCN}^-] = 2.344 \text{ M}$. The difference between the two determinations gives the total perchlorate concentration.

Lithium perchlorate was prepared by dissolving reagent grade lithium carbonate in a slight excess of 72% perchloric acid. The lithium perchlorate precipitated upon reduction of the volume of solution and was recrystallized. Stock solutions of lithium perchlorate were analyzed with ion exchange techniques described above.

For the methanol-chromium(III) experiments reagent grade methanol was used without further purification. The mercuric nitrate solutions were prepared by dissolving 6 g of reagent grade mercuric nitrate dihydrate in the appropriate methanol-water solution (~ 160 ml) containing ~ 0.1 M HClO_4 .

Induced Solvolysis of $\text{CrCH}_2\text{Cl}^{2+}$ and $(\text{CH}_3\text{OH})\text{CrCH}_2\text{Cl}^{2+}$.—Acidic solutions ($[\text{H}^+] = \sim 0.1$ M) of chloromethylchromium(III) in water-methanol solutions were mixed at room temperature with solutions of mercury(II) nitrate with the same methanol-water ratio. Identical volumes of the two solutions were used; the final volume was ~ 300 ml, and the analytical concentration of Cr(III) was 10^{-3} to 10^{-4} M. The induced solvolysis was followed spectrophotometrically to ensure complete aquation. The rate was noticeably dependent upon the concentration of methanol. For the slowest reaction (high methanol) the reaction required approximately 15 minutes to go to completion.

After the dealkylation was complete, hydrochloric acid was added to complex excess Hg^{2+} and HgCH_2Cl^+ before placing the solutions on ion-exchange columns. The chromium(III) ions were absorbed on a ion-exchange column (Dowex 50W - X8) and washed with 100 ml of 0.1 M HCl followed by 100 ml of 0.1 M HClO_4 . The chromium species were eluted with 4 M H_2SO_4 . After 25 ml of eluent had been collected, the column was allowed to stand for 3 hours. Then the rest of the chromium species were eluted. It was found that 96-100% of the chromium could be collected in 100 ml of eluent. The methanol analysis described below was performed using 50 ml of this solution and 5 ml aliquots of the remaining solution were used for total

chromium determination using the chromate method of analysis.⁴⁶

Analysis for methanol bound to chromium(III) was made by a method similar to the one developed by Jayne and King.⁴⁷ However, some modifications were employed in this study. The procedure for a typical analysis is as follows.

The standard solution of the oxidizing reagent composed of Ce^{IV} and Cr^{VI} was prepared by dissolving 27.413 g of ceric ammonium nitrate (0.05 mol) and 4.9037 g of potassium dichromate (0.01667 mol) in one liter of 4 N sulfuric acid. With these amounts the total oxidizing normality is 0.100 N. A 0.025 N iron(II) solution was made by dissolving $\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ in 4 N sulfuric acid. This solution was standardized each day prior to use.

To analyze for methanol, a 50 ml aliquot containing ~ 0.2 mmol of CH_3OH was pipetted into a 500-ml flask set in cold water. After cooling for several minutes, 15 ml of the oxidizing reagent and 70 ml of 18 M sulfuric acid was added in such a manner that the final temperature of the solution was 80° . The flask was covered and allowed to stand for four hours. Then, 140 ml of water was added and the solution allowed to cool in cold water.

After the temperature of the solution had been lowered to room temperature or below, the excess oxidizing agent was titrated with iron(II) using ferroin indicator -- an indicator useful for dichromate titrations only in highly acidic media (ca. 4-6 M).

For each individual determination a blank was done using the identical procedure with no methanol. In general, the blank was no greater than 0.00005 equiv.

Equilibrium Studies.—One method used to evaluate the equilibrium constant for the reaction was based upon the spectrophotometric analysis of solutions containing varying concentrations of SCN^- . The procedure was as follows. Appropriate volumes of stock solutions of LiClO_4 , HClO_4 , and LiSCN were measured into a volumetric flask (generally 50 ml size). This was allowed to thermostat in a 25° water bath for 20 minutes. Then an appropriate amount of monochloromethylchromium was added and the volume made up with distilled water. This solution was then allowed to thermostat for an additional 5 minutes so that equilibrium could be attained.

The absorbances were obtained using a Cary Model 14 spectrophotometer. The appropriate absorbance blank of $\text{CrCH}_2\text{Cl}^{2+}$ with no added LiSCN was obtained under identical experimental conditions. These data permitted the evaluation of the stability constant according to equations given in the Results Section of this thesis.

An independent determination of the equilibrium constant was afforded by determinations based on the data from the rate experiments. In the so-called "kinetic" equilibrium studies, pseudo-first-order plots of $\log|D_t - D_\infty|$ vs time (D_t is the absorbance at time t and D_∞ is the absorbance after the reaction has been completed) were extrapolated to zero time to obtain the total change in absorbance for the reaction. The total absorbance changes at various $[\text{LiSCN}]$ were then plotted according to the appropriate equation given in the text.

Kinetic Experiments.—Reactions were followed using a Cary Model 14 recording spectrophotometer. The reaction cell consisted of two

compartments both connected to a mixing chamber as shown in Figure 11. Approximately equal volumes of liquid were placed in each compartment with approximately equal concentrations of acid. After the cell had been thermostatted for ten minutes it was inverted three times to mix the reactants and placed in the spectrophotometer. Average dead time was ~ 7 seconds. Preliminary tests using 1 M HClO_4 on one side and distilled water on the other side showed no detectable difference in acidity of aliquots taken from either side of the cell after mixing.

The reaction cell was thermostatted at 25° during the reaction by circulating water through coils surrounding the water-filled cell holder.

The infinity absorbance reading decreased slightly over long periods of time owing to decomposition of the product. We empirically found a wavelength which minimized this error. It should be emphasized that the change in absorbance resulting from the secondary reaction was never great and, indeed, since studies showed the reaction was independent of wavelength, the precaution was not necessary.

Treatment of the Data.—All rate runs were carried out with $[\text{SCN}^-]_0 \gg [\text{CrR}^{2+}]_0$. The data were analyzed according to eq 36 where D_t is the absorbance at time t , D_0 is the initial absorbance and D_∞ is the

$$\ln|D_t - D_\infty| = \ln|D_0 - D_\infty| - k_{\text{obs}} t \quad (36)$$

absorbance after the reaction was complete. The observed rate constant was determined by the slope of a plot of $\ln|D_t - D_\infty|$ vs time.

The observed rate constants were fitted to an equation of the form

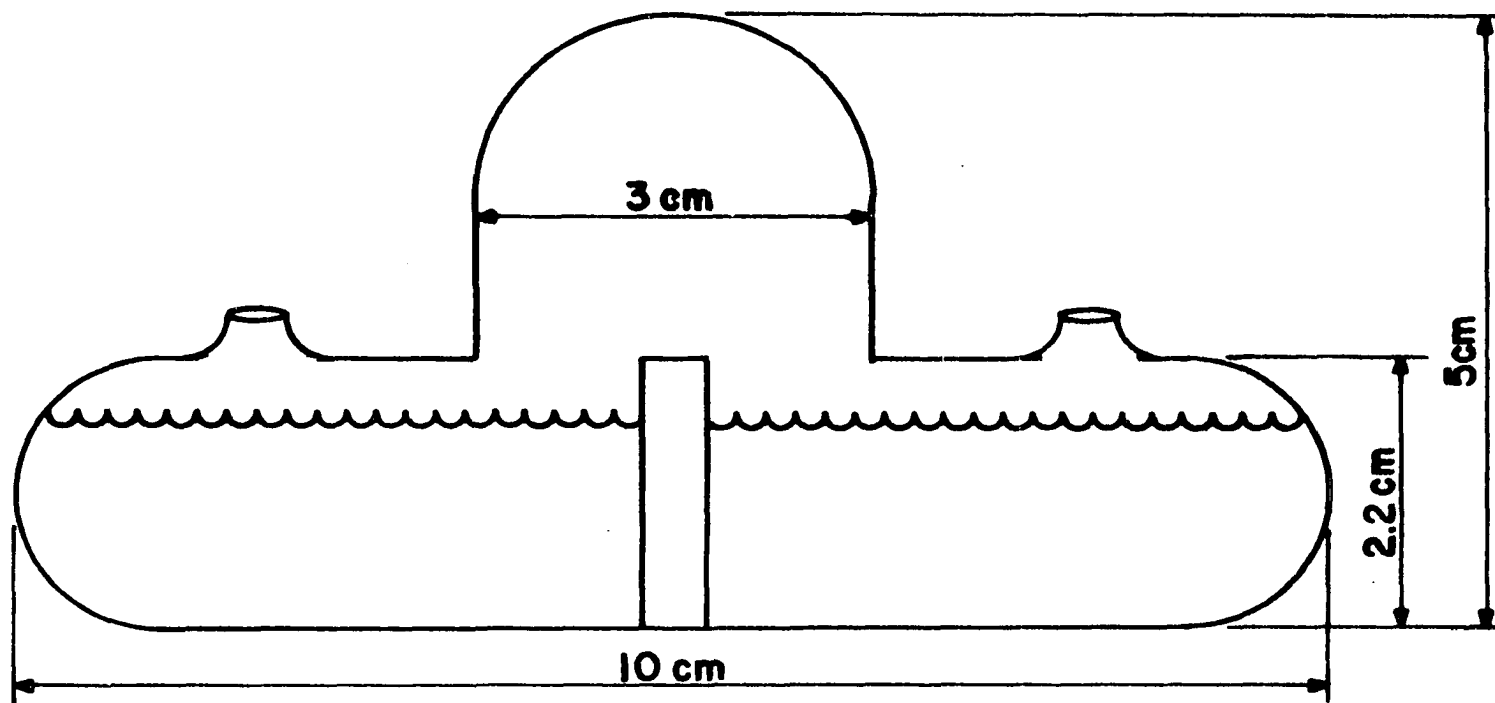


Figure 11.—Reaction cell used for kinetic experiments.

$$k_{\text{obs}} = \frac{A[\text{SCN}^-] + B}{1 + C[\text{SCN}^-]} \quad (37)$$

using a nonlinear least squares program.¹⁶

RESULTS

Spectra.--The spectrum of each of the two alkylchromium(III) complexes, $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} , was measured in aqueous 1.0 M HClO_4 . The tabulated molar absorptivities of $\text{CrCH}_2\text{Cl}^{2+}$ are listed in Table XII while the spectrum appears in Figure 12. The corresponding data for CrCHCl_2^{2+} appear in Table XIII and Figure 13.

Also illustrated in Figure 12 is the spectrum of the product of the reaction of $\text{CrCH}_2\text{Cl}^{2+}$ and SCN^- , $\text{Cr}(\text{CH}_2\text{Cl})(\text{NCS})^+$. The molar absorptivities of this complex are listed in Table XIV. The spectrum was obtained by measuring absorbance changes which occurred when LiSCN was added to a solution of $\text{CrCH}_2\text{Cl}^{2+}$. These absorbance changes are related to the difference between the molar absorptivities of $\text{CrCH}_2\text{Cl}^{2+}$ and $\text{CrCH}_2\text{Cl}(\text{NCS})^+$ by eq 38 where

$$\frac{\Delta D}{\ell[\text{CrCH}_2\text{Cl}^{2+}]_{\text{tot}}} = \frac{(\epsilon_{\text{CrCH}_2\text{Cl}(\text{NCS})^+} - \epsilon_{\text{CrCH}_2\text{Cl}^{2+}})}{1 + K[\text{SCN}^-]} K[\text{SCN}^-]. \quad (38)$$

ΔD is the absorbance increase, K is the equilibrium constant for reaction 37 which has been determined independently, ℓ is the optical path length, $[\text{CrCH}_2\text{Cl}^{2+}]_{\text{tot}}$ is the total concentration of the alkylchromium(III) both complexed and uncomplexed, and ϵ is the molar absorptivity of the respective complexes. This equation was solved for a series of five different thiocyanate concentrations at each wavelength studied and the difference in molar absorptivities reported is

Table XII
Spectrum of $\text{CrCH}_2\text{Cl}^{2+}$ ^a

λ nm	$\text{M}^{-1}\text{cm}^{-1}$	λ nm	$\text{M}^{-1}\text{cm}^{-1}$
650	3.42	430	72.8
640	3.71	420	122
630	3.99	410	177
620	4.42	400	215
610	4.99	393 ^b	225
600	5.85	390	224
590	6.99	380	204
580	8.42	370	173
570	11.1	360 ^c	163
560	14.3	350	183
550	17.0	340	228
540	20.3	330	291
530	22.4	320	408
520	23.5	310	603
517 ^b	23.7	300	989
510	23.5	290	1630
500	21.4	280	2500
490	18.5	270	3220
480	15.8	260	3560
470 ^c	14.7	250	3170
460	16.0	240	2480
450	22.8	236 ^c	2240
440	39.9	230	2300

^aAqueous solution. ^bMaximum. ^cMinimum.

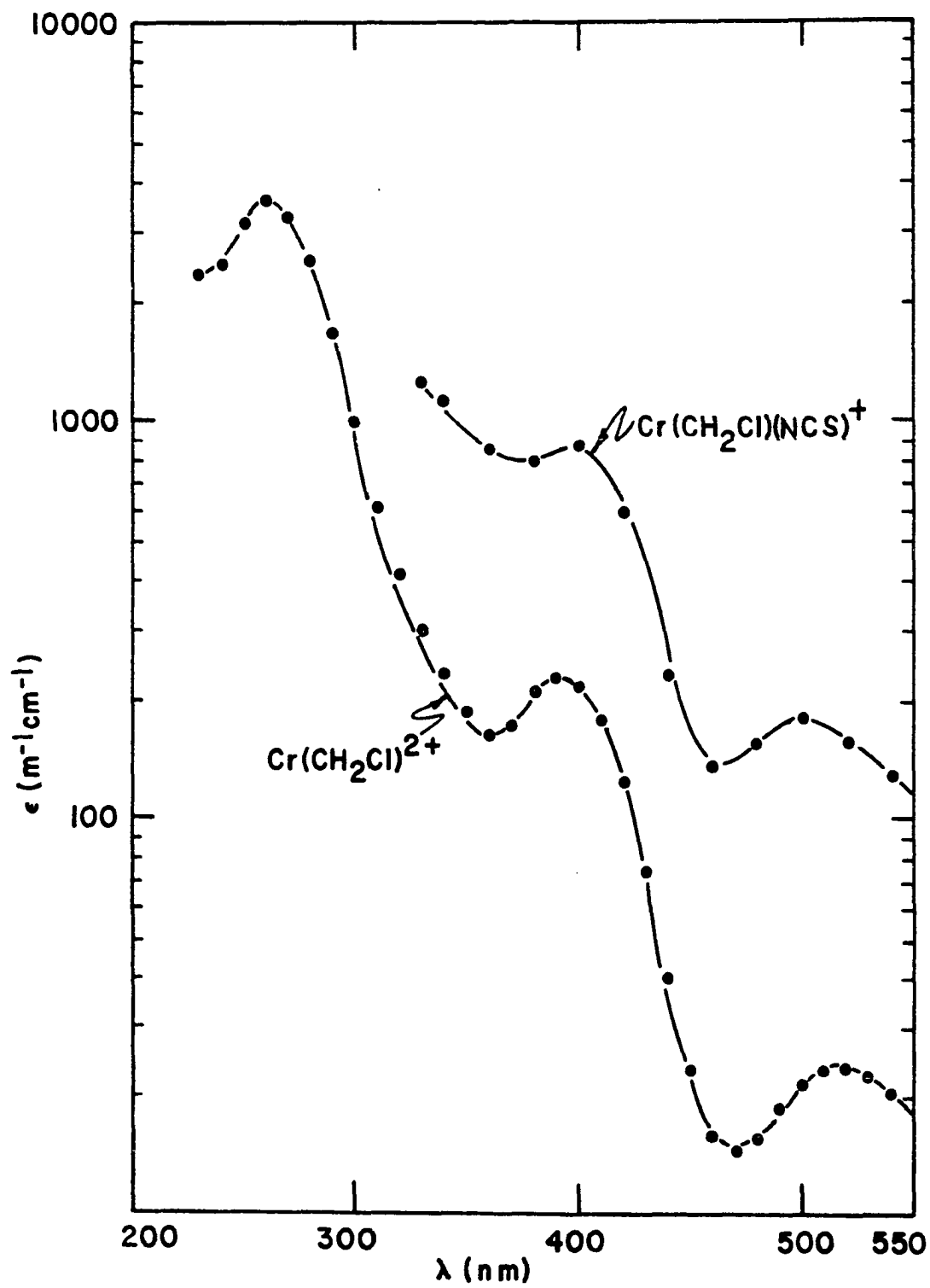


Figure 12.—Spectra of $\text{CrCH}_2\text{Cl}^{2+}$ and $\text{CrCH}_2\text{Cl}(\text{NCS})^+$.

Table XIII
Spectrum of CrCHCl_2^{2+} ^a

λ nm	$M^{-1} \text{cm}^{-1}$	λ nm	$M^{-1} \text{cm}^{-1}$
600	6.93	390	157
590	8.87	380	140
580	11.3	370	125
570	15.7	365 ^c	124
560	20.9	360	128
550	26.5	350	149
540	32.5	340	230
530	37.1	330	379
520	39.4	320	595
514 ^b	39.9	310	936
510	39.7	300	1530
500	37.1	290	2440
490	32.6	280	3500
480	28.2	270	4220
470 ^c	26.4	267 ^b	4290
460	28.4	260	4090
450	39.0	250	3110
440	57.7	240	2530
430	86.4	230	3090
420	119	226 ^b	3193
410	147	220	2990
400	160	215 ^c	2750
397 ^b	161	210	2810

^a Aqueous solution. ^b Maximum. ^c Minimum.

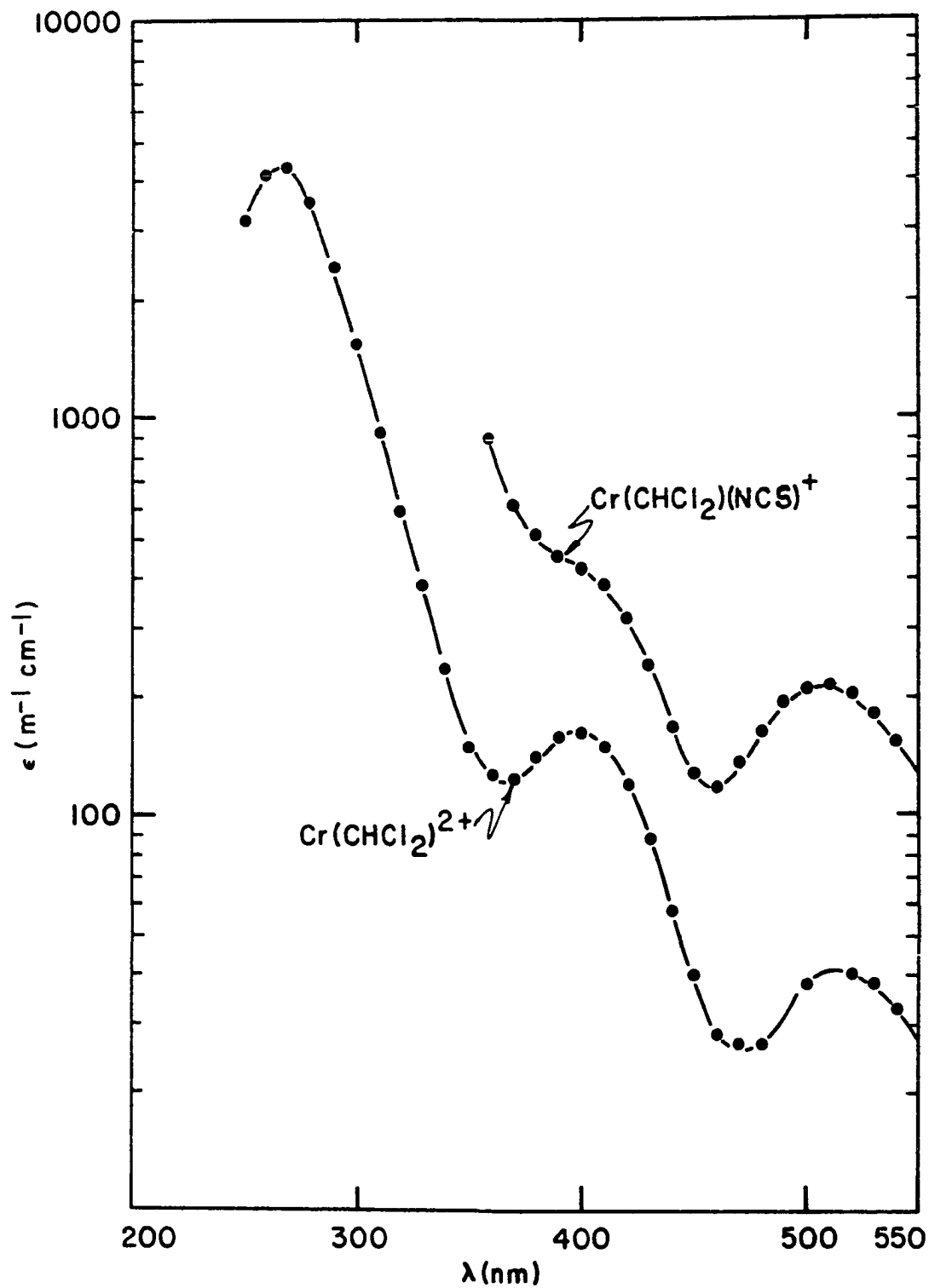


Figure 13.—Spectra of CrCHCl_2^{2+} and $\text{CrCHCl}_2(\text{NCS})^+$.

Table XIV
Spectrum of $\text{Cr}(\text{CH}_2\text{Cl})(\text{NCS})^+$

λ nm	$\Delta\epsilon_0^a$ $\text{M}^{-1}\text{cm}^{-1}$	ϵ^b $\text{M}^{-1}\text{cm}^{-1}$
600	39.5	45.4
580	50.8	59.2
560	73.7	97.0
540	109	129
520	147	171
500	157	179
480	138	154
460	120	136
440	189	229
420	462	584
400	650	865
380	580	784
360	696	859
340	888	1120
330	930	1220

^a $\Delta\epsilon = \epsilon_{\text{CrCH}_2\text{Cl}(\text{NCS})^+} - \epsilon_{\text{CrCH}_2\text{Cl}^{2+}}$; average of five determinations.

^bCalculated by the equation $\epsilon = \epsilon_{\text{CrCH}_2\text{Cl}^{2+}} + \Delta\epsilon_0$.

the average of those five determinations. The concentrations of thiocyanate were chosen such that between 20 and 60% of the alkylchromium(III) was in the complexed form. Since the molar absorptivity of $\text{CrCH}_2\text{Cl}^{2+}$ is known independently, the absorptivities of the thiocyanate complex can be calculated.

A less precise method was used in determining the spectrum of $\text{Cr}(\text{CHCl}_2)(\text{NCS})^+$ shown in Figure 13. A known amount of CrCHCl_2^{2+} was added to a 1.6 M lithium thiocyanate. An apparent molar absorptivity was obtained which was subsequently corrected upward by 4%, to allow for the uncomplexed CrCHCl_2^{2+} . The correction was based on the experimentally determined equilibrium constant (12.1 M^{-1}) and the known molar absorptivity of CrCHCl_2^{2+} . The molar absorptivities are listed in Table XV.

The low energy maxima of the thiocyanate complexes are shifted to higher energies from the aquo-alkylchromium(III) complexes. These maxima for $\text{Cr}(\text{CH}_2\text{Cl})(\text{NCS})^+$ and $\text{Cr}(\text{CHCl}_2)(\text{NCS})^+$ occur at 500 nm and 510 nm respectively.

Stoichiometry.—The spectrum of a solution of 0.001 M $\text{CrCH}_2\text{Cl}^{2+}$ or 0.001 M CrCHCl_2^{2+} changes as lithium thiocyanate is varied from 0.01 to 1.0 M. This behavior implies that the alkylchromium(III) is in equilibrium with a complex containing at least one thiocyanate as shown in eq 39. Although equilibrium studies reported

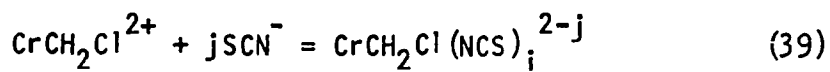


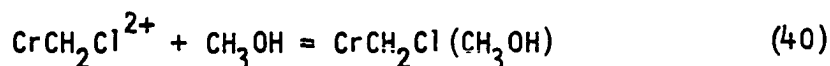
Table XV
Spectrum of $\text{Cr}(\text{CHCl}_2)(\text{NCS})^+$ ^a

λ nm	$\text{M}^{-1}\text{cm}^{-1}$	λ nm	$\text{M}^{-1}\text{cm}^{-1}$
600	38.9	470	134
590	49.0	460	119
580	60.8	450	127
570	75.3	440	167
560	97.2	430	234
550	124	420	311
540	152	410	381
530	179	400	426
520	203	390	455
510	210	380	501
500	209	370	615
490	191	358	873
480	163		

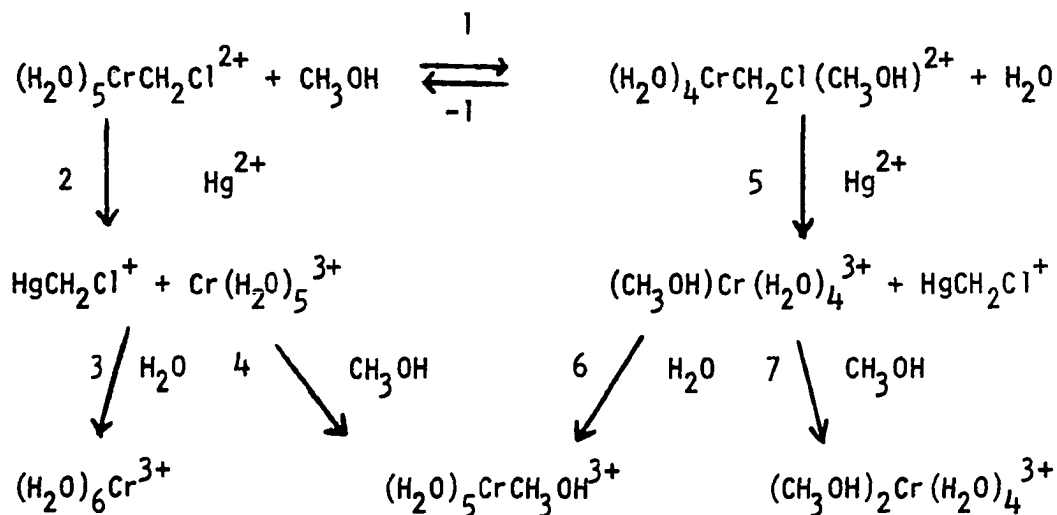
^a Measured in 1.6 M SCN^- and corrected for uncomplexed CrCHCl_2^{2+} using K given in text.

later are consistent only with $j = 1$, it is desirable to obtain an independent confirmation that one and only one ligand is entering the first coordination sphere of the chromium(III) ion.

The products could not be isolated as solids, nor could they be obtained in solution free of thiocyanate due to the high lability of alkylchromium(III). Therefore the stoichiometry of the reaction of CrR^{2+} with SCN^- could not be studied directly. However, the stoichiometry of a related reaction of $\text{CrCH}_2\text{Cl}^{2+}$ with CH_3OH shown in eq 40 could be studied using the method developed by Ferraris



and King⁴⁸ in their study of mercury(II)-induced aquation of halo-chromium(III) in water-methanol solutions. The concept of the experiment is embodied in the following reaction scheme.



When methanol is added to a solution of $\text{CrCH}_2\text{Cl}^{2+}$, the equilibrium is established via reaction 1 and -1. When mercury(II) is added, the alkyl groups are removed forming five coordinate intermediates via reactions 2 and 5. The five coordinate intermediates can then react with either a water molecule (reactions 3 or 6) or a methanol molecule (reactions 4 and 7). Given these reactions, in the limit of high methanol, first the equilibrium (1,-1) will be saturated and second, the five coordinate intermediate will react predominantly via reaction 7. Thus the average number of methanol molecules per chromium atom in the collection of all chromium products (Cr^{3+} , $\text{CrCH}_3\text{OH}^{3+}$, $\text{Cr}(\text{CH}_3\text{OH})_2^{3+}$) designated as \bar{n} , should be a function of mole fraction methanol (Z) which approaches 2.0 in the limit of high methanol as can be seen by the following equations.

$$\bar{n} = \frac{\text{Total [Methanol] in Cr(III) products}}{[\text{Cr(III)}]_{\text{total}}}$$

$$\bar{n} = \frac{[\text{Cr}(\text{CH}_3\text{OH})^{3+}] + 2[\text{Cr}(\text{CH}_3\text{OH})_2^{3+}]}{[\text{Cr}^{3+}] + [\text{Cr}(\text{CH}_3\text{OH})^{3+}] + [\text{Cr}(\text{CH}_3\text{OH})_2^{3+}]}$$

If more than one methanol were coordinated to the chromium(III) by reactions not shown in the reaction scheme, then \bar{n} would be higher than 2.0. Were no methanol coordinated prior to dealkylation by mercury(II), then \bar{n} would approach 1.0 as in the case of halochromium(III). The quantity \bar{n} has been measured in solutions containing various concentrations of methanol. The results are listed in Table XVI.

Table XVI
 Average Value of \bar{n} ^a
 in Methanol-Water Solutions

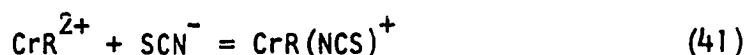
Complex	z^b				
	0	0.28	0.46	0.64	0.87
$\text{CrCH}_2\text{Cl}^{2+}$	0.03	0.86	1.40	1.65	1.90
CrBr^{2+} ^c	--	0.199	0.330	0.465	0.71

^a \bar{n} is defined as the average number of bound methanol molecules per chromium atom; room temperature; $[\text{HClO}_4] \simeq 0.1 \text{ M}$. ^b z = mole fraction of methanol considering only solvent components. ^cReference 48.

Included in this table are the results of Ferraris and King's⁴⁸ work with CrBr^{2+} for comparison. The values of \bar{n} listed in Table XVI are plotted vs mole fraction methanol in Figure 14. Provided that the curve remains smooth in the experimentally inaccessible region of $Z > 0.87$, the limit of \bar{n} appears to be 2.0.

Recovery of Reactants.—As a check to insure that there are no irreversible steps in the reaction of $\text{CrCH}_2\text{Cl}^{2+}$ and SCN^- , an experiment was performed to show that $\text{CrCH}_2\text{Cl}^{2+}$ could be recovered from the equilibrium solution. A reaction was carried out with a known concentration of $\text{CrCH}_2\text{Cl}^{2+}$ at 1.17 M SCN^- . At this concentration of thiocyanate, 93% of the $\text{CrCH}_2\text{Cl}^{2+}$ is in the complexed form. The reaction solution was placed on a column of cation exchange resin, Dowex 50W-X8. Thiocyanate was rinsed off with distilled water; reversal of the reaction caused the release of coordinated SCN^- . After this, the $\text{CrCH}_2\text{Cl}^{2+}$ complex remaining on the column was eluted as quantitatively as possible with 1.0 M perchloric acid. The concentration of the eluted chromium complex was determined spectrophotometrically at 393 nm. The recovery was 86%. This result suggests that the complexation is a reversible reaction but the possibility of partial decomposition on the resin column cannot be eliminated since 14% of the $\text{CrCH}_2\text{Cl}^{2+}$ is unaccounted for.

Equilibrium Studies.—For a reaction which proceeds according to eq 41, the total change in absorbance between



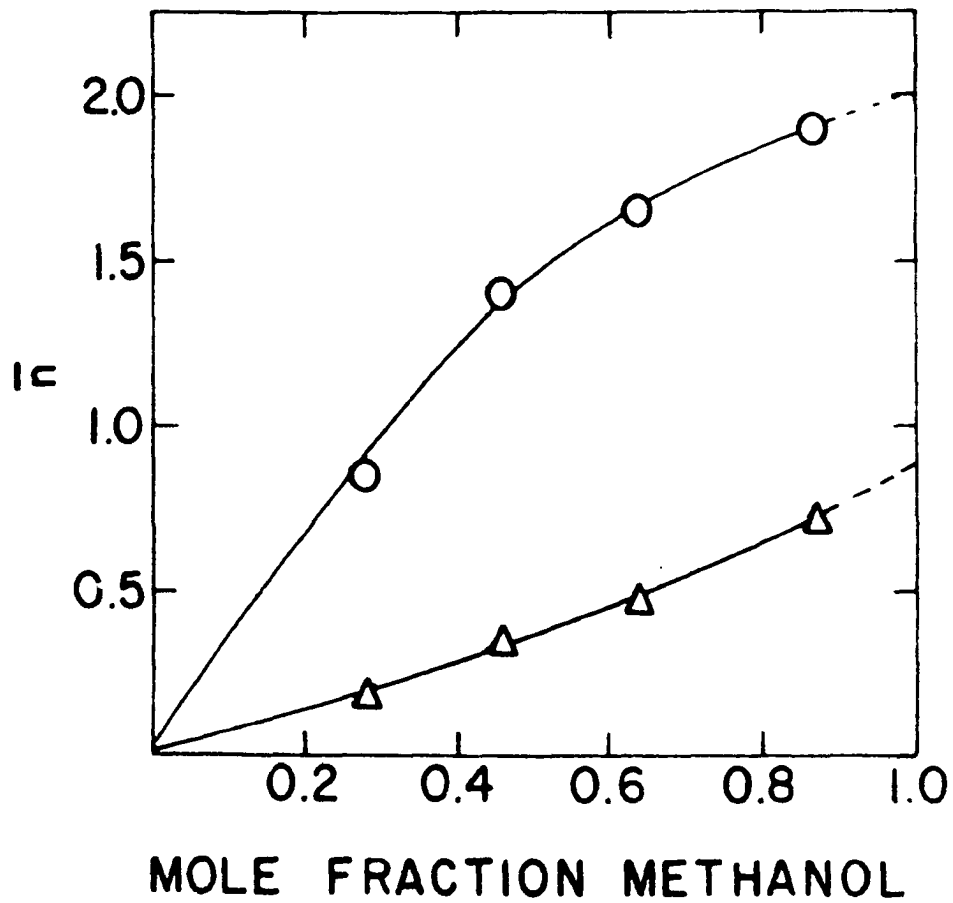


Figure 14. \bar{n} as a function of mole fraction methanol. o = $\text{CrCH}_2\text{Cl}^{2+}$; this work; Δ = CrBr^{2+} , Reference 48.

a solution of CrR^{2+} before the addition of thiocyanate and the solution after equilibrium has been obtained is related to the equilibrium constant of the system. There are two generally recognized methods for measuring this change in absorbance. In the first method the change in absorbance is obtained by measuring the absorbances of solutions containing known concentrations of thiocyanate and CrR^{2+} . Then the absorbance of a like amount of CrR^{2+} with no added thiocyanate is subtracted to obtain the static absorbance change, ΔD_s . The second method determines the change in absorbance by extrapolating absorbance traces of kinetic runs back to zero time (or the more accurate equivalent of taking the antilog of the zero time intercept of a first-order plot of $\log |D_t - D_\infty|$ vs time). This gives the kinetic absorbance change designated ΔD_k .

Given a system described by eq 40 it can be shown that ΔD is related to the equilibrium constant, K , by eq 42 and 43 where $\Delta \epsilon_0$ is the difference in molar absorptivity of CrR^{2+} and $\text{CrR}(\text{NCS})^+$,

$$\Delta \epsilon = \frac{\Delta D}{\ell [\text{CrR}^{2+}]_{\text{tot}}} \quad (42)$$

$$\frac{\Delta \epsilon}{\ell [\text{SCN}^-]} = -K \Delta \epsilon + K \Delta \epsilon_0 \quad (43)$$

$\epsilon_{\text{CrR}(\text{NCS})^+} - \epsilon_{\text{CrR}^{2+}}$, and ℓ is the optical path length.

If ℓ and $[\text{CrR}^{2+}]_{\text{tot}}$ are equal for a series of measurements, then eq 44 can be derived where ΔD_0 is the change in absorbance expected

$$\frac{\Delta D}{[\text{SCN}^-]} = -K\Delta D + \Delta D_o K \quad (44)$$

if all the CrR^{2+} were complexed. This equation was used to plot some of the data rather than eq 43.

In the present investigation both values, ΔD_s and ΔD_k , were measured for $\text{CrCH}_2\text{Cl}^{2+}$ as a function of added thiocyanate and both gave identical results. ΔD_s was measured as a function of added thiocyanate at four different wavelengths: 351, 470, 500, and 550 nm. The data listed in Table XVII are plotted according to eq 44 in Figure 15. Least-squares fits of the data give the following values for K: 11.5, 11.8, 12.0, and 11.7 M^{-1} at each of the respective wavelengths.

ΔD_k was measured as a function of added thiocyanate at only one wavelength, 351 nm. The data listed in Table XVIII obey eq 43 as evidenced by the linearity of the plot shown in Figure 16. A least-squares fit of the data gives the following parameters: $K_{\text{app}} = 11.6 \text{ M}^{-1}$ and $\Delta \epsilon_o = 446 \text{ M}^{-1} \text{ cm}^{-1}$. The average deviation between experimental and calculated values for ΔD is 3.8% with no noticeable trend in the error.

Only ΔD_k was measured for the CrCHCl_2^{2+} system. The results listed in Table XIX obey eq 43 and give the least-squares parameters of 12.1 M^{-1} and $638 \text{ M}^{-1} \text{ cm}^{-1}$ for K_{app} and $\Delta \epsilon_o$ respectively. The data are plotted in Figure 17. Again the fit was good with the average deviation being 4.5%.

Table XVII

Absorbances of Various Equilibrium Solutions of
Lithium Thiocyanate and $\text{CrCH}_2\text{Cl}^{2+}$ at Different Wavelengths^a

$\text{Li}[\text{SCN}]$ $M \times 10^2$	$\text{CrCH}_2\text{Cl}^{2+}$ $M \times 10^3$	ΔD_s^b $\lambda=351$	ΔD_s^c $\lambda=470$	ΔD_s^c $\lambda=500$	ΔD_s^c $\lambda=550$
2.19	2.26	0.411	0.251	0.334	0.204
3.76	2.26	0.610	0.379	0.510	0.315
5.85	2.26	0.803	0.508	0.679	0.421
8.77	2.26	0.966	0.603	0.816	0.503
13.22	2.26	1.178	0.740	1.007	0.611
20.5	2.26	1.408	0.902	1.232	0.745
35.1	2.26	1.678	1.102	1.525	0.913

^a ΔD_s is defined as the difference in absorbance of a solution of $\text{CrCH}_2\text{Cl}^{2+}$ containing LiSCN and a like solution of $\text{CrCH}_2\text{Cl}^{2+}$ with no added LiSCN. ^b2 cm pathlength. ^c10 cm pathlength.

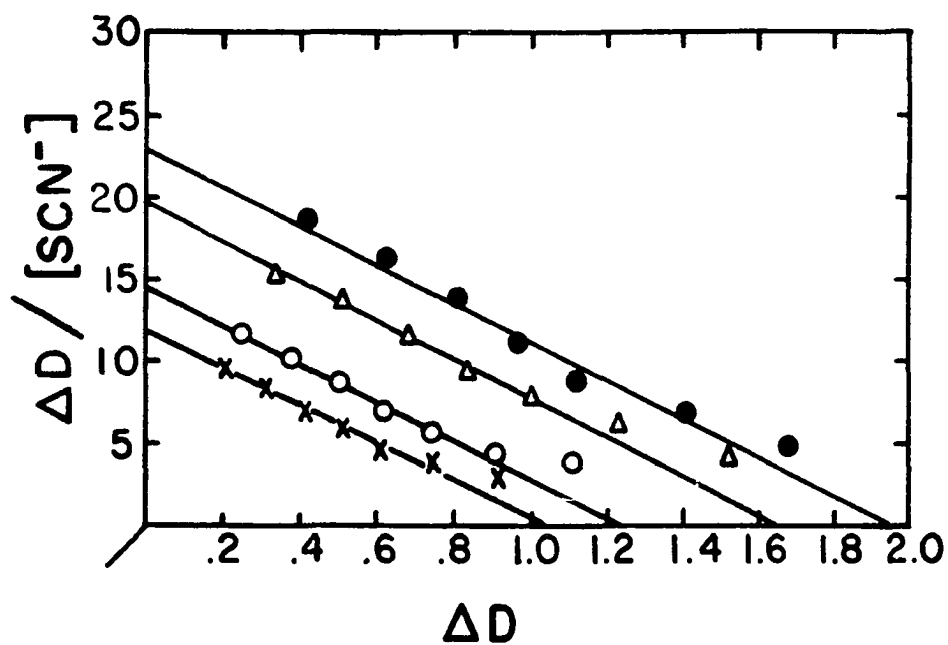


Figure 15.—Equilibrium data for the reaction of $\text{CrCH}_2\text{Cl}^{2+}$ and SCN^- plotted according to eq 44. x, $\lambda = 550 \text{ nm}$; o, $\lambda = 470 \text{ nm}$; Δ , $\lambda = 500 \text{ nm}$; \bullet , $\lambda = 351 \text{ nm}$.

Table XVIII
 Equilibrium Studies of the
 Reaction of $\text{CrCH}_2\text{Cl}^{2+}$ with $\text{SCN}^{-\text{a}}$

$[\text{SCN}^-]$ $\text{M} \times 10^2$	$[\text{CrCH}_2\text{Cl}^{2+}]$ $\text{M} \times 10^4$	ΔD_k obs ^b	ΔD_k calc ^c	$\bar{\Delta\epsilon}$	$\frac{\bar{\Delta\epsilon}}{[\text{SCN}^-]}$
60.0	3.33	1.320	1.246	414	690
40.0	3.33	1.210	1.117	380	949
20.0	3.33	0.978	0.995	307	1530
10.0	3.33	0.753	0.765	236	2360
8.00	3.31	0.617	0.681	195	2430
6.00	3.31	0.548	0.581	173	2880
4.00	3.31	0.421	0.448	133	3320
2.00	2.96	0.240	0.238	84.7	4240
1.60	2.96	0.197	0.198	69.5	4350
1.60	5.56	0.374	0.372	70.3	4390
1.00	2.96	0.142	0.131	50.1	5010
1.00	5.56	0.250	0.247	47.0	4700
0.60	5.56	0.169	0.155	31.8	5290
0.40	2.96	0.0551	0.0561	19.5	4860

^a $\lambda = 350.7 \text{ nm}$; $\mu = 1.0 \text{ M}$ maintained with LiClO_4 ; $[\text{HClO}_4] = 0.2 \text{ M}$; 25° .

^bChange in absorbance obtained by extrapolating rate data to zero time; optical pathlength is 9.57 cm . ^cAverage deviation is 3.8% .

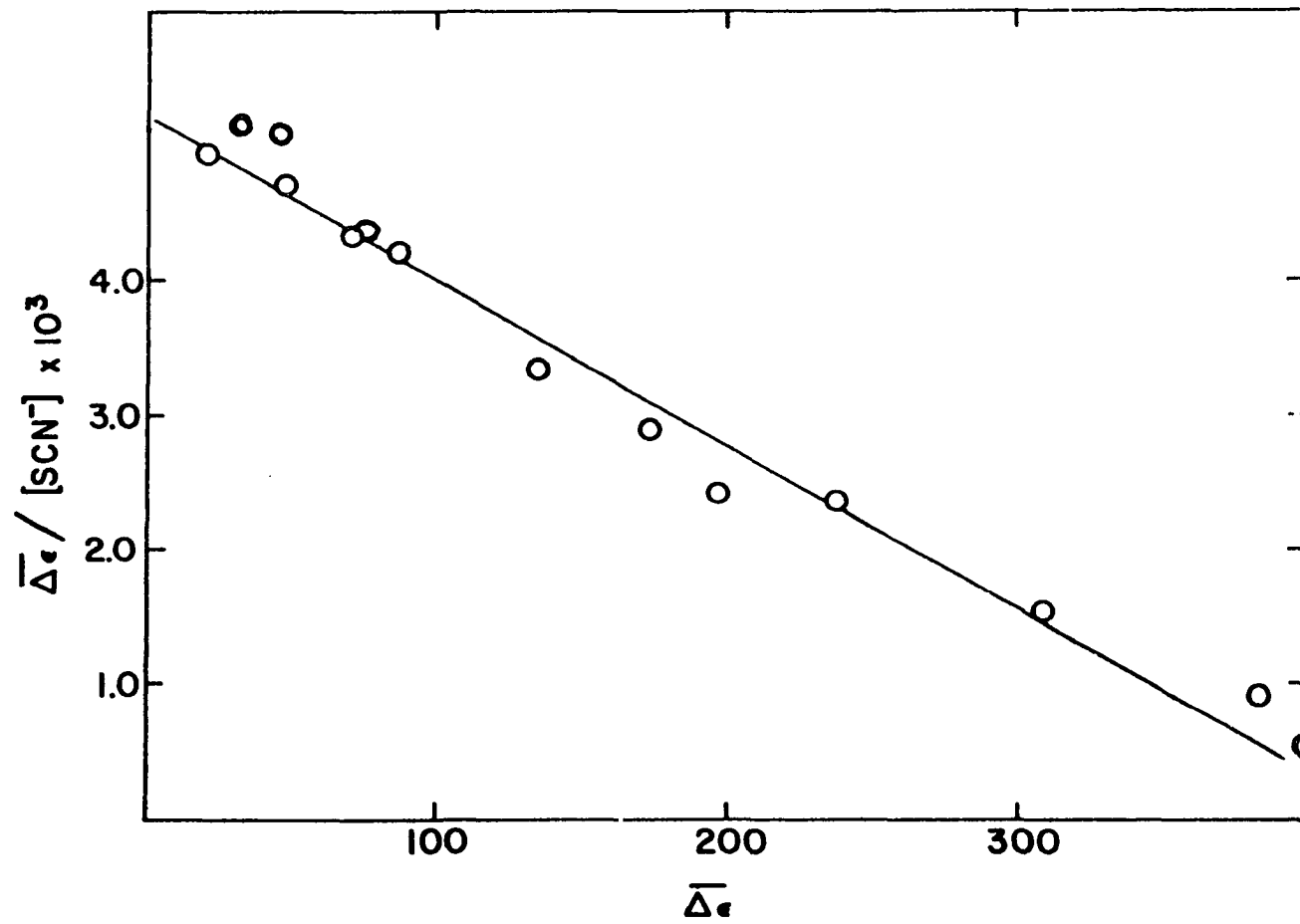


Figure 16.—Equilibrium data for the reaction of $\text{CrCH}_2\text{Cl}^{2+}$ and SCN^- plotted according to eq 43.

Table XIX
Equilibrium Studies of the
Reaction of CrCHCl_2^{2+} with SCN^- ^a

$[\text{SCN}^-]$ $\text{M} \times 10^2$	$[\text{CrCHCl}_2^{2+}]$ $\text{M} \times 10^4$	obs ^b	ΔD_k	calc ^c	$\overline{\Delta\epsilon}$	$\frac{\overline{\Delta\epsilon}}{[\text{SCN}^-]}$
75.0	2.00	1.15		1.10	600	800
60.0	1.69	0.956		0.908	591	985
50.0	1.63	0.911		0.854	584	1170
40.0	2.11	1.03		1.07	510	1280
40.0	2.00	0.885 ^d		1.01	462	1160
20.0	2.11	0.894		0.912	443	2230
15.0	1.63	0.591		0.642	379	2530
10.0	2.11	0.705		0.706	349	3490
5.0	4.16	0.910		0.958	229	4580
2.5	4.16	0.583		0.590	146	5840
1.0	4.10	0.295		0.270	71.2	7120

^a $\lambda = 358 \text{ nm}$; $\mu = 1.0 \text{ M}$ maintained with LiClO_4 ; $[\text{HClO}_4] = 0.2 \text{ M}$; 25° .

^bChange in absorbance obtained by extrapolating rate data to zero time; optical pathlength is 9.57 cm . ^cCalculated using parameters given in text; average deviation is 4.5% . ^dExcluded in computing least squares parameters.

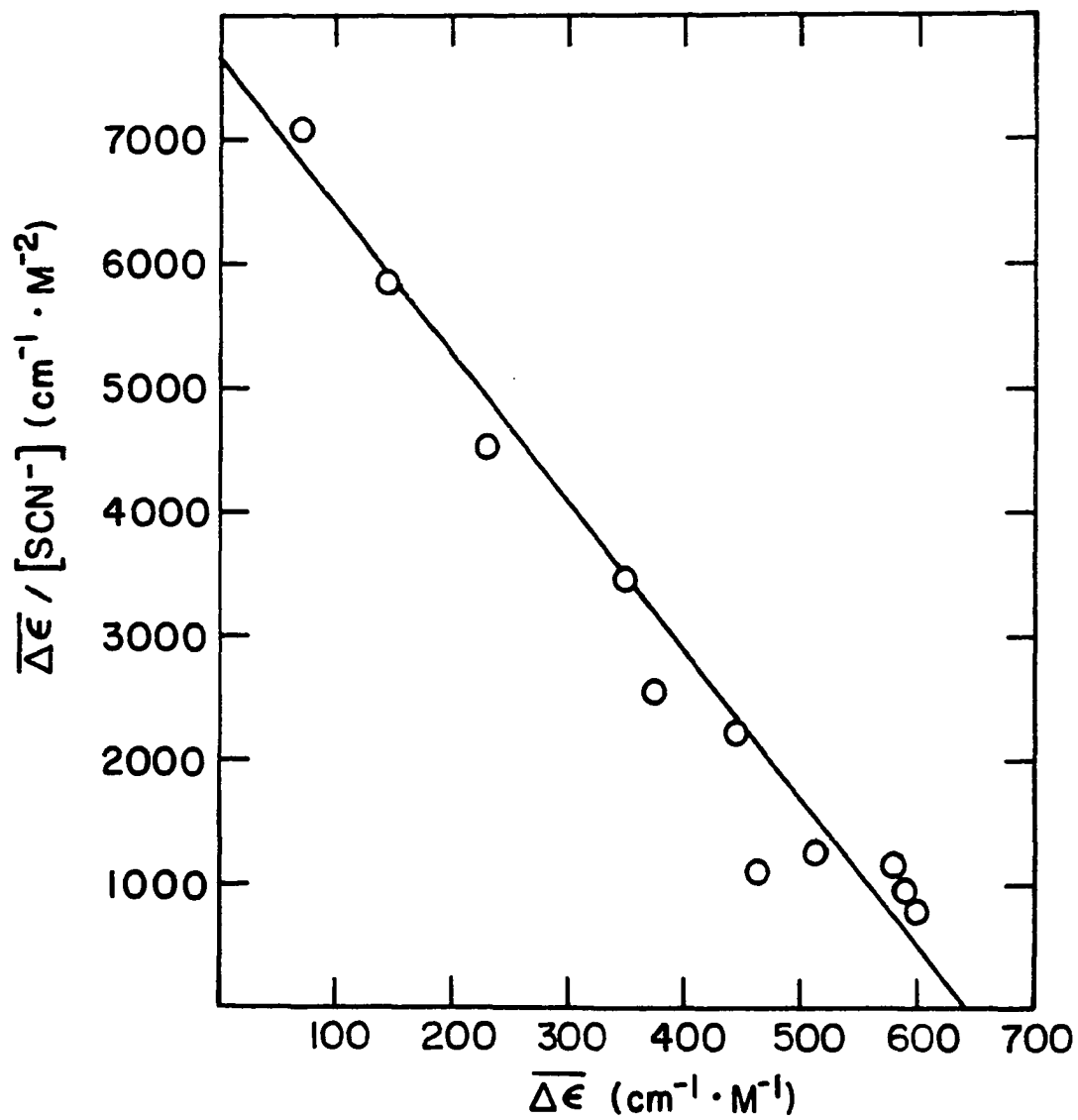


Figure 17.—Equilibrium data for the reaction of CrCHCl_2^{2+} and SCN^- plotted according to eq 43.

Ion Pairing.—The fact that ΔD_s and ΔD_k both give identical results suggests that there is no prior equilibria involving thiocyanate. To ensure against the possibility that this is a result of identical molar absorptivities rather than lack of equilibria, the initial absorbance reading of a reaction solution was measured at 300 nm. The absorbance was identical with the absorbance of an alkylchromium(III) solution with no added thiocyanate. Were ion pairing significant, a difference in absorbance would be expected since the spectra of ion pairs generally differ significantly from the spectra of the ions themselves in this region.

Kinetic Studies.—With thiocyanate in large excess compared to the alkylchromium(III) complex the reaction followed the first-order rate law shown in eq 45. From the slopes of the plots of

$$\ln|D_t - D_\infty| = \ln|D_0 - D_\infty| - k_{\text{obs}} t \quad (45)$$

$\ln|D_t - D_\infty|$ vs time, values of k_{obs} were calculated for each run.

Since the alkylchromium(III) was the limiting reagent, eq 45 is consistent with a rate law of the form where $[\text{CrR}^{2+}]_{\text{tot}}$ is the reactant

$$\frac{-d}{dt} \{ [\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e \} = k_{\text{obs}} \{ [\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e \} \quad (46)$$

concentration at time t and $[\text{CrR}^{2+}]_{\text{tot}}^e$ is its equilibrium concentration. The quantity $-d/dt\{[\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e\}$ is commonly referred

to as the rate of approach to equilibrium. It can be shown⁴⁹ that the observed rate constant for an approach to equilibrium is the sum of the forward and reverse rate constants. The values of this observed rate constant, k_{obs} , for both $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} at different thiocyanate concentrations are listed in Tables XX and XXI respectively. The observed rate constant is not a simple function of the thiocyanate concentration. The order in thiocyanate varied from zero at low thiocyanate to approximately one at intermediate concentrations and then fell to zero again in the limit of high thiocyanate.

To reduce the complexity of this equilibrium system it proved useful to separate the observed rate constant into its two component parts, the forward rate constant k_f and the reverse rate constant k_r . These individual rate constants could then be analyzed separately to obtain the form of the rate law.

For an equilibrium system for which the equilibrium constant is known, the forward rate constant, k_f , can be obtained from the observed rate by eq 47. Likewise the reverse rate constant, k_r , also can be

$$k_f = k_{\text{obs}} / [1 + (K[\text{NCS}^-])^{-1}] \quad (47)$$

obtained using eq 48. Eq 47 and 48 are true regardless of mechanism

$$k_r = k_{\text{obs}} / [(1 + K[\text{NCS}^-])] \quad (48)$$

or complexity of the rate law. These derived rate constants, k_f and k_r , were calculated in the present system with the following results.

Table XX
 Rate Constants ($\text{sec}^{-1} \times 10^2$)
 for the Reaction of $\text{CrCH}_2\text{Cl}^{2+}$ with SCN^{-} ^a

$[\text{H}^+]^b$	$[\text{SCN}]^b$	k_{obs}	k_f	k_r	k_{calc}^c	deviation ^d
2.00	8.00	9.25	8.33	0.92	9.08	1.8
2.00	7.68	8.25	7.41	0.58	8.93	8.2
2.00	6.40	8.35	7.35	1.00	8.26	1.0
2.00	6.00	7.47	6.54	0.93	8.00	7.1
2.31	5.00	7.19	6.13	1.06	7.35	2.2
2.00	4.00	6.43	5.29	1.14	6.57	2.2
2.31	3.20	6.36	5.00	1.36	5.86	7.9
2.00	2.00	4.68	3.27	1.41	4.61	1.5
2.00	1.60	4.46	2.90	1.56	4.11	7.8
2.00	1.00	3.28	1.76	1.52	3.31	0.9
2.00	0.800	2.90	1.40	1.50	3.01	3.3
5.00	1.00	3.23	1.73	1.50	3.31	2.5
9.00	1.00	3.04	1.63	1.41	3.31	8.9

^a $\mu = 1.0$ M maintained with LiClO_4 ; $[\text{SCN}^-]_0 \geq 10 [\text{CrCHCl}_2^{2+}]$. ^b $M \times 10$.

^cCalculated from parameters in Table XXII. ^dPer cent.

Table XXI
 Rate Constants ($\text{sec}^{-1} \times 10^2$)
 for the Reaction of CrCHCl_2^{2+} with SCN^{-} ^a

$[\text{H}^+]^b$	$[\text{SCN}]^b$	k_{obs}	k_f	k_r	k_{calc}^c	deviation ^d
2.00	7.50	2.52	2.30	0.224	2.55	1.1
2.00	6.00	2.40	2.14	0.260	2.33	2.9
2.00	5.00	2.28	1.99	0.290	2.15	5.7
2.00	4.00	1.76	1.49	0.272	1.93	9.7
2.00	4.00	1.91	1.62	0.290	1.93	1.0
2.00	2.00	1.43	1.05	0.380	1.36	4.9
2.00	1.50	1.20	0.807	0.393	1.19	0.8
2.00	1.00	0.969	0.560	0.409	0.985	1.7

^a $\mu = 1.0 \text{ M}$ maintained with LiClO_4 ; $[\text{SCN}^-]_0 \geq 10 [\text{CrCHCl}_2^{2+}]$. ^b $\text{M} \times 10$.

^c Calculated from parameters in Table XXII. ^d Per cent.

The forward rate constant was analyzed first. The order in thiocyanate was not constant but varied between 1.0 and zero. This suggests a form shown in eq 49. A test of this form would be a plot

$$k_f = \frac{A[\text{NCS}^-]}{1 + C[\text{NCS}^-]} \quad (49)$$

of $(k_f)^{-1}$ vs $[\text{SCN}^-]^{-1}$ which should be a straight line with a slope of $(A)^{-1}$ and intercept of (C/A) . The appropriate plots for the $\text{CrCH}_2\text{Cl}^{2+} \text{--SCN}^-$ system and the $\text{CrCHCl}_2^{2+} \text{--SCN}^-$ system are shown in Figures 18 and 19. The plots give good straight lines.

By dividing eq 47 by eq 48, eq 50 can be derived. Since

$$\frac{k_f}{k_r} = K[\text{SCN}^-] \quad (50)$$

$k_f = A[\text{SCN}^-]/[1 + C[\text{SCN}^-]]$, it can be shown using eq 50 that k_r must necessarily have a form shown in eq 51 where $B = (A/K)$. To test

$$k_r = \frac{B}{1 + C[\text{SCN}^-]} \quad (51)$$

this hypothesis, $(k_r)^{-1}$ was plotted as a function of $[\text{SCN}^-]$. This should give a straight line with a slope of (C/B) and an intercept of B^{-1} . Figures 20 and 21 show these plots.

By examining eq 49 and 51 one can establish that they are not independent. The quantity C is common to both equations. Original

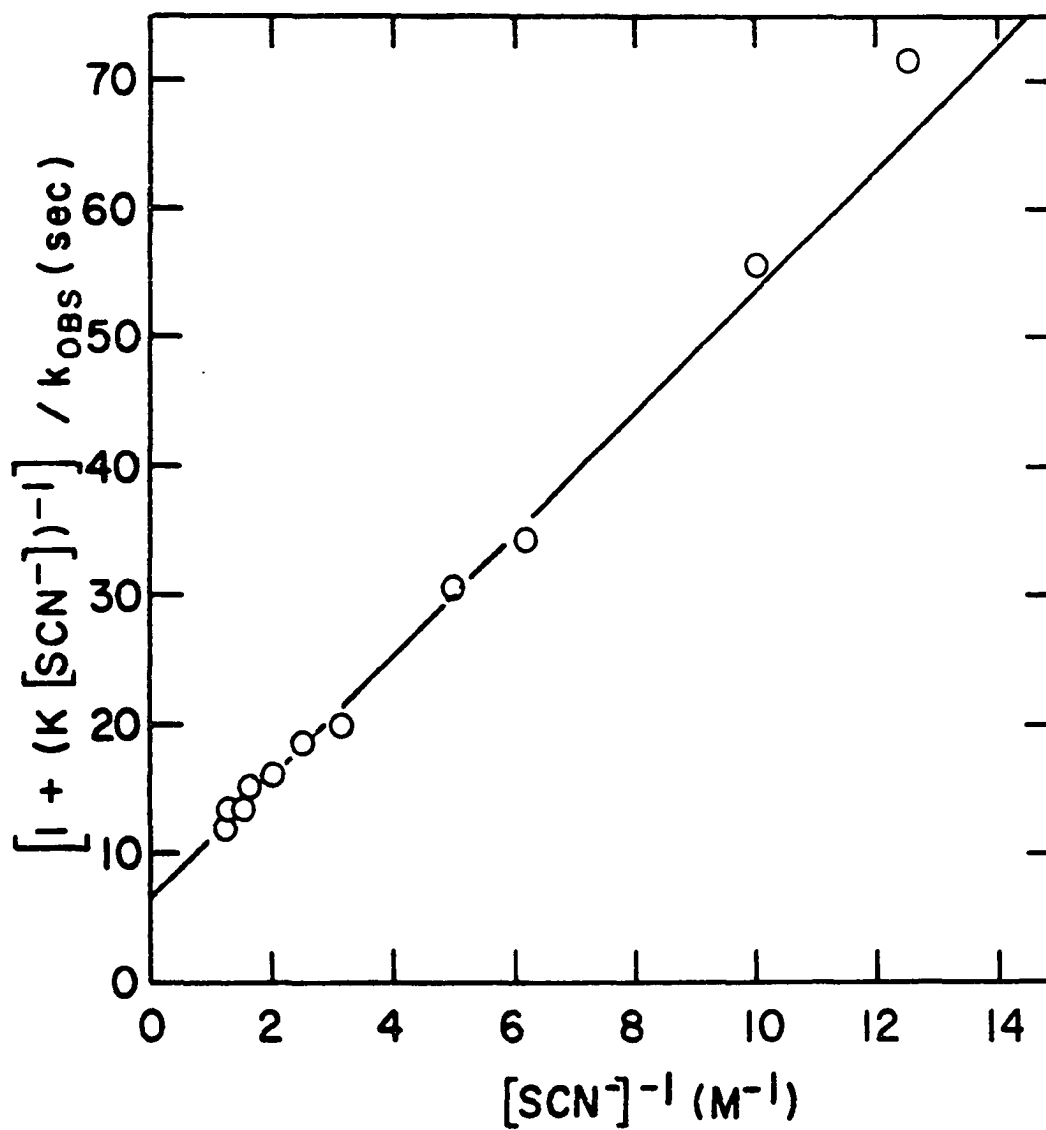


Figure 18. $-\text{CrCH}_2\text{Cl}^{2+}$ kinetic data for the apparent forward reaction plotted to test eq 49.

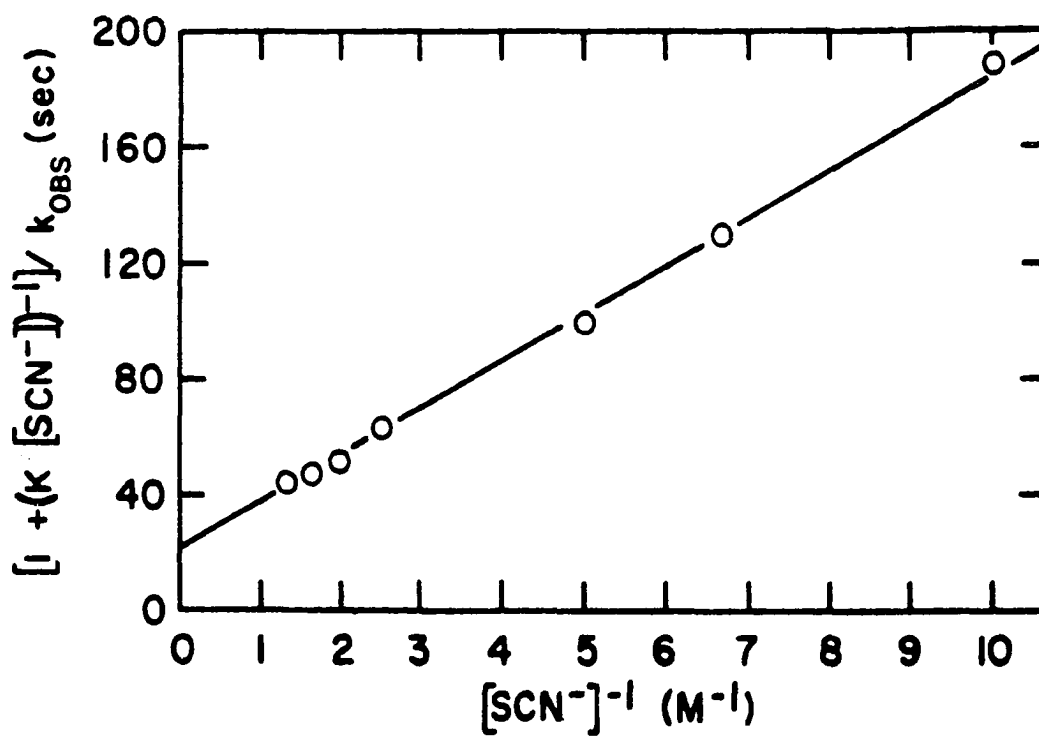


Figure 19.— CrCHCl_2^{2+} kinetic data for the apparent forward reaction plotted to test eq 49.

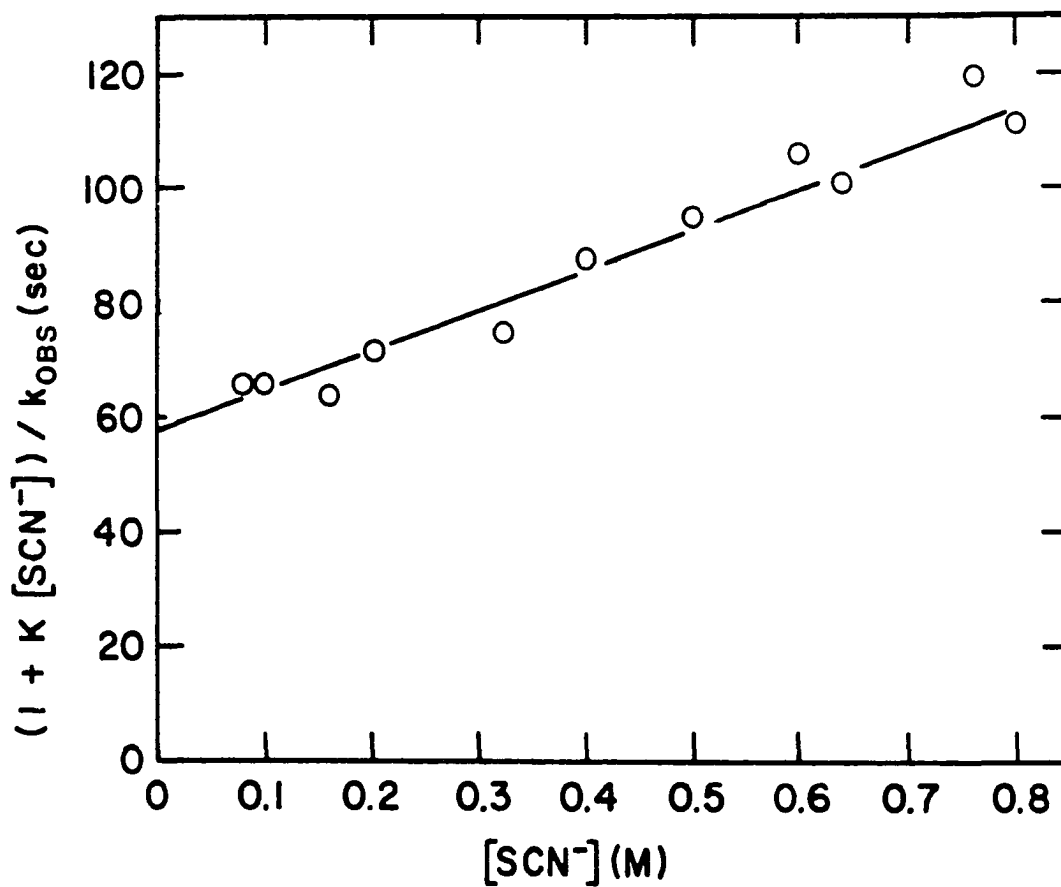


Figure 20.— $\text{CrCH}_2\text{Cl}^{2+}$ kinetic data for the apparent reverse reaction plotted to test eq 51.

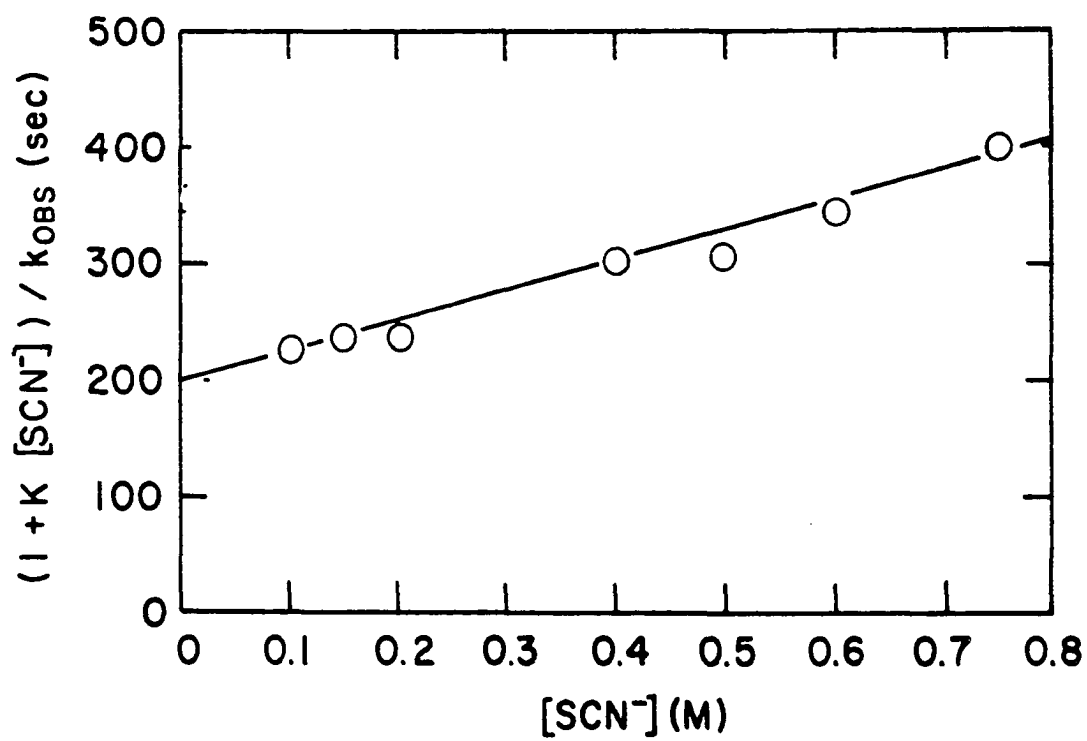


Figure 21. —CrCHCl₂²⁺ kinetic data for the apparent reverse reaction plotted to test eq 51.

plots of the type shown in Figures 18 and 20 gave slightly different values for C for the $\text{CrCH}_2\text{Cl}^{2+}\text{--SCN}^-$ system (1.30 M^{-1} in eq 49 and 1.15 M^{-1} in eq 51). To obtain the best fit of the data eq 49 and 51 were combined to give eq 52. The observed rate constants for both

$$k_{\text{obs}} = k_f + k_r = \frac{A[\text{SCN}^-] + B}{1 + C[\text{SCN}^-]} \quad (52)$$

$\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} systems were fitted to eq 18 to obtain the best fit of the data with the ratio (A/B) held constant at 11.6 M^{-1} . The values for A, B, and C for the two systems are given in Table XXII. The lines in Figures 18, 19, 20 and 21 are drawn according to these values. The calculated rate constants using these parameters are given in the respective tables of observed rate constants. The average percent deviations between calculated and observed rate constants were 4.0 ($\text{CrCH}_2\text{Cl}^{2+}$) and 3.5 (CrCHCl_2^{2+}).

Kinetic Runs at Low Thiocyanate.—After the rate law had been determined, studies were attempted at low thiocyanate to extend the concentration range of the excess reagent. The results are listed in Table XXIII. These runs begin to deviate significantly from eq 18, the rates being lower than expected. Although no definite explanation can be made of this deviation, two sources of error seem possible. The decomposition of products which was insignificant at higher concentrations where the rate was relatively high may become important at low thiocyanate. If the mechanism involves a steady-state intermediate, low thiocyanate may lead to a build-up of intermediate leading to progressively poorer kinetics.

Table XXII

Rate Constants for the
Reaction of CrR^{2+} with SCN^{-} ^a

	$\text{CrCH}_2\text{Cl}^{2+}$ ^b	CrCHCl_2^{2+} ^c
A	$0.198 \text{ sec}^{-1} \text{ M}^{-1}$	$0.0610 \text{ sec}^{-1} \text{ M}^{-1}$
B	0.0171 sec^{-1}	0.00504 sec^{-1}
C	1.17 M^{-1}	1.31 M^{-1}

^aObtained from a least-squares fit of eq 20 with data obtained with $[\text{SCN}^{-}] \geq 0.08 \text{ M}$. ^bAverage deviation is 4.5% considering data used in least-squares determination. ^cAverage deviation is 3.5% considering data used in least-squares determination.

Table XXIII
Kinetic Runs at Low Thiocyanate^a

Complex	[H ⁺] M x 10	[SCN ⁻] M x 10 ²	k _{obs} sec ⁻¹ x 10 ²
CrCH ₂ Cl ²⁺	2.00	6.00	2.40
	2.00	4.00	2.10
	2.00	2.00	1.73
	2.00	1.60	1.55
	2.00	1.50	1.54
	2.00	1.00	1.40
	2.00	0.600	1.16
	2.00	0.500	1.23
	2.00	0.400	1.18
	2.00	0.200	1.19
	2.00	0.200 ^b	1.22
	2.00	0.100 ^b	1.10
CrCHCl ₂ ²⁺	2.00	5.00	0.510
	2.00	2.50	0.339
	2.00	1.00	0.278

^aμ = 1.0 M maintained with LiClO₄. ^bDilution experiment.

Two of the rate constants reported in Table XXIII were obtained by diluting an equilibrium mixture and observing the re-equilibration. The initial thiocyanate concentration was 0.188 M before the dilution to a lower value.

[H⁺] Dependence.—The [H⁺] was varied in three experiments while the [SCN⁻] was held constant at 0.1 M. The results are listed in Table XX and are plotted in Figure 22. The observed rate constants varied by only 6% when the [H⁺] was varied between 0.2 M and 0.9 M. Such a small variation is within experimental error considering the change in medium. The reaction can be considered essentially independent of [H⁺] within the acid range studied.

Effect of Cr²⁺.—Chromium(II) (prepared by the reduction of Cr³⁺ with zinc amalgam) was added to a reaction solution from which oxygen had been excluded by bubbling with a stream of nitrogen. No retardation of the rate was observed with concentrations of Cr²⁺ up to 0.01 M.

HF Reaction.—HF reacts with CrCH₂Cl²⁺ to form a fluoro substituted complex. However, in 0.2 M acid the equilibrium is unfavorable and high concentrations of HF are needed to form appreciable amounts of the product. This results in a peculiar situation. The predominant species in solution are HF, CrCH₂Cl²⁺, Cr(CH₂Cl)F⁺, and H⁺. The concentration of fluoride ion is very small (10⁻⁴ M) and can be neglected for any equilibrium measurements. However, the fluoride ion may very well be the reactive form so that it is important to either know the fluoride concentration or keep it constant

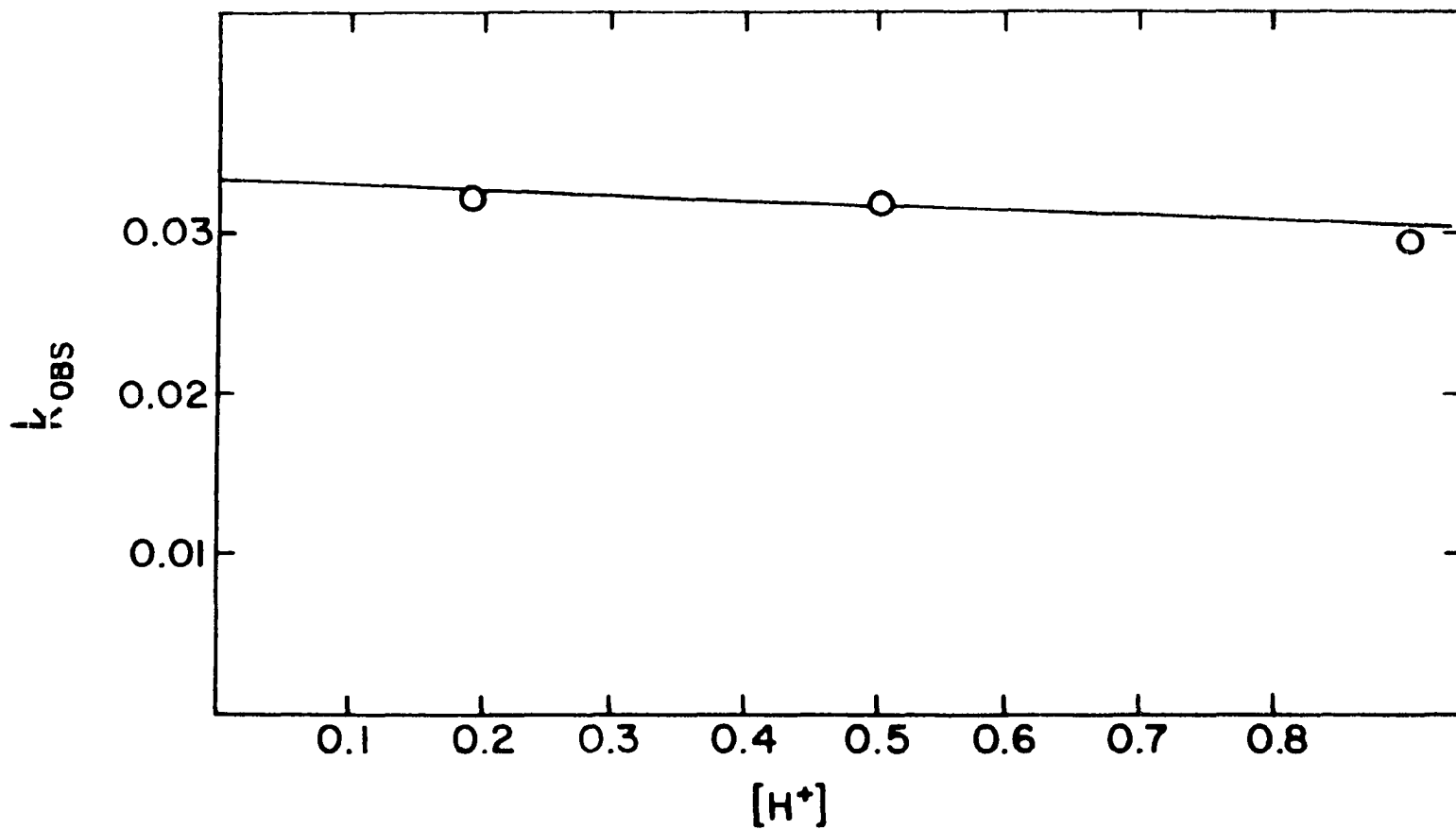
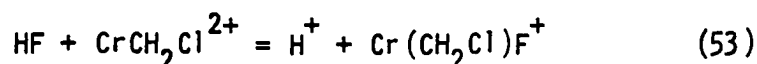


Figure 22. — k_{obs} of the reaction between $CrCH_2Cl^{2+}$ and SCN^- as a function of $[H^+]$.

relative to the HF concentration. For solutions containing high concentrations of HF a further equilibrium between HF and F^- to form HF_2^- is known to be important ($K = 3.9 M^{-1}$ at 0.53 M ionic strength).⁵⁰ Presuming that HF_2^- has a different reactivity than F^- , this equilibrium would be reflected in the rate of anation of $CrCH_2Cl^{2+}$. Since the rate law for anation is expected to exhibit complicated kinetics anyway, we felt that any attempts to characterize the mechanism with this added equilibrium were ambiguous at best and more probably impossible.

Therefore, only a very limited number of kinetic runs were done and no attempt was made to analyze the kinetic data.

The equilibrium constant was obtained from the data listed in Table XXIV. For reasons cited above the data should give a good equilibrium constant for the reaction. The least-squares fit of the



ΔD_s to eq 43 for the reaction of HF with $CrCH_2Cl^{2+}$ gave $K = 0.32$ and $\Delta \epsilon_o = 56.8 M^{-1} cm^{-1}$ with $[H^+]$ kept constant at 0.2 M. The calculated ΔD_s using these parameters were in good agreement with the observed values with an average deviation of 2%.

Table XXIV
Kinetic and Equilibrium Results of the
Reaction of Monochlorochromium(III) with Hydrofluoric Acid^a

[HF] M x 10	[CrCH ₂ Cl ²⁺] M x 10 ³	ΔD_k exp ^b	calc ^c	k_{obs} sec ⁻¹ x 10 ²
2.00	2.33	0.244	0.249	1.19
4.00	2.33	0.411	0.402	1.60
5.75	2.33	0.473	0.494	1.79
8.00	2.33	0.580	0.581	2.27
3.81	2.33	0.382	0.390	1.71

^a $\mu = 1.0$ M maintained with LiClO₄; [HClO₄] = 0.2 M. ^b $l = 5$ cm; $\lambda = 350.7$ nm. ^c Calculated using parameters given in text; average deviation is 2%.

DISCUSSION

The stoichiometry studies with methanol tend to confirm that $\text{CrCH}_2\text{Cl}^{2+}$ reacts with methanol to form a 1:1 complex. It is perhaps appropriate to comment at this time on the shape of the curve in Figure 14. The shape of the curve is a function of the rate constants shown in the reaction scheme on p 72. However individual rate constants or the equilibrium constant cannot be obtained from the data at hand owing to changes in activity of the ions as the solvent is changed from pure water to very concentrated solutions of methanol. Nevertheless, it may be worthwhile to point out that the shape of the curve is consistent with, if not proof of, the proposed reaction scheme. The scheme proposes that an equilibrium (reactions 1 and -1) is being saturated. Since \bar{n} is a function of the saturation of an equilibrium it would be expected to change rapidly initially as methanol is added but gradually become insensitive to further increases of methanol. Graphically, this is manifested in a "flattening out" of a plot of \bar{n} vs $[\text{CH}_3\text{OH}]$. This is the type of behavior exhibited in the $\text{CrCH}_2\text{Cl}^{2+} \text{ -- } \text{CH}_3\text{OH}$ system.

The question must be considered whether the existence of the species $\text{Cr}(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})(\text{CH}_2\text{Cl})^{2+}$ is sufficient evidence to suggest the existence of $\text{Cr}(\text{H}_2\text{O})_4(\text{SCN})(\text{CH}_2\text{Cl})^+$. It might be argued that the formation constants for the methanol complexes are such that although only one methanol coordinates to the chromium(III), the more strongly coordinating thiocyanate ligand will form the more highly substituted complexes. Although no direct evidence can be cited to refute this argument, the data of Jayne and King⁴⁷ tend to support the argument that the mono-substituted

complex is the result of kinetic control rather than thermodynamic control. They report that the equilibrium constant for the formation of the di-substituted methanol complex of Cr^{3+} in methanol-water solution is only a factor of 2 less than the equilibrium constant for the formation of the mono-substituted complex. Provided the same relative stability is true for Cr^{2+} -methanol complexes one would expect a large fraction of the complex to exist as the di-methanol product and higher complexes were all the positions of $\text{Cr}(\text{H}_2\text{O})_5\text{CH}_2\text{Cl}^{2+}$ subject to rapid substitution. At high mole fraction of methanol, this would result in an \bar{n} of greater than 2. The fact that \bar{n} does not exceed 2 suggests that the substitution product isolated is the result of only one coordination site on chromium(III) being labilized. If this analysis is correct, then on the time scale of this experiment, only one thiocyanate can coordinate to the metal regardless of the thermodynamic stability of the more highly substituted complexes.

The structure of the product has not been definitely established. It was not possible to obtain data which would give more structural information than the electronic spectrum. However, without evidence to the contrary the trans structure is the preferred configuration. The most compelling reason to suggest a trans structure is that only one coordination site on the chromium(III) is labilized. There is no reason that only one cis position should be labilized. One would expect all four positions to be labilized. To be sure, the second anation should be somewhat slower due to a coulombic effect but still experimentally observable. The fact that only one product is formed with only one ligand added

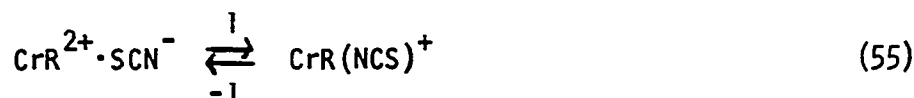
suggests that cis activation is not occurring. Moore, Basolo, and Pearson⁵¹ have used a similar argument to suggest trans activation in water exchange reactions of $\text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}$. In this example, one water exchanged much faster than the other four.

Since thiocyanate is an ambident ion, both S- and N- bonded structures are possible. Both thiocyanatopentaaquo-⁵² and isothiocyanatopentaaquochromium(III)⁵³ have been reported. The S- bonded structure has a maximum shifted to lower energy compared to hexaaquochromium(III) while the N- bonded complex has a maximum at higher energy than hexaaquochromium(III). The shift of the absorbance maximum to higher energy caused by the complexation of thiocyanate in the present system suggests that the most stable isomer of $\text{CrR}(\text{NCS})^+$ is N- bonded.

Kinetics and Mechanism.—The initial observation concerning the alkyl complexes is that they are extremely labile compared to other chromium(III) complexes. For example at 0.1 M SCN^- , $\text{CrCH}_2\text{Cl}^{2+}$ reacts 10^6 times faster than does $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The comparison can be made only at a given $[\text{SCN}^-]$ since the rate law for the anation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ has a different form.

The mechanism for the reactions of $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} cannot be unambiguously assigned. As stated in the introduction, any reaction which has an $[(A[\text{SCN}^-] + B)/(1 + C[\text{SCN}^-])]$ form of the rate law is subject to two alternate interpretations -- an ion pairing mechanism or a steady-state intermediate mechanism. Each of these mechanisms will be discussed in terms of the present reaction.

If one chooses to assign an ion pairing mechanism to the reaction of CrR^{2+} with SCN^- then eq 54 and 55 are the reaction scheme. The pseudo-

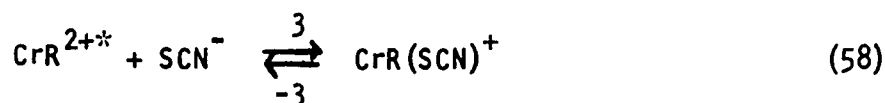
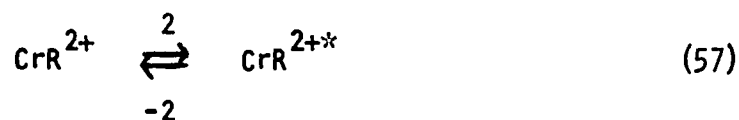


first-order rate constant for the approach to equilibrium would have a form shown in eq 56 (see Appendix for derivation).

$$k_{\text{obs}} = \frac{(k_1 + k_{-1})K_{1P}[\text{SCN}^-] + k_{-1}}{1 + K_{1P}[\text{SCN}^-]} \quad (56)$$

Equating the experimentally determined parameters, A, B and C, with the proper quantities in this mechanism one can calculate the values for k_1 , k_{-1} and K_{1P} for the $\text{CrCH}_2\text{Cl}^{2+}$ complex. The respective values are 0.181 sec^{-1} , 0.0171 sec^{-1} and 1.17 M^{-1} . The calculated values for CrCHCl_2^{2+} are 0.0560 sec^{-1} , 0.00504 sec^{-1} and 1.31 M^{-1} .

The alternate mechanism can be described by eq 57 and 58. In this



scheme, CrR^{2+*} represents a steady state intermediate whose structure is not known. The observed rate constant for the approach to equilibrium is given by eq 59 (see Appendix for derivation). From eq 59 and the

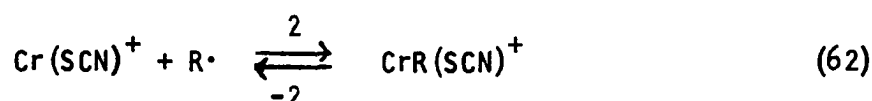
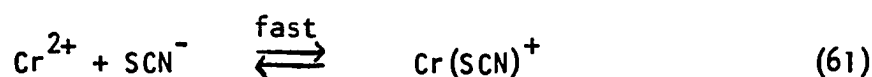
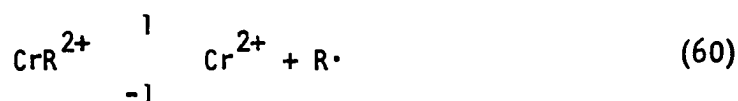
$$k_{\text{obs}} = \frac{k_{-3} + \frac{k_2 k_3}{k_{-2}} [\text{SCN}^-]}{1 + \frac{k_3}{k_{-2}} [\text{SCN}^-]} \quad (59)$$

experimental parameters, one can calculate values for the individual rate constants. For $\text{CrCH}_2\text{Cl}^{2+}$ the rate constants k_2 , k_{-3} and k_3/k_{-2} are 0.155 sec^{-1} , 0.0171 sec^{-1} and 1.17 M^{-1} . The rate constants for CrCHCl_2^{2+} in the same order are 0.0466 sec^{-1} , 0.00504 sec^{-1} and 1.31 M^{-1} .

The ion pairing mechanism is not unreasonable. The ion pairing constant for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with SCN^- has been determined to be 7 M^{-1} .⁵³ A seven-fold decrease in the ion pairing constant is consistent with the reduced charge on $\text{CrCH}_2\text{Cl}^{2+}$ or CrCHCl_2^{2+} . However, there is evidence to argue against this interpretation. The initial absorbance measured at 300 nm of a solution containing $\text{CrCH}_2\text{Cl}^{2+}$ and SCN^- is identical to a solution of $\text{CrCH}_2\text{Cl}^{2+}$ with no added SCN^- . This strongly suggests that no ion pairs are formed since the spectra of ion pairs are expected to differ significantly from the spectra of the ions themselves in the region 250 to 350 nm. The fact that $\Delta D_k = \Delta D_s$ also suggests no ion-pairing for the same reason.⁵⁴

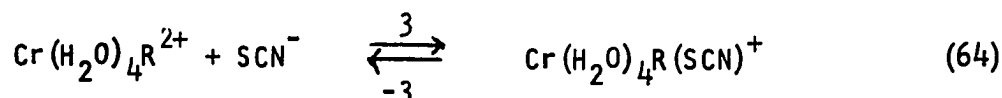
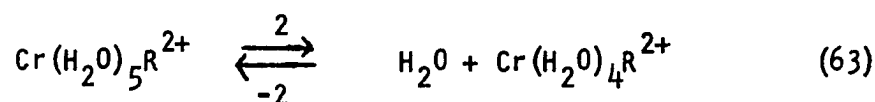
The steady-state mechanism requires that $\Delta D_s = \Delta D_k$ for all wavelengths. In this respect the steady-state mechanism better correlates with the data. The following discussion will be based on a steady-state interpretation. However, the possibility of an ion pairing mechanism cannot be definitely eliminated.

Due to the special nature of alkylchromium(III) complexes a steady-state intermediate cannot automatically be described as a five-coordinate intermediate in a D mechanism. As mentioned previously, Swaddle has found a Cr^{2+} intermediate in the aquation of pyridiomethylchromium(III). If such a dissociation were occurring in the present system one could visualize a reaction scheme illustrated by eq 60, 61 and 62. The addi-



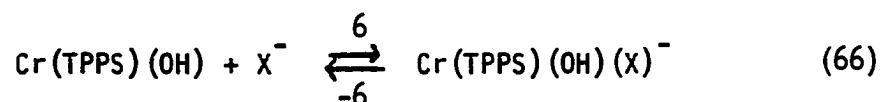
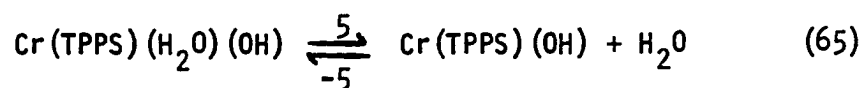
tion of Cr^{2+} to a reaction solution should increase the rate of reaction -1. This would retard the overall anation reaction. Since added Cr^{2+} was found to have no effect, a mechanism involving free Cr^{2+} can be eliminated.

The D mechanism is the only other plausible alternative. The D mechanism for the $\text{CrR}^{2+} \text{--} \text{SCN}^-$ system is shown in eq 63 and 64. The



coordinated water has been included to illustrate the dissociative nature

of the reaction scheme. Five coordinate intermediates in chromium(III) reactions are not without precedent. King⁴⁸ has shown that $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ is a reactive intermediate in mercury(II)-induced aquation of halochromium(III) complexes. More recently, Fleischer⁵⁵ has postulated that the chromium(III) salt of tetra(p-sulfonatophenyl)porphine (TPPS) anates via a five coordinate intermediate (eq 65 and 66). This chromium(III) complex



is similar to CrR^{2+} in that the anation reactions are faster than "normal" chromium(III) reactions. However, there are differences.

$\text{Cr}(\text{TPPS})(\text{H}_2\text{O})(\text{OH})$ does not exhibit D type behavior. The anation rate is first order in chromium complex and first order in entering ligand up to the highest ligand concentration studied. Fleischer attributes this to the higher reactivity of the intermediate toward water than toward thiocyanate. Hence, the apparent forward rate constant for anation of $\text{Cr}(\text{TPPS})(\text{H}_2\text{O})(\text{OH})$ would be $k_5 k_6 / k_{-5}$.

In the present system, the intermediate does not discriminate to such an extent. In fact, the ratio of k_3/k_{-2} shows that in aqueous solution, the probability of a water or a thiocyanate entering is about equal for both $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} at 1 M $[\text{SCN}^-]$. This difference in reactivity of the intermediates in the two systems may in part be due to the reduced charge of the porphine complex which would cause the porphine complex to

have a smaller affinity for SCN^- than CrR^{2+} .

Although five coordinate chromium(III) has been observed in other systems, a D rate law has not been reported for other chromium(III) complexes. Apparently, the alkyl ligand is quite effective in weakening the trans ligand-metal bond through a σ -type trans effect. The rate constants of $\text{CrCH}_2\text{Cl}^{2+}$ and CrCHCl_2^{2+} are consistent with this view. The addition of an electron withdrawing group (Cl^-) lowers the rate of approach to equilibrium. It is interesting to note that each rate constant k_2 , k_{-2} , k_3 , k_{-3} is decreased by approximately the same percentage going from $\text{CrCH}_2\text{Cl}^{2+}$ to CrCHCl_2^{2+} . This indicates that the labilization process to a first approximation is independent of the ligand in the labilized position.

If CrR^{2+} reacts via a D mechanism, then k_2 should be independent of the entering ligand. Unfortunately, in acid solution, the number of available ligands is rather limited. No reaction was observed with Cl^- , Br^- , or I^- . (A result not unexpected considering the SCN^- reaction has an equilibrium constant of only 11.6 M^{-1}). HF does react but kinetic analysis is not possible. Thus, we have been unable to demonstrate that k_2 is the same regardless of entering ligand. Until such time that a confirmation is forthcoming (perhaps by measurement of the water exchange rate), the possibility exists that the reaction occurs via an ion pairing mechanism.

PART III. KINETIC STUDIES OF THE FORMATION OF A CYANIDE
BRIDGED ADDUCT OF TWO CATIONIC METAL COMPLEXES

This work has been previously published. The reader is referred
to Reference 56.

ACKNOWLEDGEMENTS

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APPENDIX

For the following derivations, these symbols will be used:

$[]^o$ = initial concentration

$[]^e$ = concentration at equilibrium

$$[\text{CrR}^{2+}]_{\text{tot}} = [\text{CrR}^{2+}] + [\text{CrR}^{2+} \cdot \text{SCN}^-]$$

I. The Ion-Pairing Mechanism (eq 54 - 55)

Equation 56 in the text can be derived in the following manner.

$$\frac{d[\text{CrR}(\text{NCS})^+]}{dt} = - \frac{d[\text{CrR}^{2+}]_{\text{tot}}}{dt} = k_1[\text{CrR}^{2+} \cdot \text{SCN}^-] - k_{-1}[\text{CrR}(\text{NCS})^+] \quad (67)$$

Since

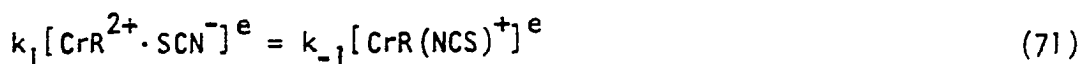
$$[\text{CrR}^{2+} \cdot \text{SCN}^-] = \frac{K_{\text{IP}}[\text{SCN}^-]}{1 + K_{\text{IP}}[\text{SCN}^-]} [\text{CrR}^{2+}]_{\text{tot}} \quad (68)$$

and

$$[\text{CrR}(\text{NCS})^+] = [\text{CrR}^{2+}]_{\text{tot}}^o - [\text{CrR}^{2+}]_{\text{tot}}, \quad (69)$$

$$- \frac{d[\text{CrR}^{2+}]_{\text{tot}}}{dt} = \left(\frac{k_1 K_{\text{IP}}[\text{SCN}^-]}{1 + K_{\text{IP}}[\text{SCN}^-]} + k_{-1} \right) [\text{CrR}^{2+}]_{\text{tot}} - k_{-1} [\text{CrR}^{2+}]_{\text{tot}}^o. \quad (70)$$

At equilibrium



$$\frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} [\text{CrR}^{2+}]_{\text{tot}}^e = k_{-1} [\text{CrR}(\text{NCS})^+]^e \quad (72)$$

By eq 69 and 70

$$\left(\frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} \right) [\text{CrR}^{2+}]_{\text{tot}}^e = k_{-1} \{ [\text{CrR}^{2+}]_{\text{tot}}^o - [\text{CrR}^{2+}]_{\text{tot}}^e \} \quad (73)$$

Rearranging

$$[\text{CrR}^{2+}]_{\text{tot}}^o = \left[\frac{\left(\frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} + k_{-1} \right)}{k_{-1}} \right] [\text{CrR}^{2+}]_{\text{tot}}^e \quad (74)$$

Substituting this result in eq 70 and collecting terms

$$-\frac{d[\text{CrR}^{2+}]_{\text{tot}}}{dt} = \left(\frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} + k_{-1} \right) \{ [\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e \} \quad (75)$$

Since $[\text{CrR}^{2+}]_{\text{tot}}^e$ is a constant,

$$-\frac{d[\text{CrR}^{2+}]_{\text{tot}}^e}{dt} = 0 \quad (76)$$

Adding eq 75 and 76

$$-\frac{d}{dt} \{ [\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e \} = \left\{ \frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} + k_{-1} \right\} \{ [\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e \} \quad (77)$$

Integration of eq 77 gives eq 78

$$\ln \{ [\text{CrR}^{2+}]_{\text{tot}} - [\text{CrR}^{2+}]_{\text{tot}}^e \} = \ln \{ [\text{CrR}^{2+}]_{\text{tot}}^o - [\text{CrR}^{2+}]_{\text{tot}}^e \} - \left(\frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} + k_{-1} \right) t \quad (78)$$

Eq 78 is identical to eq 46 in the text which defines k_{obs} . Therefore one can equate corresponding coefficients,

$$k_{\text{obs}} = \left(\frac{k_1 K_{\text{IP}} [\text{SCN}^-]}{1 + K_{\text{IP}} [\text{SCN}^-]} + k_{-1} \right) \quad (79)$$

by obtaining a common denominator, eq 56 follows directly from eq 79.

II. The Steady State Mechanism (eq 57 - 58)

By definition of steady-state

$$\frac{d[\text{CrR}^{2+\ddagger}]}{dt} = 0 = k_2 [\text{CrR}^{2+}] + k_{-3} [\text{CrR}(\text{NCS})^{\ddagger}] - k_{-2} [\text{CrR}^{2+\ddagger}]_{\text{ss}} - k_3 [\text{SCN}^-] [\text{CrR}^{2+\ddagger}]_{\text{ss}} \quad (80)$$

$$\therefore [\text{CrR}^{2+*}]_{ss} = \frac{k_2[\text{CrR}^{2+}] + k_{-3}[\text{CrR}(\text{NCS})^+]}{k_{-2} + k_3[\text{SCN}^-]} \quad (81)$$

Since

$$\frac{d[\text{CrR}(\text{SCN})^+]}{dt} = k_3[\text{SCN}^-][\text{CrR}^{2+*}] - k_{-3}[\text{CrR}(\text{SCN})^+] \quad (82)$$

then

$$\frac{d[\text{CrR}(\text{SCN})^+]}{dt} = k_3[\text{SCN}^-] \left[\frac{k_2[\text{CrR}^{2+}] + k_{-3}[\text{CrR}(\text{NCS})^+]}{k_{-2} + k_3[\text{SCN}^-]} \right] - k_{-3}[\text{CrR}(\text{SCN})^+] \quad (83)$$

Multiplying through and putting both over a common denominator

$$\frac{d[\text{CrR}(\text{SCN})^+]}{dt} = \frac{k_2k_3[\text{SCN}^0] - k_{-2}k_{-3}[\text{CrR}(\text{NCS})^+]}{k_{-2} + k_3[\text{SCN}^-]} \quad (84)$$

Using eq 85 and 86 and identical techniques used in 8-10 one can obtain eq 87.

$$[\text{CrR}(\text{NCS})^+] = [\text{CrR}^{2+}]^0 - [\text{CrR}^{2+}] \quad (85)$$

$$\left(\frac{k_2k_3[\text{SCN}^-]}{k_{-2} + k_3[\text{SCN}^-]} \right) [\text{CrR}^{2+}]^e = \left(\frac{k_{-2}k_{-3}}{k_{-2} + k_3[\text{SCN}^-]} \right) [\text{CrR}(\text{NCS})^+]^e \quad (86)$$

$$-\frac{d\{[\text{CrR}^{2+}] - [\text{CrR}^{2+}]_e\}}{dt} = \left(\frac{k_2 k_3 [\text{SCN}^-] + k_{-2} k_{-3}}{k_{-2} + k_3 [\text{SCN}^-]} \right) \{[\text{CrR}^{2+}] - [\text{CrR}^{2+}]_e\} . \quad (87)$$

Integration of eq 87 yields eq 88 identical in form to eq 46.

$$\ln\{[\text{CrR}^{2+}] - [\text{CrR}^{2+}]_e\} = \ln\{[\text{CrR}^{2+}]^o - [\text{CrR}^{2+}]_e\} - \left(\frac{k_2 k_3 [\text{SCN}^-] + k_{-2} k_{-3}}{k_{-2} + k_3 [\text{SCN}^-]} \right) t . \quad (88)$$

Therefore one can equate corresponding coefficients and obtain eq 89 which is equivalent to eq 59 in the text.

$$k_{\text{obs}} = \left(\frac{k_2 k_3 [\text{SCN}^-] + k_{-2} k_{-3}}{k_{-2} + k_3 [\text{SCN}^-]} \right) \quad (89)$$