$(CH_3)_4Pb$ by literature procedures. Anal. Calcd for $C_2H_6PbN_2O_6$: C, 6.65; H, 1.66; N, 7.76; Pb, 57.34; NO_3^-, 34.35. Found: C, 6.66; H, 1.66; N, 6.02; Pb, 57.48; NO_3^-, 34.65. Anal. Calcd for C_3H_9PbCl: C, 12.52; H, 3.13; Pb, 72.01. Found: C, 12.64; H, 3.15; Pb, 72.85.

Determination of Pb^{2+} and NO_3^-. Pb^{2+} was determined by EDTA titration[27] or atomic absorption spectrometry (Techtron AA5 Spectrometer, Varian Corp.) and NO_3^- by gravimetry.[28]

Spectrophotometric Titrations. Titrations were performed anaerobically in 1-cm quartz cells. Typically 10^{-4} M solutions of $(CH_3)_2Co(chel)$ were titrated with standard solutions of Pb^{2+}, $(CH_3)_3PbCl$, or $(CH_3)_2Pb(NO_3)_2$ by following the absorbance decrease at 442 nm for $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ or at 405 nm for $(CH_3)_2Co((1-)N_4)$. The overall reactions were titrated by injecting small volumes of the electrophile from a 1-μL syring directly into the cuvette containing a known amount of the organocobalt complex solution. Within several minutes, absorbances decreased to a constant value, and more titrant was added. Attempts to observe the first step of the biphasic reactions of Pb^{2+} and $(CH_3)_2Pb(NO_3)_2$ failed although titrant additions were separated by only 10s.

^{1}H NMR Titrations. All titrations were performed anaerobically in 5-mm NMR tubes. In a typical experiment a 0.50 mL aliquot of a 0.030 M solution of $(CH_3)_2Co(chel)$ in CH_3CN-d_3 was titrated with standard electrophile solutions from a 100-μL syringe. ^{1}H NMR

studies were done after cooling the titrant to -40 °C by means of a dry ice–*o*-xylene–*m*-xylene slush.

GLC Studies. Anaerobic solutions of $(CH_3)_2Co(chel)$ (4×10^{-3} M) were placed in 50-mL Hypo vials that were sealed with serum caps. An appropriate amount of a standardized electrophile solution was added, and the evolved CH_4 and $(CH_3)_4Pb$ were sampled with a gastight syringe and determined by GLC.

Determination of Pb. $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ (13.67 mg, 0.301 mmol) was dissolved in 5.00 mL of CH_3CN in a Hypo vial. The vial was sealed with a serum cap and purged with nitrogen before 34 μL of a 0.220 M Pb^{2+} solution was added. After completion of the reaction, the solution was filtered through a 0.40 μm polycarbonate membrane. The resulting black solid was washed with CH_3CN and air-dried. The solid was placed in a glass capillary, and its X-ray diffraction pattern was obtained. A similar experiment with $(CH_3)_2Co((1-)N_4)$ also gave a black solid. Both solids were identified as Pb^0 on the bases of their X-ray diffraction patterns.

Nephelometric Titration. Solutions of $(CH_3)_2Co(chel)$ (10^{-4} M) were titrated with small aliquots of 0.220 M Pb^{2+}. Changes in solution scattering were monitored during titration by Pb^{2+} by irradiating the solutions at 500 nm and measuring scattered light at the same wavelength.

Registry No. $(CH_3)_2Co((1-)N_4)$, 33569-60-7; $[(CH_3)_2Co(N_4)]$-ClO_4, 77310-45-3; Pb^{2+}, 14280-50-3; $(CH_3)_2Pb(NO_3)_2$, 39152-70-0; $(CH_3)_3PbCl$, 1520-78-1; $(CH_3)_4Pb$, 75-74-1.

(27) Flaschka, H. A. "EDTA Titrations, An Introduction to Theory and Practice"; Pergamon Press: New York, 1964; pp 79–86.
(28) Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis including Elementary Instrumental Analysis", 3rd ed.; Longman Group Ltd.: London, England, 1961; pp 583–584.

Contribution from Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Electronic Effects and Trans Substitution in Octahedral Complexes of Chromium(III)
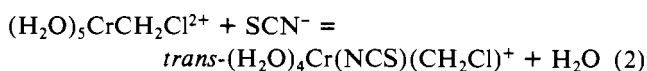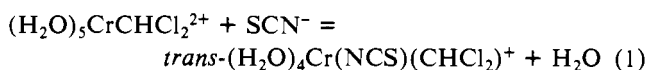
ANDREJA BAKAČ,* JAMES H. ESPENSON,* and LESLIE P. MILLER†

Kinetics and equilibrium data were determined for the formation of 1:1 adducts of NCS^- with four complexes of the general formula $(H_2O)_5CrR^{2+}$ (R = CH_2OH, CH_2OCH_3, CH_2CN, and $CH(CH_3)_2$). The kinetic data for the approach to equilibrium follow the rate law $k_{obsd} = (A[SCN^-] + B)/(1 + C[SCN^-])$ and are consistent with both a limiting S_N1 (or D) and a dissociative ion-pairing (I_D) mechanism. The rate constants of the trans-water exchange in these and two previously studied complexes of the same general type (R = $CHCl_2$ and CH_2Cl) were approximated as a ratio A/C. The correlation of these rate constants and ones for the trans-water exchange in complexes $Cr(H_2O)_5X^{2+}$ (X = I^-, Cl^-, and SCN^-) with the electron-donating ability of the labilizing groups R and X as measured by a Hammett substituent constant was examined. The same correlation was obtained for a limited number of available rate constants for the Cr–NCS bond breaking in the adducts *trans*-Cr-$(H_2O)_4R(NCS)^+$, indicating that the trans-labilizing ability of group R does not depend on the nature of the leaving group. The complex $(H_2O)_5CrCH(CH_3)_2^{2+}$ reacts with SCN^- more slowly than predicted by this correlation.

Introduction

The position trans to the alkyl group in some (halomethyl)pentaaquochromium(III) complexes is by several orders of magnitude kinetically more labile than the same position in the corresponding inorganic complexes of chromium(III).[1] Substitution of one water molecule in $(H_2O)_5CrCHCl_2^{2+}$ and $(H_2O)_5CrCH_2Cl^{2+}$ by thiocyanate ions (eq 1 and 2) occurs on the same time scale of several minutes

$(H_2O)_5CrCHCl_2^{2+} + SCN^- =$
$$\textit{trans-}(H_2O)_4Cr(NCS)(CHCl_2)^+ + H_2O \quad (1)$$

$(H_2O)_5CrCH_2Cl^{2+} + SCN^- =$
$$\textit{trans-}(H_2O)_4Cr(NCS)(CH_2Cl)^+ + H_2O \quad (2)$$

rather than hours or days normally seen for the complexes of the general formula $(H_2O)_5CrX^{2+}$. Another report[2] gives

much higher rate constant for reaction 2. We return to this discrepancy later in the paper.

Malik et al.[3] reported a rapid substitution of the fluoride ion into the coordination sphere of $(H_2O)_5CrCF_3^{2+}$. The product of this reaction, $(H_2O)_4CrF(CF_3)^+$, undergoes a Cr–C bond cleavage more rapidly than the parent pentaaquo complex. The complexes *trans*-Cr$(H_2O)_4(NCS)(CHCl_2)^+$ and *trans*-$(H_2O)_4Cr(NCS)(CH_2Cl)^+$, the products of reactions 1 and 2, also decompose by Cr–C bond-cleavage reactions more rapidly than do the parent complexes. The acceleration by anions of the Cr–C bond cleavage in the benzylpentaaquochromium(III) cation is most likely also brought about by a rapid substitution of the anions into its coordination sphere.[4]

The studies of the kinetics and mechanisms of the oxidation of α-hydroxyalkyl complexes of chromium(III)[5–7] suggested

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(1) Bushey, W. R.; Espenson, J. H. *Inorg. Chem.* **1977**, *16*, 2772.
(2) Azran, J.; Cohen, H.; Meyerstein, D. *J. Coord. Chem.* **1977**, *6*, 249.
(3) Malik, S. K.; Schmidt, W.; Spreer, L. D. *Inorg. Chem.* **1974**, *13*, 2986.
(4) Kochi, J. K.; Buchanan, D. *J. Am. Chem. Soc.* **1965**, *87*, 853.

that these organochromium complexes might be even more substitutionally labile than the ones previously reported. We therefore decided to investigate the effect(s) of the organic groups R on the rate of ligand substitution in the complexes $Cr(H_2O)_5R^{2+}$. For this purpose we studied the kinetics of substitution of four complexes (R = CH_2OH, CH_2OCH_3, $CH(CH_3)_2$, and CH_2CN) by the thiocyanate ion.

Experimental Section

Materials. The organochromium complexes were prepared according to published procedures. (Methoxymethyl)chromium(2+),[6] (hydroxymethyl)chromium(2+),[6,8] and (cyanomethyl)chromium(2+)[9] complexes were prepared by a modified Fenton's reaction using dimethyl ether, methanol, and acetonitrile as the organic substrates, respectively. (2-Propyl)chromium(2+) was made in the reaction of Cr^{2+} with 2,3-dimethyl-2-butyl hydroperoxide.[10] All the complexes except $(H_2O)_5CrCH_2OH^{2+}$ were purified by ion-exchange chromatography (Dowex 50W-X8). $(H_2O)_5CrCH_2OH^{2+}$ was prepared in situ and used without purification owing to its shorter lifetime in solution. Lithium thiocyanate was prepared from potassium thiocyanate and lithium perchlorate.[1]

Equilibrium and Kinetic Data. The spectrophotometric data necessary for evaluation of the equilibrium constants were obtained with a Cary 219 spectrophotometer. The kinetic data were obtained with a Cary 219 for slow reactions ($(H_2O)_5CrCH_2CN^{2+}$ and $(H_2O)_5CrCH(CH_3)_2^{2+}$ at low [SCN⁻]) and either a Durrum or a Canterbury SF-3A stopped-flow spectrophotometer for fast reactions. The Durrum instrument was equipped with a multimix unit,[7] and the relatively unstable complex $(H_2O)_5CrCH_2OH^{2+}$[8,10] was formed in the stopped-flow instrument by mixing the contents of the two syringes containing $CrH_2O)_6^{2+}$ and H_2O in acidified aqueous methanol (1 M) and then immediately reacted with the thiocyanate ions from the third syringe.

The absorbance measurements for the reactions of SCN⁻ with $(H_2O)_5CrCH_2OCH_3^{2+}$ and $(H_2O)_5CrCH_2OH^{2+}$ were done at the absorption maxima of the uncomplexed organochromium complexes[6,11] near 400 nm. The formation of $(H_2O)_4CrCH(CH_3)_2(NCS)^+$ was followed at 410 nm, the wavelength of its maximum absorbance (ϵ 722 M⁻¹ cm⁻¹). Owing to the low absorbance of $(H_2O)_5CrCH_2CN^{2+}$ and its thiocyanato adduct in the visible part of the spectrum, this reaction was monitored at 290 nm.

The experiments were done at 25 °C and 1.00 M ionic strength $(LiClO_4 + HClO_4)$ under air-free conditions in an atmosphere of Cr^{2+}-scrubbed nitrogen. The kinetic data were evaluated by standard methods.

Results

Equilibria. Addition of thiocyanate ion to a solution of any of the four complexes causes an increase in absorbance throughout the visible region of the spectrum, similar to the reactions of the halomethylchromium complexes with thiocyanate ion.[1] On the basis of the analysis given in ref 1, we ascribe the absorbance increase to the substitution reaction of eq 3. (Evidence that substitution occurs in the trans

$$(H_2O)_5CrR^{2+} + SCN^- =$$
$$trans\text{-}(H_2O)_4Cr(NCS)R^+ + H_2O \quad (3)$$
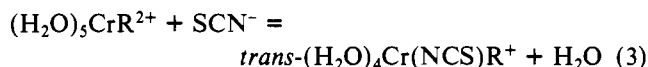
position and that the thiocyanate ion is coordinated through nitrogen was given previously.[1]) With the exception of $(H_2O)_4Cr(CH_2CN)(NCS)^+$ the adducts formed are quite unstable and decompose in acid-catalyzed hydrolysis reactions. Because of this relatively rapid decomposition, stable final absorbance readings cannot be obtained. The absorbance used in the evaluation of the equilibrium constants were obtained
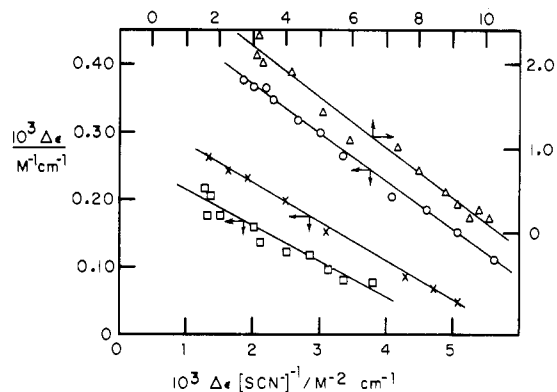

Figure 1. Plots according to eq 4 for reactions of SCN⁻ with $CrCH(CH_3)_2^{2+}$ (□), $CrCH_2OCH_3^{2+}$ (×), $CrCH_2OH^{2+}$ (○), and $CrCH_2CN^{2+}$ (△).
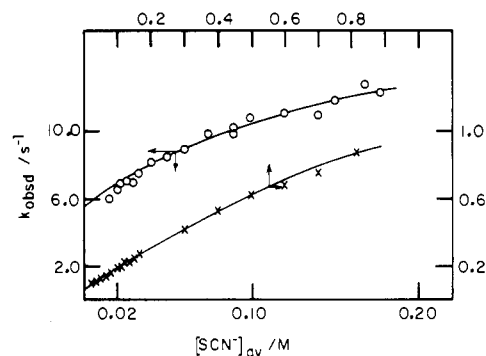
Figure 2. Plots showing a dependence of k_{obsd} on [SCN⁻] for the reactions of SCN⁻ with $CrCH_2OCH_3^{2+}$ (○) and $CrCH(CH_3)_2^{2+}$ (×). The lines are calculated from the least-squares kinetic parameters.

Table I. Summary of the Equilibrium Data for the Reaction of SCN⁻ with $(H_2O)_5CrR^{2+}$ Complexes at 25 °C and 1.00 M Ionic Strength

R	λ/nm	ϵ_0/M⁻¹ cm⁻¹ [a]	ϵ_1/M⁻¹ cm⁻¹ [b]	K_{eq}/M⁻¹
CH_2OCH_3	385	404 ± 16[c]	744 ± 30	17.2 ± 0.3
CH_2OH	392	570 ± 85[d]	(1.08 ± 0.16) × 10³	13.8 ± 0.3
$CH(CH_3)_2$	410	459 ± 18[e]	722 ± 30	19.1 ± 1.7
CH_2CN	290	(1.75 ± 0.09) × 10³ [f]	(4.78 ± 0.24) × 10³	3.46 ± 0.15
CH_2Cl[g]				10.4 ± 0.6
$CHCl_2$[g]				12.7 ± 0.8

[a] Molar absorptivity of uncomplexed $(H_2O)_5CrR^{2+}$. [b] Molar absorptivity of adduct $(H_2O)_4CrR(NCS)^+$. [c] Reference 6. [d] Reference 11. [e] Reference 25. [f] Reference 9. [g] Reference 1.

either from an analysis of the kinetic data using the Kezdy–Swinbourne method[12] for reaction 3 (R = $CH(CH_3)_2$) or by extrapolating the kinetic traces for decomposition of $(H_2O)_4CrR(NCS)^+$ to zero time (R = CH_2OH and CH_2OCH_3). The equilibrium constants were evaluated with eq 4, where ϵ_0 represents the molar absorptivity of uncomplexed

$$\Delta\epsilon = \epsilon_1 - \epsilon_0 - \frac{\Delta\epsilon}{[SCN^-]}K^{-1} \quad (4)$$

$(H_2O)_5CrR^{2+}$, ϵ_1 the molar absorptivity of its thiocyanate adduct, K the equilibrium constant, and $\Delta\epsilon$ is calculated at each thiocyanate concentration as a difference between observed molar absorptivity and ϵ_0. Figure 1 shows the plots of $\Delta\epsilon$ vs. $\Delta\epsilon/[SCN^-]$ as suggested by eq 4. The equilibrium constants and molar absorptivities evaluated from the slopes and intercepts of the straight lines are summarized in Table

(5) Espenson, J. H.; Bakač, A. *J. Am. Chem. Soc.* **1980**, *102*, 2488.
(6) Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721.
(7) Kirker, G. W. Ph.D. Thesis, Iowa State University, 1981.
(8) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.
(9) Funke, L. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 897.
(10) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.
(11) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(12) (a) Kezdy, F. J.; Kaz, J.; Bruylants, A. *Bull. Soc. Chim. Bel.* **1958**, *67*, 687. (b) Swinbourne, E. S. *J. Chem. Soc.* **1960**, 2371.

Table II. Summary of the Kinetic Parameters for the Reaction of SCN$^-$ with $(H_2O)_5CrR^{2+}$ Complexes and Trans-H_2O Exchange Rate Constants for the Complexes $(H_2O)_5CrX^{2+}$ ^{a}

R (or X)	A/M^{-1} s^{-1}	B/s^{-1}	C/M^{-1}	k_1/s^{-1}	k_3/s^{-1}	$\sigma_I{}^b$	$\sigma_p{}^b$
CH$_2$OH	638 (19)	49.4 (12)	$\leqslant 0.42^c$	$\geqslant 1520$	$\geqslant 1470$	0.05	0.01
CH$_2$OCH$_3$	96.7 (27)	5.62 (25)	4.70 (34)	20.6	15.0	0.07	0.02
CH(CH$_3$)$_2$	1.34 (2)	0.0702 (73)	0.424 (36)	3.16	3.09	−0.03	−0.15
CH$_2$CN	0.0905 (17)	0.0273 (6)	$\leqslant 0.067^c$	$\geqslant 1.35$	$\geqslant 1.32$	0.18	0.18
CH$_2$Cl^d	0.178 (4)	0.0171 (14)	0.85 (18)	0.209	0.192	0.15	0.12
CHCl$_2$^{d}	0.0624 (17)	0.004 91 (44)	1.35 (18)	0.0462	0.0413	0.30	0.32
I				2.7×10^{-4} ^{e}		0.39	0.27
Cl				2.4 (4) $\times 10^{-5}$ ^{e}		0.47	0.24
NCS				1.5 (2) $\times 10^{-5}$ ^{e}		0.42	0.38

^{a} Numbers in parentheses represent standard deviations of the last digit(s). ^{b} From: Exner, Otto. "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; p 439. ^{c} Plot of k_{obsd} vs. [SCN$^-$] is a straight line; see text. ^{d} Reference 1. ^{e} Rate constant for trans-H_2O exchange; ref 14.

I along with the previously published data on (chloromethyl)- and (dichloromethyl)chromium(III) complexes. The equilibrium constants all lie within a narrow range of values (3.5–19.1 M^{-1}).

Kinetics. Thiocyanate ions were present in large excess and in each run the data conformed to a first-order rate law yielding k_{obsd}, the rate constant for approach to equilibrium. For two of the complexes studied, CrCH$_2$OCH$_3{}^{2+}$ and CrCH(CH$_3$)$_2{}^{2+}$, the values of k_{obsd} show a nonlinear dependence on the concentration of the thiocyanate ion (Figure 2). The relation is adequately described by eq 5, analogous to the

$$k_{obsd} = (A[\text{SCN}^-] + B)/(1 + C[\text{SCN}^-]) \qquad (5)$$

reactions of CrCH$_2$Cl^{2+} and CrCHCl$_2{}^{2+}$ with thiocyanate ion.[1] From the independently determined equilibrium constant K, the composite constant k_{obsd} is transformed into k_{an}, the pseudo-first-order rate constant for the anation process (eq 6). Relation 7 then follows from eq 5, with $K = A/B$. The

$$k_{an} = k_{obsd}/(1 + (K[\text{SCN}^-])^{-1}) \qquad (6)$$

$$k_{an} = A[\text{SCN}^-]/(1 + C[\text{SCN}^-]) \qquad (7)$$

rate constants k_{an} were used to evaluate the parameters A and C according to eq 7 by a computer using nonlinear least-squares analysis. This treatment affords the following values of the parameters: CrCH$_2$OCH$_3{}^{2+}$, $A = 96.7 \pm 2.7$ M^{-1} s^{-1}, $C = 4.70 \pm 0.34$ M^{-1}; CrCH(CH$_3$)$_2{}^{2+}$, $A = 1.34 \pm 0.02$ M^{-1} s^{-1}, $C = 0.424 \pm 0.036$ M^{-1}.

The reactions of SCN$^-$ with the other two complexes, CrCH$_2$OH^{2+} and CrCH$_2$CN^{2+}, show a linear dependence of k_{obsd} on [SCN$^-$] throughout the concentration ranges studied (Figure 3). The data are consistent with a scheme of opposing pseudo-first-order reactions as in eq 8, which represents a special case of eq 5, where $C[\text{SCN}^-] \ll 1$.

$$k_{obsd} = A[\text{SCN}^-] + B \qquad (8)$$

The reaction of CrCH$_2$OH^{2+} with SCN$^-$ was studied only at low [SCN$^-$] because the reaction rates were high and at [SCN$^-$] = 0.12 M reached the limit of the stopped flow. This could be the reason why deviations from eq 8 were not observed. The reaction of CrCH$_2$CN^{2+} on the other hand was studied over a wide range of thiocyanate concentrations. The failure to observe deviations from eq 8 thus results from a very small value of $C[\text{SCN}^-]$ compared to 1. Assuming for both reactions that the point at the highest [SCN$^-$] could deviate from eq 8 by ~5% (estimated experimental error), one calculates $C \leq 0.42$ M^{-1} and ≤ 0.067 M^{-1} for CrCH$_2$OH^{2+} and CrCH$_2$CN^{2+}, respectively.

A least-squares analysis of the data according to eq 8 yields the following values of parameters: CrCH$_2$OH^{2+}, $A = 638 \pm 19$ M^{-1} s^{-1}, $B = 49.4 \pm 1.2$ s^{-1}; CrCH$_2$CN^{2+}, $A = 0.0905 \pm 0.0017$ M^{-1} s^{-1}, $B = 0.0273 \pm 0.0006$ s^{-1}. The equilibrium constants K_k, evaluated from these kinetic parameters by use
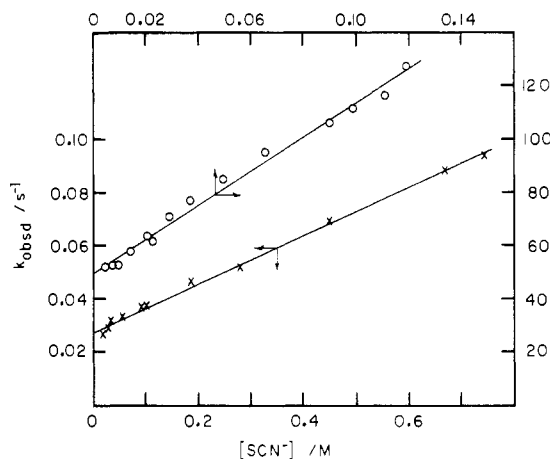
Figure 3. Plots showing a linear dependence of k_{obsd} on [SCN$^-$] for the reaction of SCN$^-$ with CrCH$_2$OH^{2+} (○) and CrCH$_2$CN^{2+} (×).

of relation $K_k = A/B$, are in very good agreement with the ones determined independently in the equilibrium (K) experiments: CrCH$_2$OH^{2+}, $K_k = 12.9 \pm 0.7$ M^{-1}, $K = 13.8 \pm 0.3$ M^{-1}; CrCH$_2$CN^{2+}, $K_k = 3.32 \pm 0.14$ M^{-1}, $K = 3.46 \pm 0.15$ M^{-1}. The summary of all the kinetic data is given in Table II.

Evaluation of the Kinetic Parameters from k_{aq}. For the two complexes obeying the rate law of eq 5 (CrCH$_2$OCH$_3{}^{2+}$ and CrCH(CH$_3$)$_2{}^{2+}$), the parameters B and C can also be evaluated from the rate constant for the reverse of reaction 3, k_{aq}. Combining eq 5 and 7 with the relation $k_{obsd} = k_{an} + k_{aq}$, one obtains eq 9, which suggests that a plot of $1/k_{aq}$ vs. [SCN$^-$]

$$k_{aq} = B/(1 + C[\text{SCN}^-]) \qquad (9)$$

should be a straight line with an intercept of $1/B$ and a slope of C/B. For the other two complexes, CrCH$_2$OH^{2+} and CrCH$_2$CN^{2+}, $C[\text{SCN}^-] \ll 1$ and k_{aq} should be independent of [SCN$^-$]. Figure 4 illustrates this analysis for two of the complexes studied, CrCH$_2$OCH$_3{}^{2+}$ and CrCH$_2$OH^{2+}. The linear plot of $1/k_{aq}$ vs. [SCN$^-$] for the former complex gives $B = 5.40 \pm 0.10$ s^{-1} and $C/B = 0.782 \pm 0.034$ s M^{-1}. For comparison, values of B and C/B determined from k_{an} are 5.62 ± 0.25 s^{-1} and 0.836 $\pm$ 0.097 s M^{-1}, respectively. Similarly, one calculates $B = 0.0671 \pm 0.0008$ s^{-1} and $C/B = 4.83 \pm 0.51$ s M^{-1} using k_{aq} for the reaction of SCN$^-$ with CrCH(CH$_3$)$_2{}^{2+}$. The agreement with the parameters evaluated from the rate constants k_{an} ($B = 0.0702 \pm 0.0073$ s^{-1}, $C/B = 6.04 \pm 1.14$ s M^{-1}) is again satisfactory, especially when one considers that most of the kinetic data were obtained under the conditions where the anation reaction was dominant.

In the reaction of SCN$^-$ with CrCH$_2$OH^{2+}, k_{aq} is independent of [SCN$^-$] (Figure 4), as expected. This treatment affords a value of B (48.2 $\pm$ 1.6 s^{-1}) that is within experimental error identical with the intercept in Figure 3 (49.4 $\pm$ 1.2 s^{-1},
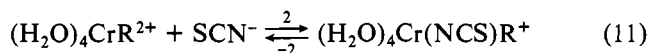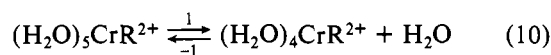
Table II). Also for the reaction of $CrCH_2CN^{2+}$ one obtains $k_{aq} = 0.0269 \pm 0.0010$ s^{-1}, in excellent agreement with the value of B listed in Table II (0.0273 $\pm$ 0.0006 s^{-1}).

None of the kinetic or equilibrium data showed any acid dependence in the range studied (0.01–0.40 M). Also the data for the $CrCH_2OCH_3^{2+}$ reaction with SCN$^-$ are unaffected by the presence of 1 M methanol. We take that as evidence that the data for $CrCH_2OH^{2+}$, obtained in 1 M methanol, are strictly comparable to the data for other complexes in this work which were studied in purely aqueous solutions.
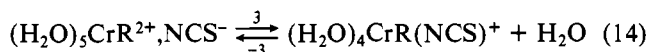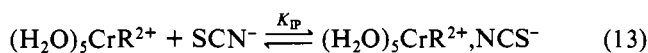
A brief study of the reaction of $CrCHCl_2^{2+}$ with SCN$^-$ was done using the stopped-flow technique in an effort to reproduce the results reported in ref 2. No fast reaction was observed at [H$^+$] = 0.50 M, [SCN$^-$] = 0.10–0.31 M, and [$CrCHCl_2^{2+}$] = (1.35–6.75) $\times$ 10^{-3} M. The experiments were done at room temperature and without adjusting the ionic strength to duplicate the conditions of ref 2 as closely as possible. Only a relatively slow reaction, the one reported by Bushey and Espenson,[1] was observed. We then searched for a possible impurity that would either catalyze the reaction of $CrCHCl_2^{2+}$ with SCN$^-$ or react itself with one of the reactants in a fast reaction, producing an increase in absorbance. We found that we were able to reproduce both the kinetic and equilibrium data of ref 2 within a reasonable error when small amounts of iron(III) perchlorate ($\sim$2 $\times$ 10^{-5} M) were added to the solutions of $CrCHCl_2^{2+}$. Identical results were obtained even when $CrCHCl_2^{2+}$ was omitted so that Fe^{3+} and SCN$^-$ were the only reactants.[13] In view of these results, all the data pertaining to the reaction of SCN$^-$ with $CrCHCl_2^{2+}$ and $CrCH_2Cl^{2+}$ cited in this work were taken from Bushey and Espenson.[1]

Discussion

The form of the general rate law of eq 5 is consistent with either a limiting S_N1 (or D) mechanism (eq 10–12) or an ion pair (or I) mechanism (eq 13–15).

$$(H_2O)_5CrR^{2+} \underset{-1}{\overset{1}{\rightleftarrows}} (H_2O)_4CrR^{2+} + H_2O \quad (10)$$

$$(H_2O)_4CrR^{2+} + SCN^- \underset{-2}{\overset{2}{\rightleftarrows}} (H_2O)_4Cr(NCS)R^+ \quad (11)$$

$$k_{obsd} = \frac{(k_1k_2/k_{-1})[SCN^-] + k_{-2}}{1 + (k_2/k_{-1})[SCN^-]} \quad (12)$$

$$(H_2O)_5CrR^{2+} + SCN^- \overset{K_{IP}}{\rightleftarrows} (H_2O)_5CrR^{2+},NCS^- \quad (13)$$

$$(H_2O)_5CrR^{2+},NCS^- \underset{-3}{\overset{3}{\rightleftarrows}} (H_2O)_4CrR(NCS)^+ + H_2O \quad (14)$$

$$k_{obsd} = \frac{(k_3 + k_{-3})K_{IP}[SCN^-] + k_{-3}}{1 + K_{IP}[SCN^-]} \quad (15)$$

An associatively controlled ion pair (or I_A) mechanism is not considered likely for these reactions. Strong labilizing groups such as the ones used in this study promote dissociative mechanisms. Also, for several complexes of the general type $(H_2O)_5CrX^{2+}$, the kinetics of the exchange of the trans H$_2$O have been studied.[14] On the basis of activation parameters, an I_D mechanism was suggested. The $(H_2O)_5CrR^{2+}$ complexes, even more reactive in their substitution reactions, would

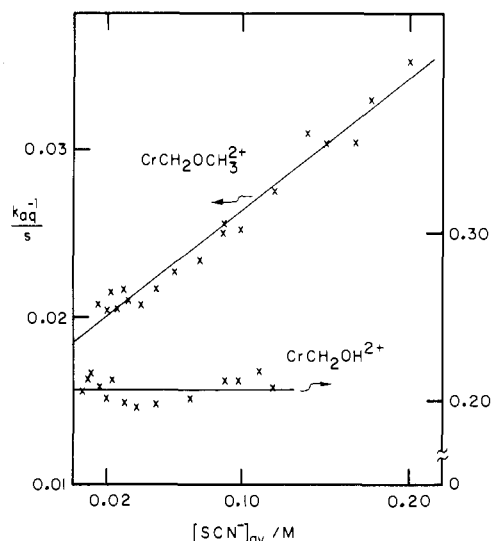**Figure 4.** Plot showing a constancy of $1/k_{aq}$ for $CrCH_2OH^{2+}$–SCN$^-$ reaction and a linear dependence of $1/k_{aq}$ on [SCN$^-$]$_{av}$ for $CrCH_2OCH_3^{2+}$–SCN$^-$ reaction as suggested by eq 9.
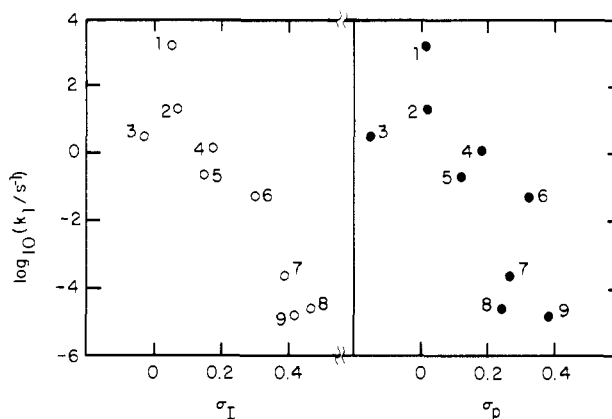

Figure 5. Plots showing the trend in the values of k_1 with Hammett substituent constants σ_I and σ_p for complexes $(H_2O)_5CrR^{2+}$ (R = CH$_2$OH (1), CH$_2$OCH$_3$ (2), CH(CH$_3$)$_2$ (3), CH$_2$CN (4), CH$_2$Cl (5), and CHCl$_2$ (6)) and $(H_2O)_5CrX^{2+}$ (X = I (7), Cl (8), and NCS (9)). Values of log k_1 for $CrCH_2OH^{2+}$ and $CrCH_2CN^{2+}$ represent the lower limits (see text).

thus not be expected to react by associative processes.

A distinction between a D and I_D mechanism is often based on the ratio A/C, which represents a rate-limiting dissociation of the coordinated trans water, k_1, in the former mechanism and the sum $k_3 + k_{-3}$ in the latter. A constancy of the ratio A/C for a series of incoming ligands is considered a strong evidence for a D mechanism.[15] It is quite possible though in the present system that an approximately constant value of A/C for a particular organochromium complex could be obtained with a series of ligands such as SCN$^-$, F$^-$, and N^{3-}, even if an I_D mechanism applies. Since $k_{-3} \ll k_3$, the constants k_1 and k_3 in the two mechanisms have almost identical values (Table I). It has been pointed out before[16] that these two rate

(13) The rate constants measured under these conditions are different from the published data for the reaction Fe^{3+} + SCN$^-$ = FeNCS^{2+} (k = 127 + 20/[H$^+$]): Below, J. F., Jr.; Connick, R. E.; Coppel, C. P. *J. Am. Chem. Soc.* **1958**, *80*, 2961. The concentrations of SCN$^-$ used by Azran et al. are quite high and formation of higher complexes, Fe(NCS)$_2^+$, Fe(NCS)$_3$, etc., is quite likely under these conditions. The rate constant measured thus represents the overall rate constant for all the complexation processes.

(14) Bracken, D. E.; Baldwin, H. W. *Inorg. Chem.* **1974**, *13*, 1325.

(15) This point could not be checked in the present system. Although a large number of ligands caused a significant acceleration of the Cr–C bond cleavage (presumably by first binding to the organochromium complex), only the reactions with SCN$^-$, N$_3^-$, and F$^-$ were accompanied by formation of sufficiently stable complexes and large enough absorbance changes. Owing to the high proton basicity of the latter two ligands, the reaction rates are almost certain to show a pronounced acid dependence, as its has been shown for the reaction of the fluoride ion with Cr(H$_2$O)$_5$CF$_3^{2+}$.[3] Interpretation of the data under such conditions becomes ambiguous (see, for example: Carlyle, D. W.; Espenson, J. H. *Inorg. Chem.* **1967**, *6*, 1967) and for this reason the reactions with N$_3^-$ and F$^-$ were not studied.
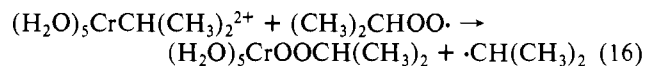
constants can reasonably be approximated as the water exchange rate constants k_{exch} in the absence and presence of the entering ligand, respectively. Also, the available evidence suggests that k_{exch} is not significantly altered by outer-sphere complex formation.[17,18] On the basis of these grounds, the ratio A/C is taken as the rate constant for the trans-water exchange in the organochromium complexes studied. For sake of convenience, the notation used throughout the rest of the Discussion is the one adopted for the D mechanism. The principal point to be made is not the distinction between D and I_D mechanisms but the substituent effects on the dissociatively controlled rate constant governing the reaction.

The data in Table II indicate that the rate constant for trans-water exchange increases with the electron-donating properties of the group R. A more quantitative approach is shown in Figure 5, which depicts the dependence of the constant k_1 on the Hammett substituent constant σ_I. Also in Figure 5 are shown the rate constants for the trans-water exchange in three complexes of the type $(H_2O)_5CrX^{2+}$ (X = I$^-$, Cl$^-$, and SCN$^-$).[14] For all the complexes studied (with the exception of CrCH(CH$_3$)$_2^{2+}$), the rate constant k_1 monotonically increases with a decrease in σ_I. Admittedly there is a significant scatter of the data. However, bearing in mind the very rough approximation made in using σ_I values to represent the electron-donating properties of R and X through the purely inorganic $(H_2O)_5Cr$, we feel that the correlation is good and, more to the point, not accidental. The rate constants k_1 span a range of 8 orders of magnitude for the variation of σ_I from −0.05 to +0.47. If the dependence is assumed to be linear, one calculates a reaction constant $\rho \simeq -17$. A similar type of relationship between different parameters that measure the electron-donating properties of the labilizing group and the rate of the trans-ligand substitution was observed for a number of cobaloximes.[19-23] For example, the rates of pyridine dissociation from neutral and anionic alkyl(pyridine)cobaloximes[21] are linearly related to the Taft substituent constant σ^* by reaction constant ρ^* values of −4.1 and −5.6, respectively (although exclusion of the values for R = CH$_3$, CH$_2$Cl, and CH$_2$I was necessary to realize this correlation[21]). Quantitative details aside, it is clear that the inductive effects of the trans-alkyl or substituted-alkyl groups are substantial. Furthermore, in a qualitative sense, they accord with the effects found in organic reactions. That is to say, a relatively electron-donating R group accelerates the rate of dissociatively controlled ligand substitution and vice versa. It is a much more difficult matter, however, to settle which of the substituent-constant series from organic reactions might be used to correlate data for these reactions quantitatively so as to afford a measure of the importance of the trans-inductive effect in a given ligand substitution reaction series (and, consequently, to permit the assessment of the extent to which dissociative activation controls the mechanism). The σ_I constants—and the older σ^* constants, concerning which certain problems for alkyl groups have recently[24] been pointed out—are derived from reactions in which allowance must be made for the very appreciable steric influence of the aliphatic substituent. Any steric influence a trans ligand would have in coordination

chemistry might be of quite a different character in that it is not in a position to directly interact with the leaving or entering ligand. Rather its steric effects would include any structural changes in the reactant complex such as distortion of the cis ligands from coplanarity or lengthening of the metal–ligand bond trans to it (such effects are termed "ground-state influences"), as well as those structural changes in the activated complex that reflect varying steric requirements of a given ligand to an extent which is different from the ground state. Given these considerations it is not unreasonable to consider the applicability of a series of substituent constants derived from reaction series in which steric effects are nonexistent; the Hammett substituent constants σ_p are one such set. Figure 5 also shows a plot made on such a basis. Aside from the single alkyl complex examined (R = CH(CH$_3$)$_2$), the remaining points show a rough correlation. Great significance should not be attributed to the value of the reaction constant so calculated ($\rho = -23$); it would be a gross oversimplification to expect that electronic effects be transmitted to the trans-positioned reaction center of a metal complex in a fashion exactly paralleling that for para substitutents on a benzene ring. Again, at the present stage of development, the correlations should be taken only to show the direction and magnitude of the polar effects.

The rate constants k_{-2} for the dissociation of SCN$^-$ from $(H_2O)_4CrR(NCS)^+$ show the same qualitative trend as the constants k_1. This implies that the order of trans labilizing ability of the groups R or X (CH$_2$OH > CH$_2$OCH$_3$ > CH(CH$_3$)$_2$ > CH$_2$CN > CH$_2$Cl > CHCl$_2$ > I > Cl $\gtrsim$ NCS) is independent of the nature of the leaving group.

The much slower reaction of the (2-propyl)pentaaquochromium(III) complexes than predicted by its σ_I value is puzzling. Indeed, the extrapolated value ($k_1 \approx 10^{4-5}$ s^{-1} or $A \approx 10^{3.5-4.5}$ M^{-1} s^{-1}) would suggest that the reaction 16[25] could

$$(H_2O)_5CrCH(CH_3)_2^{2+} + (CH_3)_2CHOO \cdot \rightarrow$$
$$(H_2O)_5CrOOCH(CH_3)_2 + \cdot CH(CH_3)_2 \quad (16)$$

occur as fast as it does ($k_{16} = 10^{4.8}$ M^{-1} s^{-1}) by trans-ligand substitution, whereas the surprisingly small value of k_1 found experimentally suggests that the radical displacement reaction of eq 16 occurs by a different process. It is possible that, as in the cobaloximes,[26,27] (2-propyl)chromium has an unusually long metal–carbon bond which could explain its special chemistry. A possibility that other alkyl complexes that do not contain any heteroatoms also react more slowly than predicted has not been investigated. Finally, of course, there is no factual basis for insisting that the rate constant for the one-electron process of eq 16 be the same as that for the two-electron processes characteristic of ligand-substitution reactions, as the character of the transition state and the leaving group are different.

(16) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1976; p 188.
(17) Duffy, N. V.; Earley, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 272.
(18) Monacelli, F.; Viel, E. *Inorg. Chim. Acta* **1967**, *1*, 467.
(19) "Cobaloxime" is a trivial name for bis(dimethylglyoximato)cobalt.
(20) Seibles, L.; Deutsch, E. *Inorg. Chem.* **1977**, *16*, 2273.
(21) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338.
(22) Brown, K. L.; Awtrey, A. W. *Inorg. Chem.* **1978**, *17*, 111.
(23) Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1978**, *100*, 817.
(24) DeTar, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 7988.

(25) Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 2488.
(26) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.
(27) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7372.