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Kinetics of substitution of ethylbis(dimethylglyoximato)-aquocobalt(III) by hexacyanometallates

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Kinetics of substitution of ethylbis(dimethylglyoximato)-aquocobalt(III) by hexacyanometallates

by

Robert Russell

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ABSTRACT

The formation of a 1:1 adduct between ethylaquocobaloxime, cobaloxime being the trivial name for bis(dimethylglyoximato) symbolized $(dmgH)_2$, and $M(CN)_6^{n-}$ complexes for M = Fe(II), Fe(III), Co(III), and Cr(III) are reported. These adducts are formed by the displacement of the bound water in the ethylaquocobaloxime to form the complex $\{C_2H_5Co(dmgH)_2NCM(CN)_5^{n-}\}$. This substitution was studied kinetically by stopped-flow methods. Equilibrium measurements are also reported. The kinetic results are not consistent with a limiting S_N1 mechanism for all four reactions. A mechanism which can be applied to all four reactions involves a prior outer-sphere association of the ethylaquocobaloxime and $M(CN)_6^{n-}$, followed by the rate-determining loss of water.

INTRODUCTION

The sigma bonded alkyl substituent has been shown to significantly increase the rate of substitution of the ligand trans to the alkyl group relative to similar compounds not containing the metal-carbon bond (1-12). The compounds generally used to observe this effect have been alkylcobalt compounds containing a planar, tetradentate ligand system such as the corrins (1-3), bis(dimethylglyoximato) (4-7), and related ligand systems (8-12). The enhanced rate is reflected in the substitution of thiocyanate in methylaquocobaloxime ($k = 49.6\ M^{-1}sec^{-1}$) (4) which is 10^5 times faster than the substitution of thiocyanate into nitroaquocobaloxime ($k = 5.8x10^{-4}\ M^{-1}sec^{-1}$) (13).

In the cobalamin systems, vitamin B_{12}, the proposed mechanism of substitution (14,15) is a limiting S_N1 mechanism having the reaction scheme

$$R - (Co)\text{-}H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R\text{-}(Co) + H_2O \qquad (1)$$

$$R\text{-}(Co) + L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} R(Co) - L \qquad (2)$$

where the parentheses signify the planar, tetradentate ligand system, R is an alkyl group, and L the entering ligand. The rate constant for the approach to equilibrium of this mechanism is given by Eq 3, making the steady-state assumption for [R-(Co)].

$$k_{obs} = \frac{k_1 k_2[L] + k_{-1}k_{-2}}{k_{-1} + k_2[L]} \qquad (3)$$

However Eq 3 becomes

$$k_{obs} = \frac{k_1 k_2}{k_{-1}}[L] + k_{-2} \qquad (4)$$

when the relation $k_{-1} >> k_2[L]$ exists. In the cobalamin systems only Eq 4 is observed. However the limiting S_N1 mechanism is proposed for the cobalamins due to the existence of a five-coordinate species in solution (16) similar in structure to the steady-state intermediate formed in Eq 1 and the similarity of the rates of anation by various ligands as shown in Table 1. The ligand would have little effect on the rate of substitution if the intermediate were formed by loss of water. For the aquation reactions, the metal-ligand bond is no longer common to every reaction in forming the five-coordinate intermediate. This is shown in Table 1 by the variation of k_f, the rate constant for anation, by a factor of 10 and k_r, the rate constant for aquation, by a factor of 10^7.

In the vitamin B_{12} model compounds such as the cobaloximes, the existence of an appreciable concentration of a five-coordinate species in aqueous solution is not observed. However in non-coordinating solvents, the five-coordinate form is predominant for several model compounds. Alkylbis(acetylacetone)ethylenediimine cobalt (8) and alkylbis(salicylaldehyde)-ethylenediimine cobalt (9) are five-coordinate in weakly coordinating solvents such as n-propanol. When solvents are chosen

Table 1. Kinetic and equilibrium constants for cobalamin substitution reactions[a]

Ligand	$k_f(10^{-3}M^{-1}sec^{-1})$	$k_r(sec^{-1})$	K_{thermo}[b]
SCN^-	2.3	1.8	$1.2x10^3$
I^-	1.4	35	$3.2x10^1$
Br^-	1.0	590	1.9
N_3^-	1.2	0.029	$5.6x10^4$
NCO^-	0.47	1.1	$5.3x10^2$
$S_2O_3^{2-}$	0.20	.035	$7.3x10^3$
HSO_3^-	0.17		~2.2
SO_3^{2-}	<0.2	$<1x10^{-5}$	$2.2x10^7$

[a] 25.5°C, μ = 0.5M, ClO_4^- medium reference 3.

[b] Thermodynamic formation constant from references 1 and 17.

for the alkylcobaloximes which would favor the formation of a five-coordinate species, only a dimer is observed (18).

The absence of an observable five-coordinate species does not eliminate a limiting S_N1 mechanism for the substitution of the alkylcobaloximes. The effect of a more labile axial group is observed in the rates of substitution. The results for the substitution of nitroaquocobaloxime are given in Table 2. These substitute much slower than the alkylcobaloximes. Rates of substitution for a methylaquocobaloxime are given in Table 3. The effect of the alkyl group is significant. If a limiting S_N1 mechanism is operative, the effect of the alkyl group would be to weaken the trans group's bond to the cobalt, forming a compound closer in form to the five coordinate intermediate.

The limiting S_N1 mechanism has been proposed for the substitution of the alkyl cobalt compounds (4-7). Comparison of the rates of substitution of the cobalamins and cobaloximes is given in Table 4. From this comparison it is observed that both alkyl cobalt systems, cobalamin and alkylcobaloxime, have rates of substitution depending little on the entering group while the rates are largely dependent on the leaving group. This dependence which can be explained by a limiting S_N1 mechanism and the cobaloxime's ability to model other cobalamin reactions gave support to the proposed S_N1 mechanism.

The form of the kinetic results for the alkylcobaloximes is consistent with Eq 4. This is not a unique expression but

Table 2. Equilibrium and kinetic constants for substitution reactions of nitroaquocobaloxime[a]

Ligand	$10^4 k_f (M^{-1}sec^{-1})$	$10^4 k_r (M^{-1}sec^{-1})$	$K_{eq}(M)$
Cl^-	0.8	1.2	0.6
Br^-	1.6	1.2	1.3
N_3^-	5.7		
NCS^-	5.8	~0.5	11.6
HSO_3^-	85	~7	12.1

[a] Reference 13, 25°C, μ = 1.0M.

Table 3. Equilibrium and kinetic constants for the axial substitution of methylaquocobaloxime at 25.0°[a]

Ligand	$k_f(M^{-1}sec^{-1})$	$k_r(sec^{-1})$	$K_{eq}(M^{-1})$
$NH_2CH_2CF_3$	4.34	$8.37x10^{-2}$	$5.19x10^{1}$
$NH_2(CH_2)_2OCH_3$	5.22	$3.44x10^{-3}$	$1.74x10^{3}$
$NH_2(CH_2)_3OCH_3$	5.53	$2.08x10^{-3}$	$3.02x10^{3}$
$NH_2CH_2CH(OCH_3)_2$	4.79	$5.91x10^{-3}$	$7.89x10^{2}$
$NH_2(CH_2)_2CH_3$	7.48	$2.07x10^{-3}$	$4.25x10^{3}$
4-CN-py	9.21	$2.90x10^{-1}$	$3.29x10^{2}$
$4\text{-}CONH_2\text{-}py$	117	$1.56x10^{-1}$	$8.03x10^{2}$
py	114	$5.52x10^{-2}$	$2.04x10^{3}$
$4\text{-}CH_3\text{-}py$	128	$4.04x10^{-2}$	$3.25x10^{3}$
$4\text{-}NH_2\text{-}py$	196	$1.94x10^{-2}$	$1.11x10^{4}$
$HSCH_2\text{-}COOCH_3$	24.2	$2.11x10^{-4}$	$1.17x10^{5}$
$HS\text{-}CH_2CH_3$	27.3	$1.14x10^{-4}$	$2.04x10^{5}$
$HS\text{-}CH_2COOH$	12.8	$4.5x10^{-5}$	$2.73x10^{5}$
SCN^{-b}	49.6	$5.2x10^{-1}$	9.6x10
N_3^{-b}	34.7	$1.7x10^{-1}$	$2.04x10^{2}$
py^{b}	29.7	$6.2x10^{-3}$	$4.81x10^{3}$
NH_3^{b}	3.1	$8.5x10^{-4}$	$3.64x10^{3}$
OH^{-b}			2.7x10

[a] $R\text{-}NH_2$ and 4-X-py reference 7, RSH reference 6.

[b] Reference 4, 10.0°C.

Table 4. Relative range of rate and equilibrium constants for the ligation reactions of aquocobalamin and cobaloximes at 25°

Complex	Entering ligand	Rel. rate range	Rel. equil. range	$\frac{\text{Equil. range}}{\text{Rate range}}$
Aquocobalamin[a]	SCN^-, I^-, Br^-, N_3^-, NCO^-, $S_2O_3^{2-}$, HSO_3^-, SO_3^{2-}	13.5 (4.9)[a]	2.4×10^4 (2.4×10^4)[a]	1.8×10^3 (4.9×10^3)[a]
$Co(dmgH)_2(NO_2)(H_2O)$[b]	Cl^-, Br^-, N_3^-, NCS^-, HSO_3^-	1.1×10^2	4.8×10^2	4.6
$Co(dmgH)_2(I)H_2O$[b]	Cl^-, Br^-, NCS^-, HSO_3^-	10.5	1.2×10^3	1.1×10^2
$MeCo(dmgH)_2H_2O$[c]	RNH_2, X-py, RS^-	45.0 (45.0)[d]	5.3×10^3 (2.1×10^2)[d]	1.2×10^2 (4.8)[d]
$MeCo(dmgH)_2H_2O$[e]	SCN^-, N_3^-, py, CN^-, NH_3	16	1×10^4	6.2×10^2

[a] References 1, 3, 17; values in parentheses refer to monoanions only.

[b] Reference 13.

[c] References 6 and 7.

[d] Values in parentheses refer to nitrogen ligands only.

[e] Reference 4, 10°C, $\mu = 1.0M$.

can be applied to numerous kinetic mechanisms. A bimolecular reaction, a S_N2 mechanism, is also consistent with Eq 4. A S_N2 mechanism would have an observed rate law of

$$k_{obs} = k_f[L] + k_r \tag{5}$$

where k_f and k_r are the rate constants for anation and aquation respectively. However for the S_N2 mechanism, the entering ligand would have a large effect on the rate of substitution. Another mechanism consistent with the kinetic results would be a mechanism of the form

$$\text{R-(Co)-H}_2\text{O} + \text{L} \overset{K_{O.S.}}{\rightleftarrows} \{\text{R-(Co)-H}_2\text{O}\cdots\text{L}\} \tag{6}$$

$$\{\text{R-(Co)-H}_2\text{O}\cdots\text{L}\} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \text{R-(Co)-L} + \text{H}_2\text{O} \tag{7}$$

in which an outer-sphere association occurs prior to the rate determining loss of water. The observed rate constant for the approach to equilibrium is given by

$$k_{obs} = \frac{(k_3+k_{-3})K_{O.S.}[L] + k_{-3}}{1 + K_{O.S.}[L]} \tag{8}$$

Under conditions where $1 \gg K_{O.S.}[L]$, Eq 8 simplifies to

$$k_{obs} = (k_3+k_{-3})K_{O.S.}[L] + k_{-3} \tag{9}$$

Kinetically the forms of Eqs 3 and 8 have the general form of Eq 10 and a mechanism cannot be decided on the form of the

$$k_{obs} = \frac{A[L] + B}{1 + C[L]} \tag{10}$$

observed rate constant. The same is true for the Eqs 4 and 9 which are identical in form to Eq 5, the S_N2 mechanism.

Presently only one alkylcobalt system has been reported that has a kinetic rate expression of the form of Eq 10. The kinetics of substitution of alkyl- and aryl-aquo 1,3-bis-(acetylmonoximino)propanatocobalt monocation, RCo{(DOH)(DO)pn} H_2O^+, in acetone containing 1% water (10) and in aqueous solution (11) approach a rate independent of ligand concentrations. This would occur for Eq 10 at ligand concentrations where C[L] >> 1 such that k_{obs} = A. Initially (10) this was explained in terms of a limiting S_N1 mechanism. In the limiting S_N1 mechanism the rate constant k_1 and k_{-1} are unique in that they are independent of ligand. However it was found (11) that the values of "k_1" varied with entering ligand. Thus the mechanism assigned was an outer-sphere associative mechanism similar to Eqs 6 and 7.

In the alkylcobaloximes the kinetic expression can be described by the general form of Eq 5, the S_N2 mechanism. Non-alkyl cobaloximes have been observed to obey limiting S_N1 kinetics in aqueous solution. The substitution of sulfito-aquocobaloxime by sulfite (19) approaches a rate independent of sulfite concentration or $k_{obs} = k_1$. However there have been no deviations from Eq 5 for the alkylcobaloximes.

In the present study the substitution of ethylaquo-cobaloxime (Figure 1) by hexacyano metal ligands is compared to the work of George and coworkers (20) where similar

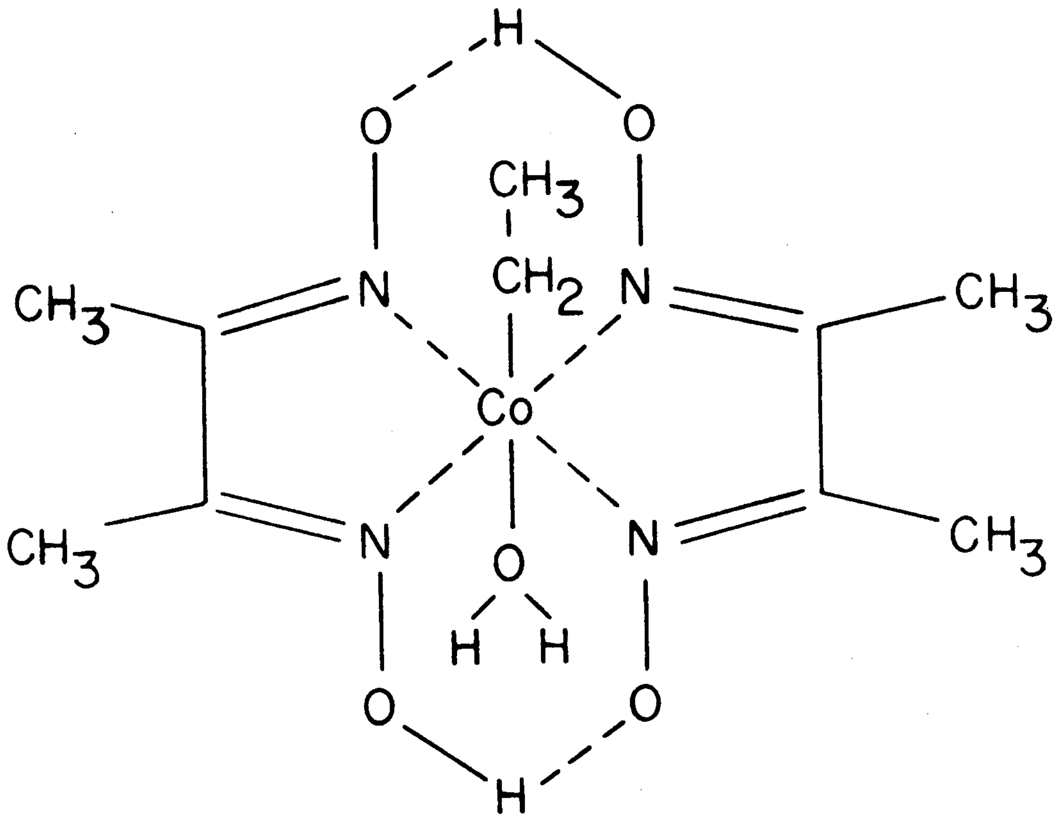

Figure 1. Ethylaquocobaloxime

hexacyano ligands substituted for the axial water of aquocobalamin. The ligands compared are $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$. For the cobalamins the bonding to the cobalt is thru the nitrogen of the cyanide. This is shown by a spectral shift similar to that observed for other nitrogen ligands and completely unlike a carbon-bonded cyanide. Thus the bonding is not thru a cyanide released from a ligand by aquation but thru one of the peripheral nitrogen atoms of the hexacyanide ligand. The alkylcobaloximes also form cyano-bridged complexes with the hexacyanide ligands. The bonding to the cobalt is again thru the nitrogen of the hexacyano complex. The kinetics of the approach to equilibrium of the reaction

$$C_2H_5Co(dmgH)_2H_2O + M(CN)_6^{n-} \overset{K}{\rightleftarrows} C_2H_5Co(dmgH)_2 - NCM(CN)_5^{n-} + H_2O \qquad (11)$$

where M = Fe(II), Fe(III), Co(III), or Cr(III), are given in this study.

EXPERIMENTAL

Materials

$C_2H_5Co(dmgH)_2H_2O$ was prepared by the method of Schrauzer (21). A suspension of 23.8 grams (0.1 mole) of cobalt(II) chloride 6-hydrate and 23.2 grams (0.2 mole) of dimethylglyoxime in 100 ml of methanol was stirred in a 500 ml three-necked flask for 5 minutes. The reaction mixture was under nitrogen until the product was separated. Subsequently, 8.0 grams (0.2 mole) of sodium hydroxide in 150 ml of water was added. The resulting solution was stirred for 15 minutes and cooled to -20°. While stirring 7.0 grams (0.113 mole) of dimethylsulfide was added. After 5 minutes, 22 grams (0.141 mole) of ethyl iodide was added. Next a solution of 4.0 grams of sodium hydroxide in 20 ml of water was added dropwise. This was immediately followed by the addition of a solution of 1.0 grams sodium hydroxide plus 0.6 grams of sodium borohydride in 10 ml of water. After stirring for 15 minutes and allowing the solution to return to room temperature, the reaction mixture was filtered. The filtrate was diluted with one volume of water, and set aside for crystallization at 0° for 24 hours. The red-orange crystals of ethyl(dimethylsulfide)cobaloxime were collected, washed with water, and air dried. Additional cobaloxime was removed from the filtrate by the addition of 10 ml of pyridine which precipitated the cobaloxime in the form ethyl(pyridine)cobaloxime. The ethyl(dimethylsulfide)cobaloxime was converted to the ethylaquocobaloxime by boiling a suspension of the dimethylsulfide complex in water for 30 minutes. The ethyl(pyridine)cobaloxime was converted to the ethylaquocobaloxime by heating to boiling the pyridine complex in dilute acid for 10 minutes. To avoid any photodecomposition all the steps were carried out in the dark.

The potassium ferricyanide used in all experiments was prepared by recrystallizing twice from distilled water reagent grade potassium ferricyanide.

The potassium chromicyanide, $K_3Cr(CN)_6$, was prepared by the method of Schaap <u>et</u> <u>al</u>. (22). A solution of 56 grams (0.12 mole) of $[Cr(H_2O)_6](ClO_4)_3$ in 500 ml of water was added dropwise to a boiling solution of 130 grams (2.0 moles) of KCN in 500 ml of water. The rate of addition was such that boiling continued and the solution was clear. The addition was accomplished in as short a time span as possible. After the addition the reaction mixture was cooled to 0°C and filtered. The filtrate, predominately the tetracyanodihydroxy complex, was deaerated with nitrogen for 1 hour. Under nitrogen, 2 ml of 0.1 M $Cr(H_2O)_6^{2+}$ was added to catalyze the anation reactions. The reaction was allowed to continue for 30 minutes. Air was then bubbled thru the solution to oxidize the chromous ion to chromium(III), which resulted in a color change of red-orange to straw yellow. The $K_3Cr(CN)_6$ salt was precipitated by the addition of 3 to 5 volumes of methanol. The solid was filtered and dried with anhydrous ethyl ether. The product was recrystallized by redissolving in a minimum of water and precipitating with an excess of methanol. The yield was 90% $K_3Cr(CN)_6$ with two recrystallizations.

The potassium cobalticyanide, $K_3Co(CN)_6$, was prepared by the method of Benedetti-Pichler (23). The intermediate $K_4Co(CN)_6$ was prepared by adding an excess of KCN to a boiling solution of $CoCl_2 \cdot 6H_2O$. The deep red solution of $K_4Co(CN)_6$ was boiled for 15 minutes which converted the complex to $K_3Co(CN)_6$. The $K_3Co(CN)_6$ precipitated from solution upon cooling. The product was recrystallized twice from distilled water.

The potassium ferrocyanide used in the experiments was prepared by recrystallizing reagent grade $K_4Fe(CN)_6$ from distilled water. The sodium ferrocyanide (24) was prepared by adding to a concentrated solution of $K_4Fe(CN)_6$, a solution of 1 M $HClO_4$. The acid form, $H_4Fe(CN)_6$, was separated by adding ethyl ether to the acidic solution. The etherate was filtered and air dried. The filtrate was dissolved in a solution of 0.5 M NaOH. The pH was maintained basic in the solution. The product was precipitated from solution by adding 2 to 4 volumes of methanol to the solution. The product was twice recrystallized by dissolving in distilled water and precipitating with methanol.

The sodium perchlorate used in all experiments was prepared by recrystallizing reagent grade sodium perchlorate twice from distilled water.

All stock acidic and basic solutions were prepared from reagent grade chemicals.

Analyses

Iron in solution was analyzed as the $Fe(H_2O)_6^{3+}$ ion. The conversion of the hexacyanide iron complexes to the aquo complex was accomplished by heating an aliquot of solution with 2 ml of $HClO_4$ to fuming. The sides of the flask were washed with distilled water and the procedure repeated. The flask was cooled, filled to the mark with distilled water, and the absorbance of the $Fe(H_2O)_6^{3+}$ ion measured at $\lambda = 238$ nm. The extinction coefficient for the $Fe(H_2O)_6^{3+}$ ion was $4.16\text{x}10^3$ $M^{-1}cm^{-1}$ (25).

Analysis for cobalt in solution was accomplished by converting the cobalt to Co^{2+} by a method analogous to the conversion of the iron complexes. The Co^{2+} ion was converted to the $Co(NCS)_4^{2-}$ complex in a 50% acetone solution. This complex has a known extinction coefficient of 1842 $M^{-1}cm^{-1}$ at $\lambda = 623$ nm (26).

Chromium in solutions of $Cr(CN)_6^{3-}$ was analyzed by conversion to the $Cr(H_2O)_6^{3+}$ by heating with perchloric acid. The chromium was converted to chromate by treatment with sodium hydroxide and hydrogen peroxide. The extinction coefficient used for the chromate was 4830 $M^{-1}cm^{-1}$ at $\lambda = 372$ nm (27).

Stock Solutions

Solutions of $C_2H_5Co(dmgH)_2H_2O$ were prepared by dissolving the cobaloxime in water and adding sufficient standardized sodium perchlorate such that ionic strength was unity. The concentration was determined spectrophotometrically at λ = 450 (ε = 1490 $M^{-1}cm^{-1}$). The solutions were stored at all times in the dark. All syringes in the stopped-flow and flasks containing ethylcobaloxime solutions were covered with aluminum foil to shield the solution from light.

All stock solutions of the ligands were prepared the day of their use. To avoid the precipitation of potassium perchlorate, the ligands were converted to the sodium salt by passing a solution of the ligand thru a Dowex 50W-X8 cation exchange column in the sodium form. The concentrations were determined spectrophotometrically at the respective ligand's absorption maximum; λ = 420 nm (ε = 1050 $M^{-1}cm^{-1}$) for $Na_3Fe(CN)_6$, λ = 300 nm (ε = 215 $M^{-1}cm^{-1}$) for $Na_3Co(CN)_6{}^{3-}$, λ = 378 nm (ε = 86 $M^{-1}cm^{-1}$) for $Na_3Cr(CN)_6$, and λ = 315 nm (ε = 315 $M^{-1}cm^{-1}$) for $Na_4Fe(CN)_6$. All solutions were known to follow Beer's law in the concentration ranges studied.

All solutions were prepared such that the ionic strength was unity at all times. The ionic strength was adjusted by the addition of standardized sodium perchlorate. The sodium perchlorate was standardized by passing an aliquot of the solution thru a Dowex 50W-X8 ion exchange column in the H^+

form. The eluent containing the acid was titrated against a standardized base to a phenolphthalein endpoint. Thus the concentration of the sodium perchlorate would be calculated knowing that the sodium:H^+ ratio is 1:1.

Procedures

The wavelengths of interest for the kinetic and thermodynamic measurements were determined by observing the change in the spectrum as a function of ligand concentration. The wavelengths chosen for the study were those wavelengths which gave the greatest change in absorbance due to formation of the product. Figures 2, 3 and 4, show preliminary experiments used to determine the wavelength of maximum absorbance change. The wavelengths used were λ = 590 nm for $Fe(CN)_6{}^{3-}$, λ = 450 nm for $Cr(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$, and $Co(CN)_6{}^{3-}$.

The spectrum of the product, the cyano-bridged complex, was determined from a spectrum of a reaction mixture. Once the equilibrium constant was known, the contribution of the individual species to the absorbance could be calculated. Thus the product spectrum could be constructed. The amount of each species present was calculated by the equilibrium

$$C_2H_5Co(dmgH)_2H_2O + L \overset{K}{\rightleftharpoons} C_2H_5(Co(dmgH)_2L + H_2O \qquad (12)$$

where L is the substituting hexacyano ligand and K the equilibrium constant. The percent of product was calculated by

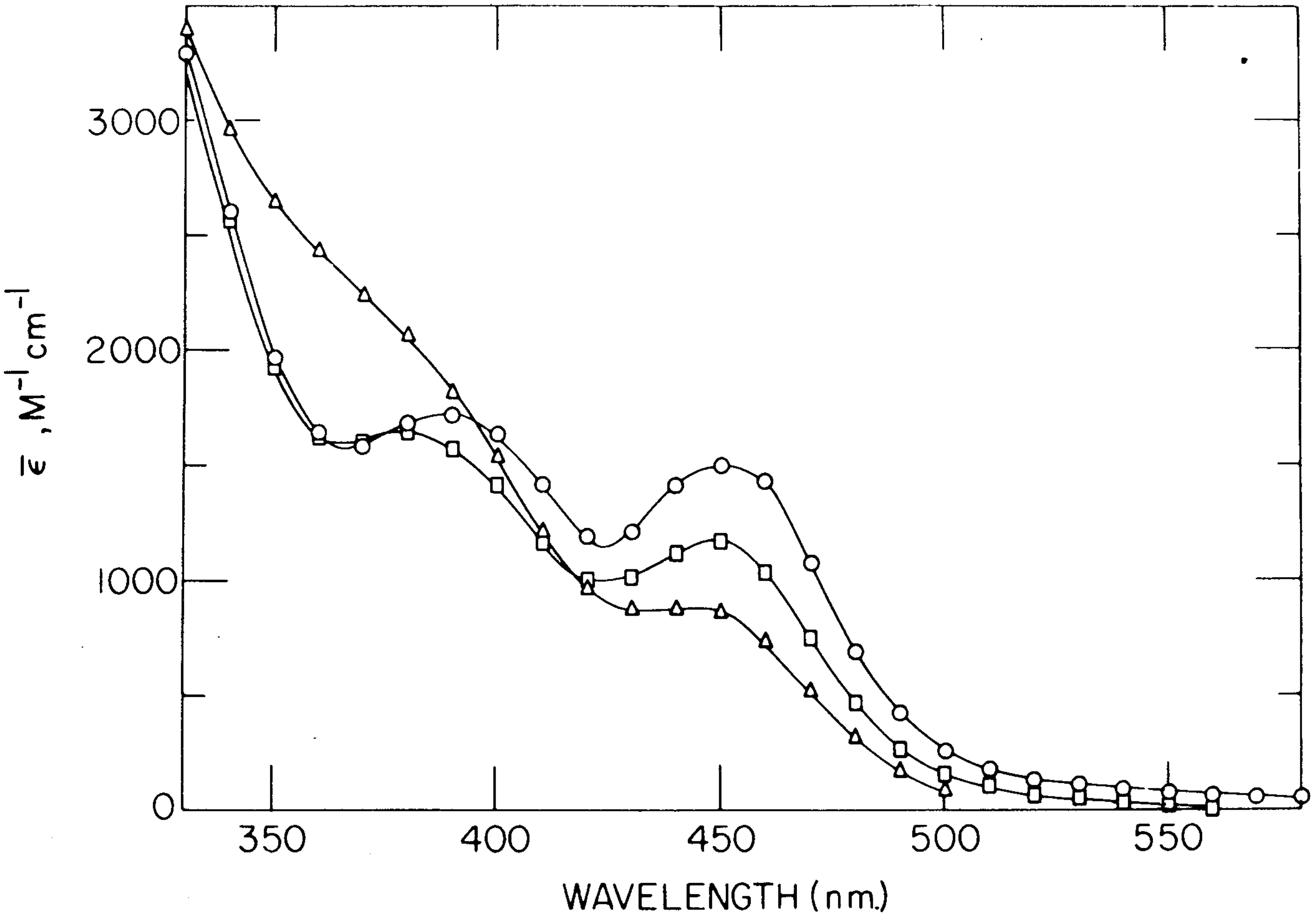

Figure 2. Preliminary spectral study to determine wavelengths to be used in the study. $C_2H_5Co(dmgH)_2H_2O$ only (circles), $C_2H_5Co(dmgH)_2H_2O$ and $3.3x10^{-3}M$ $Co(CN)_6^{3-}$ (squares) , and $C_2H_5Co(dmgH)_2H_2O$ and $3.6x10^{-3}M$ $Cr(CN)_6^{3-}$ (triangles)

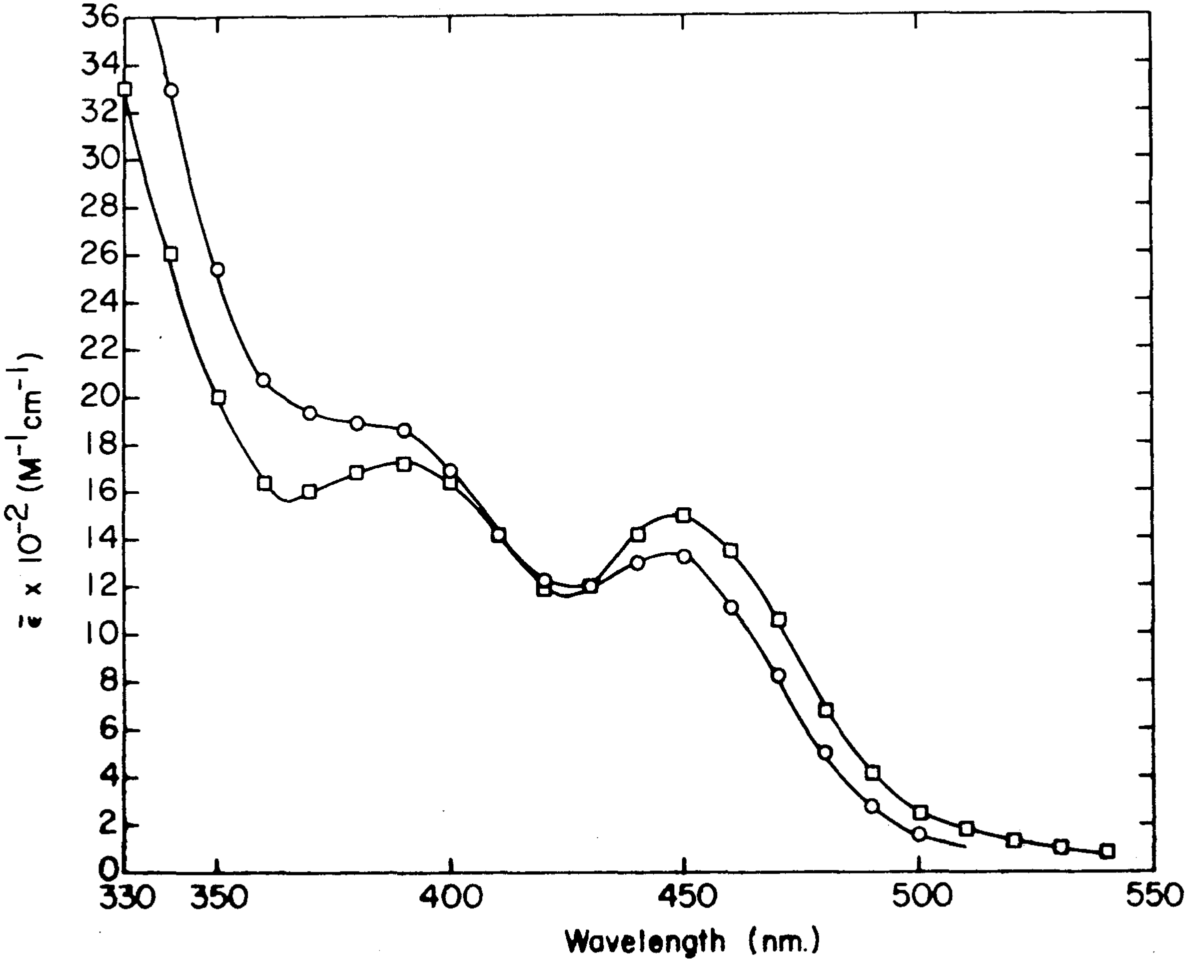

Figure 3. Preliminary spectral study to determine wavelengths to be used in the study. $C_2H_5Co(dmgH)_2H_2O$ only (squares), and $C_2H_5Co(dmgH)_2H_2O$ and $1.0x10^{-3}$M $Fe(CN)_6{}^{4-}$ (circles)

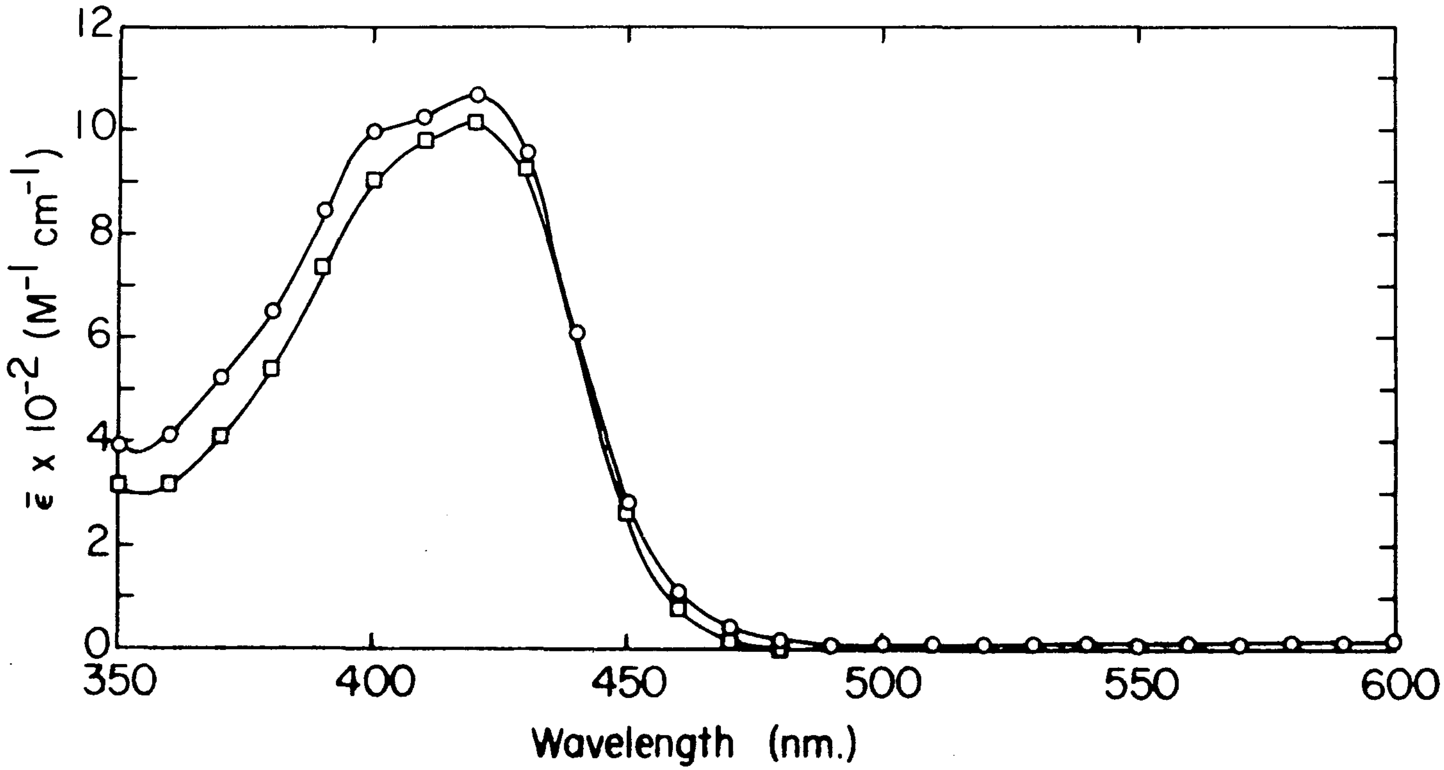

Figure 4. Preliminary spectral study to determine wavelengths to be used in the study. $Fe(CN)_6{}^{3-}$ only (squares) and $C_2H_5Co(dmgH)_2H_2O$ and $1.1x10^{-2}M$ $Fe(CN)_6{}^{3-}$ (circles)

$$\%C_2H_5Co(dmgH)_2L = \frac{KL}{1+KL} \times 100 \qquad (13)$$

and the percent of uncomplexed cobaloxime by

$$\%C_2H_5Co(dmgH)_2H_2O = \frac{1}{1+KL} \times 100 \qquad (14)$$

In the solutions where the ligand did not absorb strongly in the region where the cobaloxime has its characteristic bands (λ = 350 nm to λ = 480 nm) the ligands, $Co(CN)_6{}^{3-}$, $Cr(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$, were in large excess over the cobaloxime. For the $Fe(CN)_6{}^{3-}$ product spectrum in which the ligand absorbs (λ = 420, ε = 1050 $M^{-1}cm^{-1}$), equimolar concentrations of $Fe(CN)_6{}^{3-}$ and $C_2H_5Co(dmgH)_2H_2O$ were used. The method of producing the product spectrum was the same as for the other ligands.

All equilibria were established rapidly and could be conveniently followed using stopped-flow methods. A Durrum stopped-flow spectrophotometer equipped with a D-131 Amplifier was used in all experiments. The absorbance signal was displayed on the Tektronix 564B storage oscilloscope. The log amplifier was calibrated such that a ten volt response would correspond to one absorbance unit. With the use of the sensitivity control and the off-set control any absorbance region between 0 and 2.0 absorbance units would be expanded from 1.0 absorbance units full scale to 0.025 absorbance units full scale.

All solutions were allowed to come to temperature in the drive syringes of the stopped-flow. The drive syringes were immersed in a constant temperature waterbath.

Spectrophotometric determination of the equilibrium constant was accomplished concurrently with the kinetic measurement for the ligands studied. The kinetic measurements furnished information as to the change in absorbance from the time of mixing to the equilibrium time. A second method of determination of the equilibrium constant was employed for $Fe(CN)_6^{4-}$. Solutions of known ligand concentrations were allowed to equilibrate with $C_2H_5Co(dmgH)_2H_2O$ in volumetric flasks in a constant temperature waterbath. The absorbance was read at four wavelengths of interest; 460 nm, 450 nm, 430 nm, and 420 nm, on a Cary Model 12 recording spectrophotometer.

The pH of the solutions was measured with a Beckman expanded scale pH meter. The pH meter was calibrated with standardized solutions with an ionic strength of unity at pH 4, 7, and 11.

Treatment of Data

All kinetic runs were analyzed according to Eq 15

$$\ln |D_t - D_\infty| = \ln |D_0 - D_\infty| - k_{obs} t \tag{15}$$

where D_t is the absorbance at time t, D_0 is the initial absorbance and D_∞ is the absorbance after the reaction is complete.

The experimental rate constants, k_{obs}, were fit to Eq 16 using a linear least squares program.

$$k_{obs} = k_f[L] + k_r \tag{16}$$

Where deviation from linearity was observed in graphs of Eq 16, the experimental rate constants were fit to Eq 17

$$k_{obs} = \frac{A[L] + B}{1 + C[L]} \tag{17}$$

The equilibrium constant was determined from the kinetic runs by Eq 18

$$\varepsilon^* = \frac{\Delta D}{[Co]_o b} = (\varepsilon_o - \varepsilon_1) - \varepsilon^* \frac{1}{K[L]_o} \tag{18}$$

where $\Delta D = D_o - D_t$, ε_o and ε_1 are the molar absorptivities of the aquocobaloxime and the ligated cobaloxime respectively, $[Co]_o$ is the total cobaloxime concentration, K the equilibrium constant of interest, b the path length, and L the ligand being studied.

The equilibrium constant for $Fe(CN)_6^{4-}$ was determined by an alternate method according to Eq 19

$$\bar{\varepsilon} = \frac{D_t - \varepsilon_L[L]b}{[Co]_o b} = \varepsilon_1 + \frac{\varepsilon_o - \bar{\varepsilon}}{[L]_o} \frac{1}{K} \tag{19}$$

where $\bar{\varepsilon}$ is a newly defined quantity and ε_L is the ligand's molar absorptivity.

The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, were calculated by Eq 20

$$k = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{+\Delta S^\ddagger/R} \tag{20}$$

The form of Eq 20 for Eq 16, $k_{obs} = k_f[L] + k_r$, used was Eq 21

$$k_{obs} = \{\frac{kT}{h} e^{-\Delta H_f^{\ddagger}/RT} e^{+\Delta S_f^{\ddagger}/R}\} [L] + \{\frac{kT}{h} e^{-\Delta H_r^{\ddagger}/RT} e^{+\Delta S_r^{\ddagger}/R}\} \tag{21}$$

which was computer fit by a non-linear least squares program (28) with an IBM 360 computer.

Calculated observed rate constants were obtained from the program for the activation parameters, Eq 21. The individual rate constants were recalculated using the calculated k_{obs} and compared to the experimental k_{obs}.

RESULTS

The product spectra of the cyanobridged complexes are given in Figure 5 for the ligands $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, and in Figure 6 for $Fe(CN)_6^{3-}$. The spectrum of the $Cr(CN)_6^{3-}$ and $C_2H_5Co(dmgH)_2H_2O$ reaction, Figure 7, is not representative of the bridged complex due to a second reaction occurring. The second reaction is approximately a factor of 10 slower than the first. The spectrum of the final product is similar to the spectrum of the $C_2H_5Co(dmgH)_2CN^-$ as shown in Figure 7. The aquation of $Cr(CN)_6^{3-}$ (22) is known to be more rapid than the other ligands studied. Also the free cyanide produced is known to form a more stable complex (4) than the $Cr(CN)_6^{3-}$ with the $C_2H_5Co(dmgH)_2H_2O$. No experiments were directed at studying this second reaction. The equilibrium constants used to calculate the product spectra, Eqs 13 and 14, were the kinetic values at 25.0°: $Co(CN)_6^{3-}$ ($K = 72.8\ M^{-1}$), $Fe(CN)_6^{4-}$ ($K = 28.1\ M^{-1}$), $Fe(CN)_6^{3-}$ ($K = 78.2\ M^{-1}$).

The Reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$

The kinetics of the reaction were studied as a function of concentration, pH, and temperature. The concentration range of $Co(CN)_6^{3-}$ studied was $2.0\times10^{-3}M$ to $8.0\times10^{-2}M$ with $C_2H_2Co(dmgH)_2H_2O$ in the concentration range $1.55\text{-}3.9\times10^{-4}M$. The observed rates are given in Table 5 for 18.0°, Table 6 for 25.0°, and Table 7 for 35.0°. The data were fit to Eq 16, $k_{obs}=k_f[L]+k_r$,

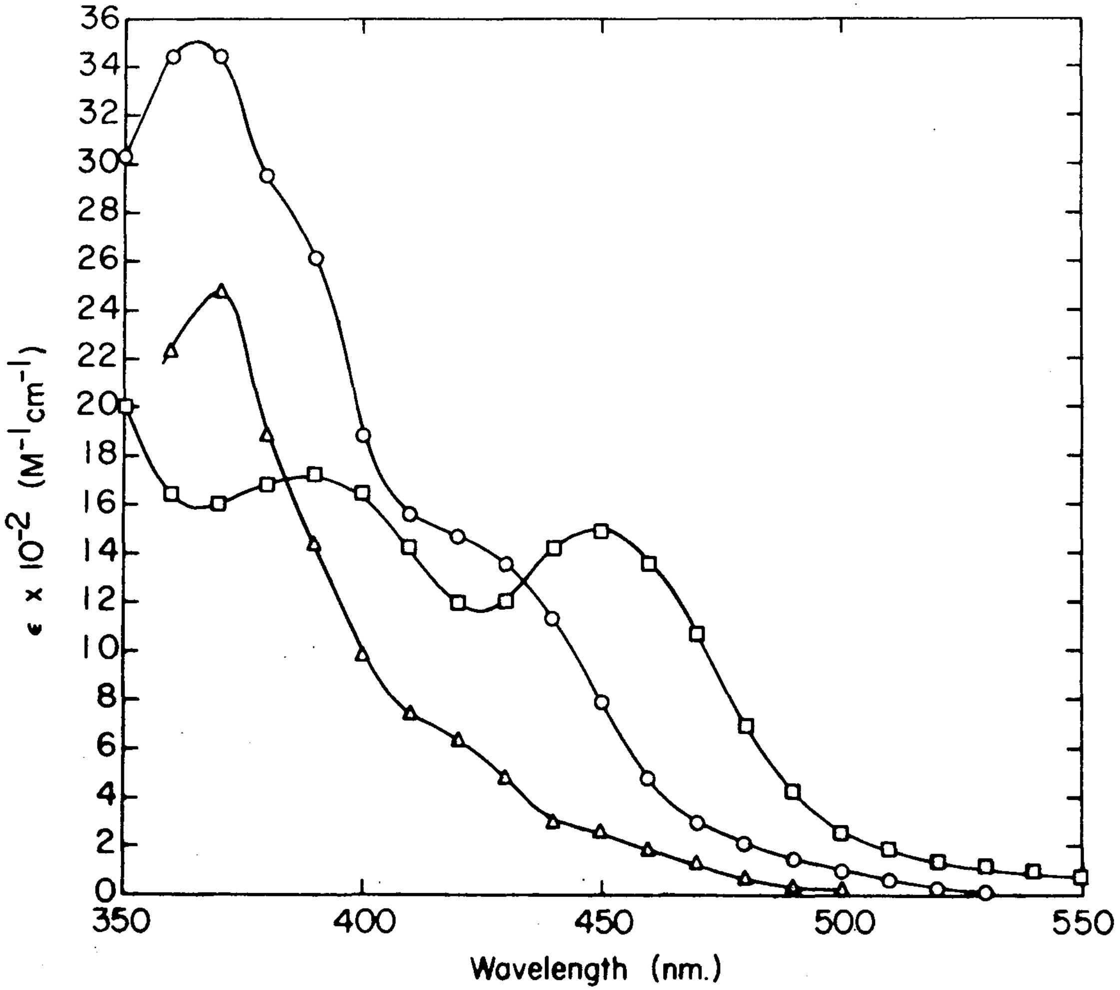

Figure 5. Product spectra of $C_2H_5Co(dmgH)_2H_2O$ (squares), $C_2H_5Co(dmgH)_2NC$-$Co(CN)_5^{3-}$ (triangles), and $C_2H_5Co(dmgH)_2NC$-$Fe(CN)_5^{4-}$ (circles)

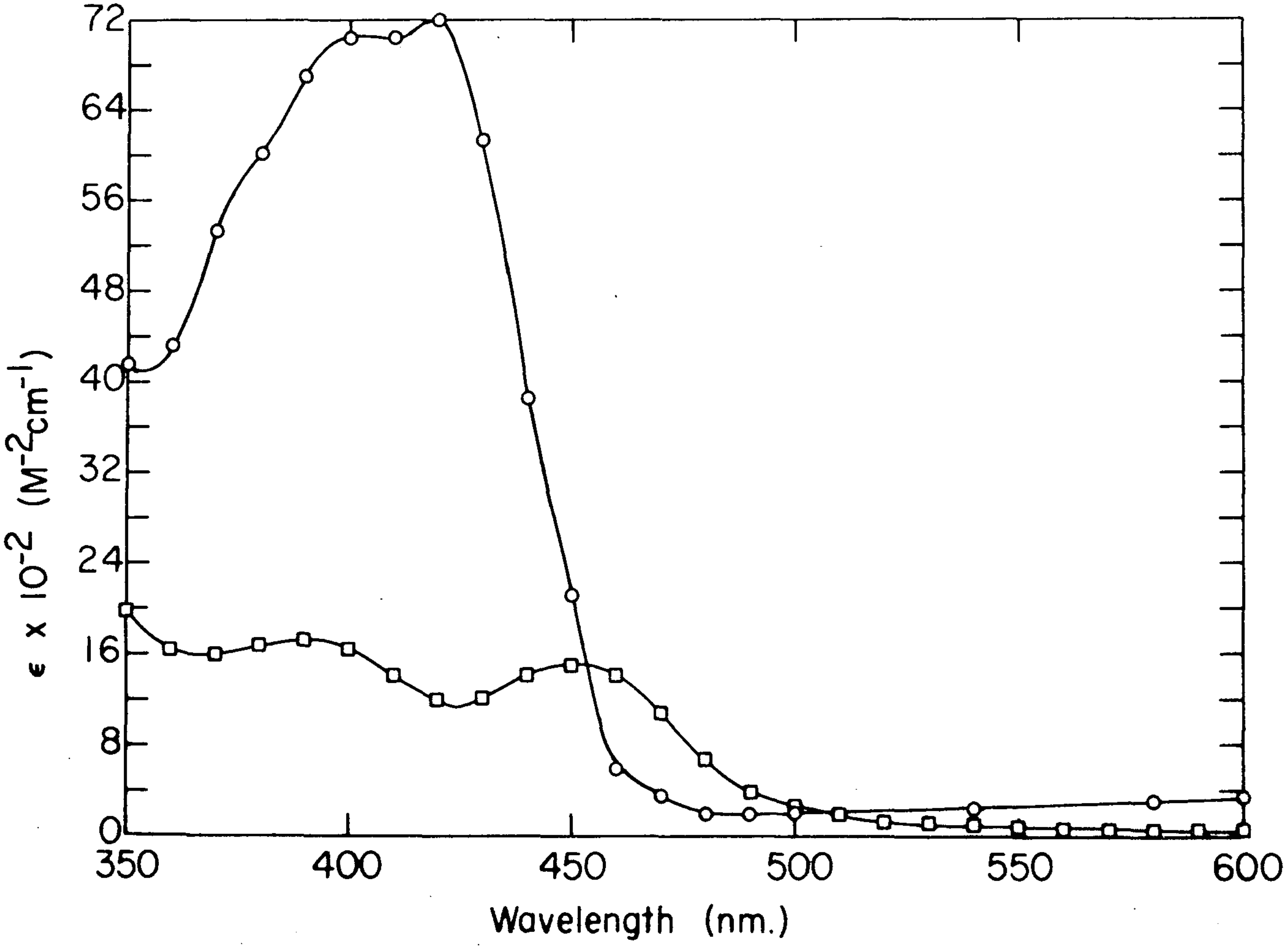

Figure 6. Product spectra of $C_2H_5Co(dmgH)_2H_2O$ (squares) and $C_2H_5Co(dmgH)_2$ $NC\text{-}Fe(CN)_5{}^{3-}$ (circles)

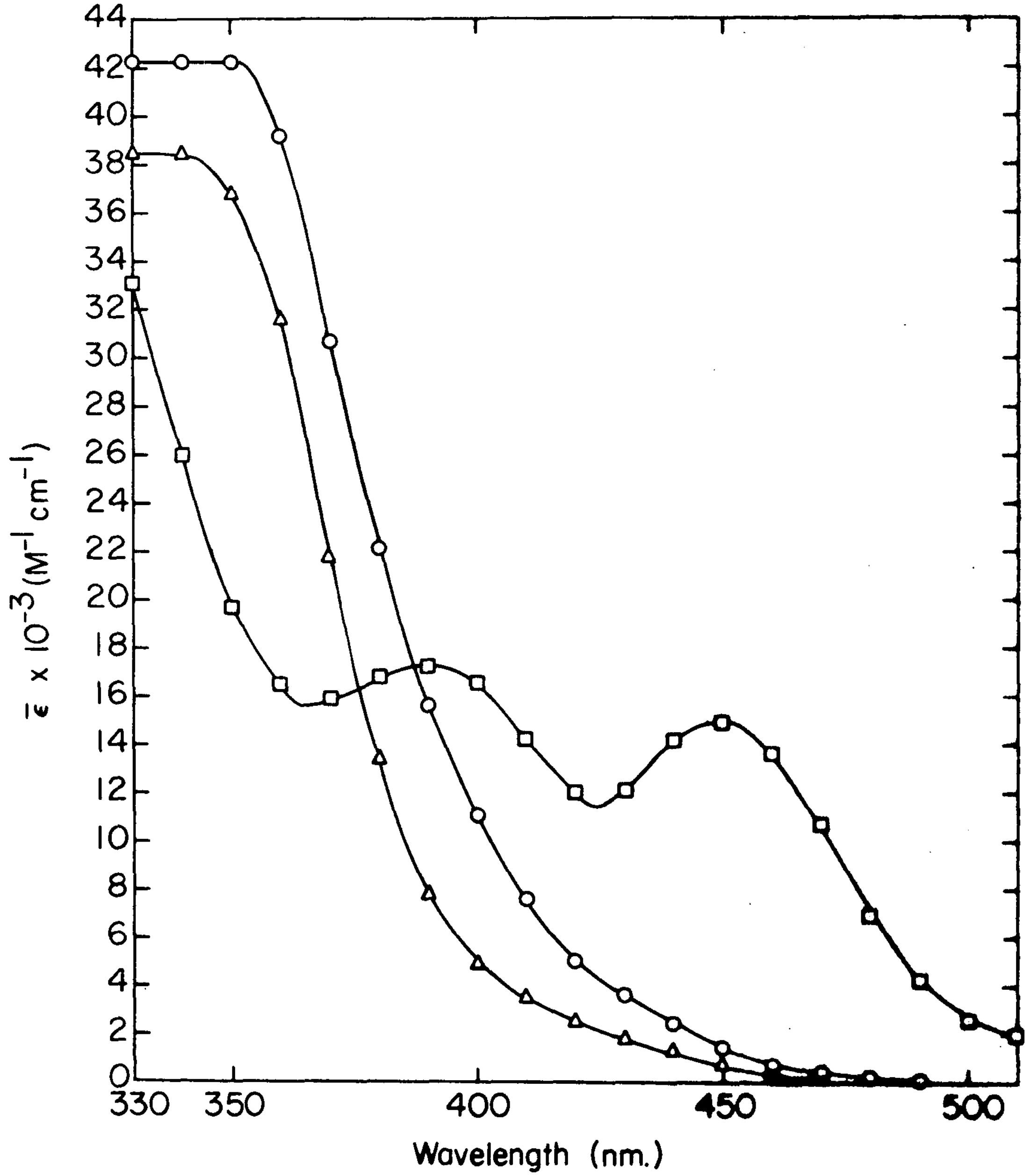

Figure 7. Product spectra of $C_2H_5Co(dmgH)_2H_2O$ (squares), "$C_2H_5Co(dmgH)_2NC\text{-}Cr(CN)_5^{3-}$" final product (circles), and $C_2H_5Co(dmgH)_2CN^-$(triangles)

Table 5. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$ at 18.0°[a]

$[Co(CN)_6^{3-}]$(M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	146	9.1	9.1
0.0068	188	10.4	10.1
0.0100	240	11.4	11.8
0.0250	375	19.8	19.7
0.0500	396	32.6	32.9

[a] μ=1.0M, λ=450nm, $[C_2H_5Co(dmgH)_2H_2O]=2.41\times10^{-4}$M.

[b] Obtained from treatment of data at the three temperatures by Eq 21.

Table 6. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$ at 25.0°[a]

$[Co(CN)_6^{3-}]$ (M)	ε^* ($M^{-1}sec^{-1}$)	k_{obs} (sec^{-1})	k_{obs}^{calc} (sec^{-1})[b]
0.0020[c]	134	15.3	14.6
0.0025[d]	141	17.1	15.1
0.0030[c]	201	15.3	15.4
0.0047[c]	302	16.8	17.0
0.0050[d]	260	17.4	17.1
0.0065[d]	321	20.0	18.7
0.0076[c]	403	18.0	19.5
0.0100[d]	401	21.7	21.2
0.0135[c]	504	23.2	24.5
0.0150[d]	501	29.2	25.8
0.0160[c]	554	26.2	26.2
0.0250[d]	621	32.8	33.6
0.0293[c]	706	38.6	37.8
0.0800[d]	681	84.8	79.2

[a] μ=1.0M, λ=450nm.

[b] k_{obs}^{calc} obtained from computer treatment of Eq 21.

[c] $[C_2H_5Co(dmgH)_2H_2O] = 1.55\times10^{-4}$M.

[d] $[C_2H_5Co(dmgH)_2H_2O] = 2.60\times10^{-4}$M.

Table 7. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$ at 35.0°[a]

$[Co(CN)_6^{3-}]$ (M)	ε^* ($M^{-1}cm^{-1}$)	k_{obs} (sec^{-1})	k_{obs}^{calc} (sec^{-1})[b]
0.005	187	41.4	40.3
0.010	307	46.4	47.9
0.025	401	71.0	70.6
0.035	440	85.0	85.8

[a] μ=1.0M, λ=450nm, $[C_2H_5Co(dmgH)_2H_2O]$ = 3.9×10^{-4}M.

[b] Calculated according to Eq 21.

to determine the dependence of the rate upon [L]. This dependence is shown in Figure 8 for 18.0°, 25.0°, and 35.0°. The value of k_f was obtained from the slope and k_r the intercept. The results are given in Table 8.

In the pH range 4.4 to 10.3 there was no dependence of the rate on H^+ as shown in Table 9. In this pH range the only species present was $Co(CN)_6^{3-}$ (29).

The equilibrium constant was determined spectroscopically according to Eq 18 from ΔD values of the kinetic runs. The plot of Eq 18 is given in Figure 9 for 18.0°, Figure 10 for 25.0°, and Figure 11 for 35.0°. At 18.0° the spectroscopic K_{eq}, $K_{eq}^{spec} = 83.0 \pm 11.4M^{-1}$, is compared to the kinetic value, $K_{eq}^{kin} = 79.3 \pm 3.6M^{-1}$. For 25.0° $K_{eq}^{spec} = 70.8 \pm 6.0M^{-1}$ is compared to $K_{eq}^{kin} = 72.8 \pm 3.6M^{-1}$. For 35.0° $K_{eq}^{spec} = 107 \pm 17M^{-1}$ is compared to $49.0 \pm 2.4M^{-1}$. These constants are given in Table 8.

The activation parameters for the reaction were calculated according to Eq 21. The forward rate, k_f, was found to have $\Delta H_f^{\ddagger} = 10.5 \pm 1.2$ kcal mol^{-1} and $\Delta S_f^{\ddagger} = -9.8 \pm 4.1$ cal°K^{-1}mol^{-1}. The reverse rate had $\Delta H_r^{\ddagger} = 16.2 \pm 1.0$ kcal mol^{-1} and $\Delta S_r^{\ddagger} = 1.0 \pm 3.4$ cal°K^{-1}mol^{-1}.

The Reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$

The kinetics of the reaction were studied as a function of ligand concentration, pH, and temperature. The concentration range of $Fe(CN)_6^{3-}$ studied was 5.0×10^{-3}M to 1.0×10^{-1}M with

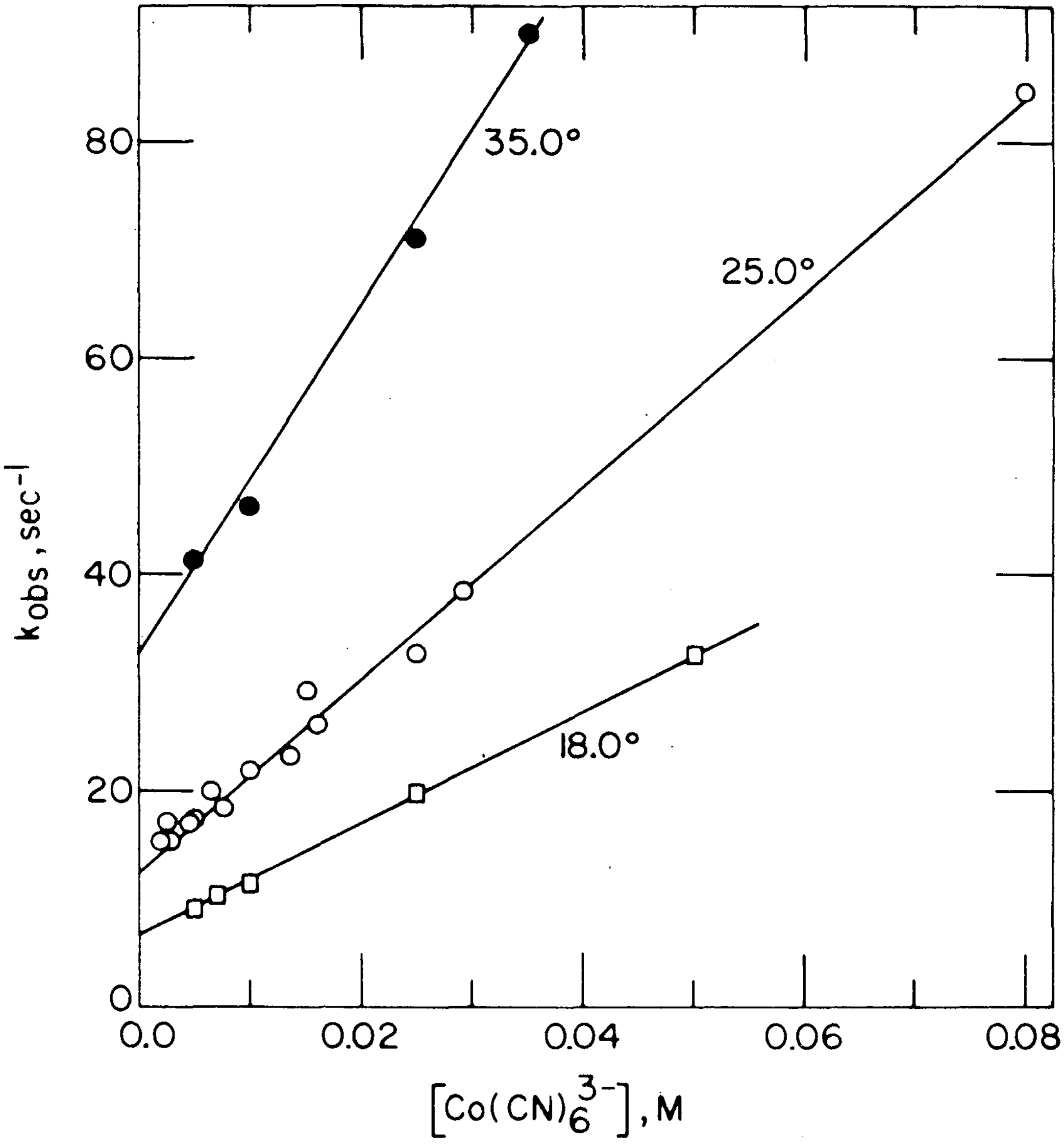

Figure 8. The dependence of k_{obs} on ligand concentration for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$

Table 8. Kinetic and equilibrium constants for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$

Temp	k_f $(M^{-1}sec^{-1})$	k_f^{calc} $(M^{-1}sec^{-1})^a$	$k_r(sec^{-1})$	$k_r^{calc}(sec^{-1})^a$	$K_{kin}{}^b$	$K_{kin}^{calc\,a}$	$K_{spec}{}^c$
18.0°	522±8	528	6.6±0.2	6.5	79.3±3.6	81.3	83.0±11.4
25.0°	896±15	828	12.3±0.4	12.9	72.8±3.6	64.1	84.6±7.3
35.0°	1510±35	1516	30.9±0.8	32.7	49.0±2.4	46.3	107±17

[a] Computer computation for Eq 21.

[b] $K_{kin} = k_f/k_r$.

[c] K_{spec} is the K obtained spectrophotometrically according to Eq 18.

Table 9. Dependence of k_{obs} on pH for the reaction of $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ with $C_2H_5Co(dmgH)_2H_2O$ at 25.0° and μ = 1.0M

$Co(CN)_6^{3-}$[a]		$Fe(CN)_6^{3-}$[b]		$Fe(CN)_6^{4-}$[c]	
pH	$k_{obs}(sec^{-1})$	pH	$k_{obs}(sec^{-1})$	pH	$k_{obs}(sec^{-1})$
4.4	24.2	3.7	44.7	5.9	1.95
8.0	25.0	6.4	41.7	6.8	1.95
10.3	23.2	11.2	43.5	7.5	1.97
				10.4	1.96

[a] $[Co(CN)_6^{3-}]$ = 0.0110M, $[C_2H_5Co(dmgH)_2H_2O]$ = 2.9×10^{-4}M.

[b] $[Fe(CN)_6^{3-}]$ = 0.0300M, $[C_2H_5Co(dmgH)_2H_2O]$ = 6.2×10^{-4}M.

[c] $[Fe(CN)_6^{4-}]$ = 0.0100M, $[C_2H_5Co(dmgH)_2H_2O]$ = 2.0×10^{-4}M.

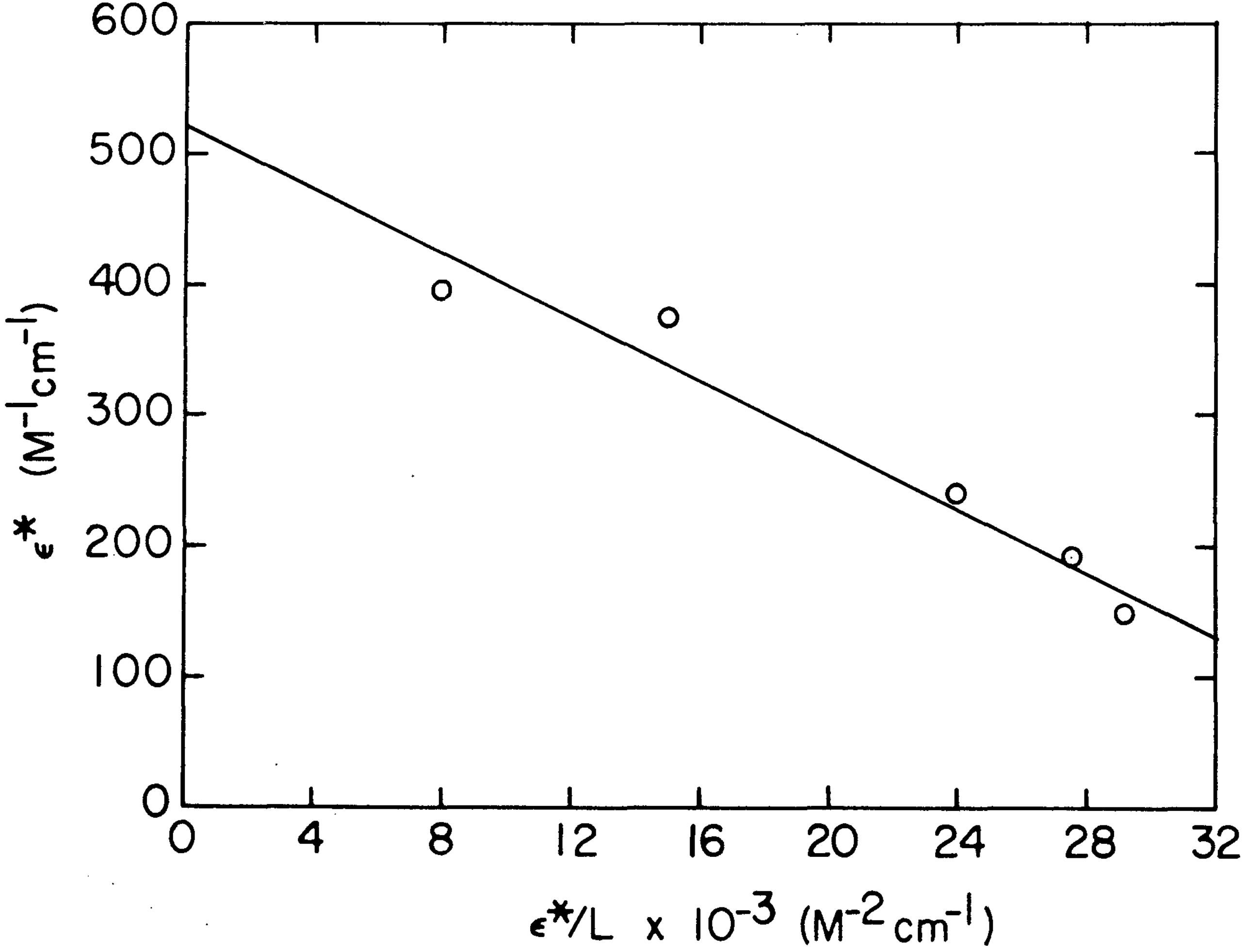

Figure 9. Plot for the calculation of K_{eq} from the absorbance changes in the kinetic runs, ΔD, for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6{}^{3-}$ at 18.0°C, resulting in $K_{eq} = 83.0 \pm 11.4\ M^{-1}$ and $\varepsilon_1 = 972 \pm 37 M^{-1}cm^{-1}$

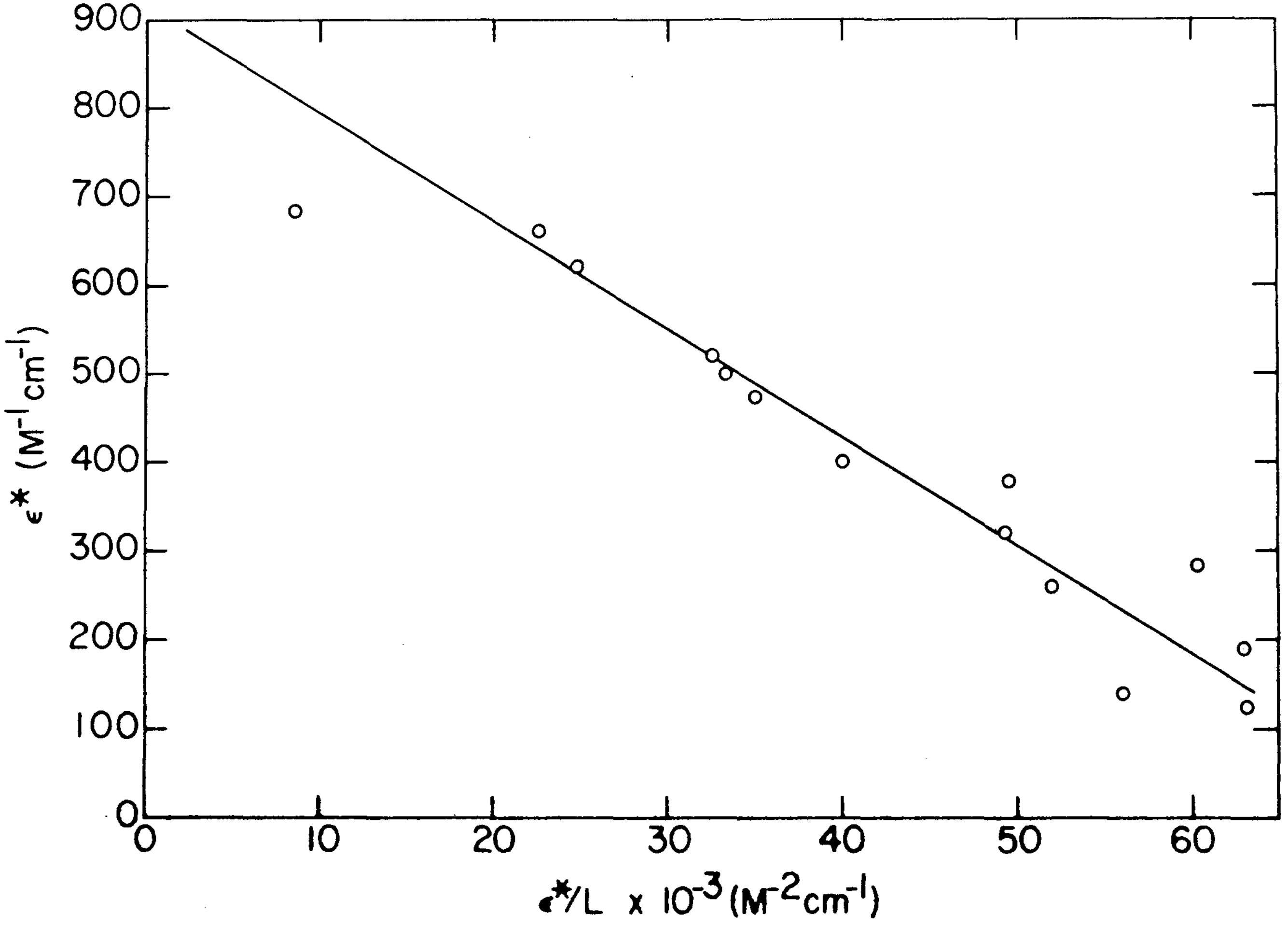

Figure 10. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$ at 25.0°C yielding $K_{eq} = 84.6 \pm 7.3\ M^{-1}$ and $\varepsilon_1 = 585 \pm 48\ M^{-1}cm^{-1}$

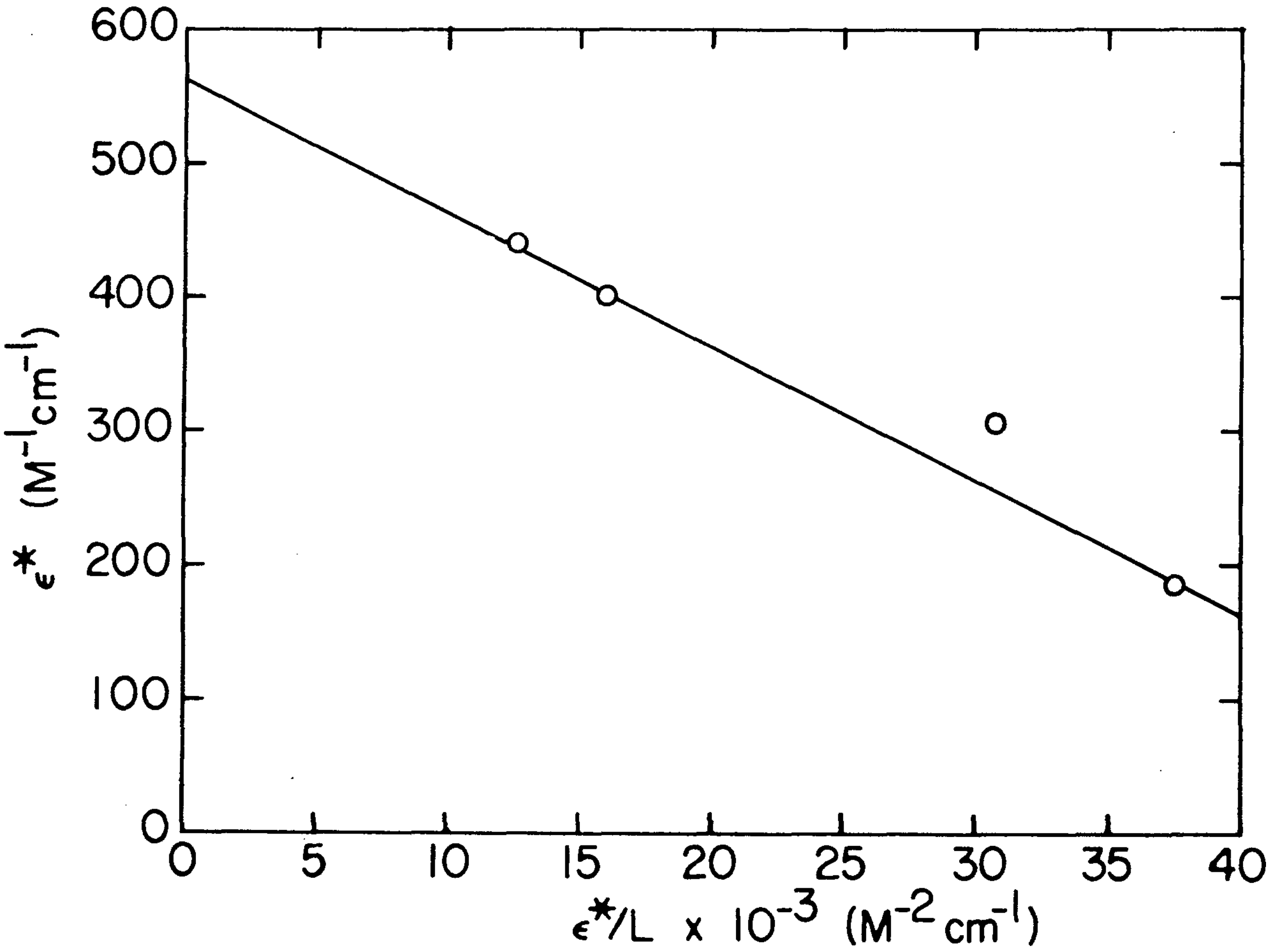

Figure 11. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Co(CN)_6^{3-}$ at 35.0°C yielding $K_{eq} = 107\underline{+}17\ M^{-1}$ and $\varepsilon_1 = 931\underline{+}39\ M^{-1}sec^{-1}$

the $C_2H_5Co(dmgH)_2H_2O$ in the range $2.5\text{-}3.0\times10^{-4}$M. The observed rate constants are given in Table 10 for 18.5°, Table 11 for 25.0°, and Table 12 for 35.0°. The data did not deviate from Eq 16, $k_{obs} = k_f[L] + k_r$. This is shown in Figure 12 for 18.5°, 25.0°, and 35.0°. The values for k_f and k_r, the slope and intercept respectively of Figure 12, are given in Table 13. As shown in Table 9 there was no dependence on pH in the region pH 3.7 to pH 11.2. In this pH range $Fe(CN)_6^{3-}$ is the only ligand species present (30).

The equilibrium constant was spectroscopically determined from ΔD values of the kinetic runs. The value of $K_{eq}(18.5°) = 106 \pm 7\ M^{-1}$ was determined spectroscopically by Figure 13. This compares to $K_{eq}(18.5°) = 112 \pm 13\ M^{-1}$ determined kinetically. The value of $K_{eq}(25.0°) = 99.9 \pm 11.6\ M^{-1}$ was obtained from Figure 14 for the spectroscopic determination. This compares to a value of $K_{eq}(25.0°) = 78 \pm 10\ M^{-1}$ obtained kinetically. The value of $K_{eq}(35.0°) = 96.8 \pm 7.9\ M^{-1}$ was determined spectroscopically by Figure 15. This compares to the kinetic value of $K_{eq}(35.0°) = 62 \pm 4\ M^{-1}$.

The values of the forward and reverse rates and the equilibrium constants for the three temperatures of the study are given in Table 13.

The activation parameters for the reaction were calculated according to Eq 21. The forward rate, k_r, had $\Delta H_f^{\ddagger} = 10.4\pm0.8$ kcal mol^{-1} and $\Delta S_f^{\ddagger} = -10.0\pm2.6$ e.u. The reverse rate, k_r, had

Table 10. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$ at 18.5°[a]

$[Fe(CN)_6^{3-}]$ (M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	88	8.1	8.6
0.0100	131	11.4	11.7
0.0200	171	18.7	18.0
0.0300	183	24.5	24.2
0.0400	208	30.9	30.5
0.0500	218	36.1	36.7

[a] μ=1.0M, λ=590nm, $[C_2H_5Co(dmgH)_2H_2O] = 2.6\times10^{-4}$M.

[b] Value obtained from computer treatment of Eq 21.

Table 11. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$ at 25.0°[a]

$[Fe(CN)_6^{3-}]$ (M)	ε^* ($M^{-1}cm^{-1}$)	k_{obs} (sec^{-1})	k_{obs}^{calc} (sec^{-1})[b]
0.0050[c]	52	15.5	15.7
0.0065[d]	65	17.7	17.1
0.0100[c]	78	21.9	20.4
0.0150[c]	94	24.5	25.1
0.0175[d]	96	28.5	27.5
0.0200[c]	104	32.2	29.8
0.0360[d]	108	46.0	44.9
0.0400[c]	111	50.1	48.7
0.0500[c]	115	60.2	58.1
0.0535[d]	-	56.3	61.4
0.0710[d]	123	79.5	78.0
0.0885[d]	-	89.3	94.5
0.1000[c]	115	108.0	105.3

[a] μ=1.0M, λ=590nm.

[b] Calculated from Eq 21 by computer.

[c] $[C_2H_5Co(dmgH)_2H_2O] = 4.0\times10^{-4}M$.

[d] $[C_2H_5Co(dmgH)_2H_2O] = 2.5\times10^{-4}M$.

Table 12. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$ at 35.0°[a]

$[Fe(CN)_6^{3-}]$(M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0040	52	35.8	36.6
0.0075	83	42.9	42.7
0.0150	116	53.7	55.6
0.0225	127	69.2	68.6
0.0300	143	81.9	81.5

[a] μ=1.0M, λ=590nm, $[C_2H_5Co(dmgH)_2H_2O]$ = 3.6×10^{-4}M.

[b] Computer fit of Eq 21.

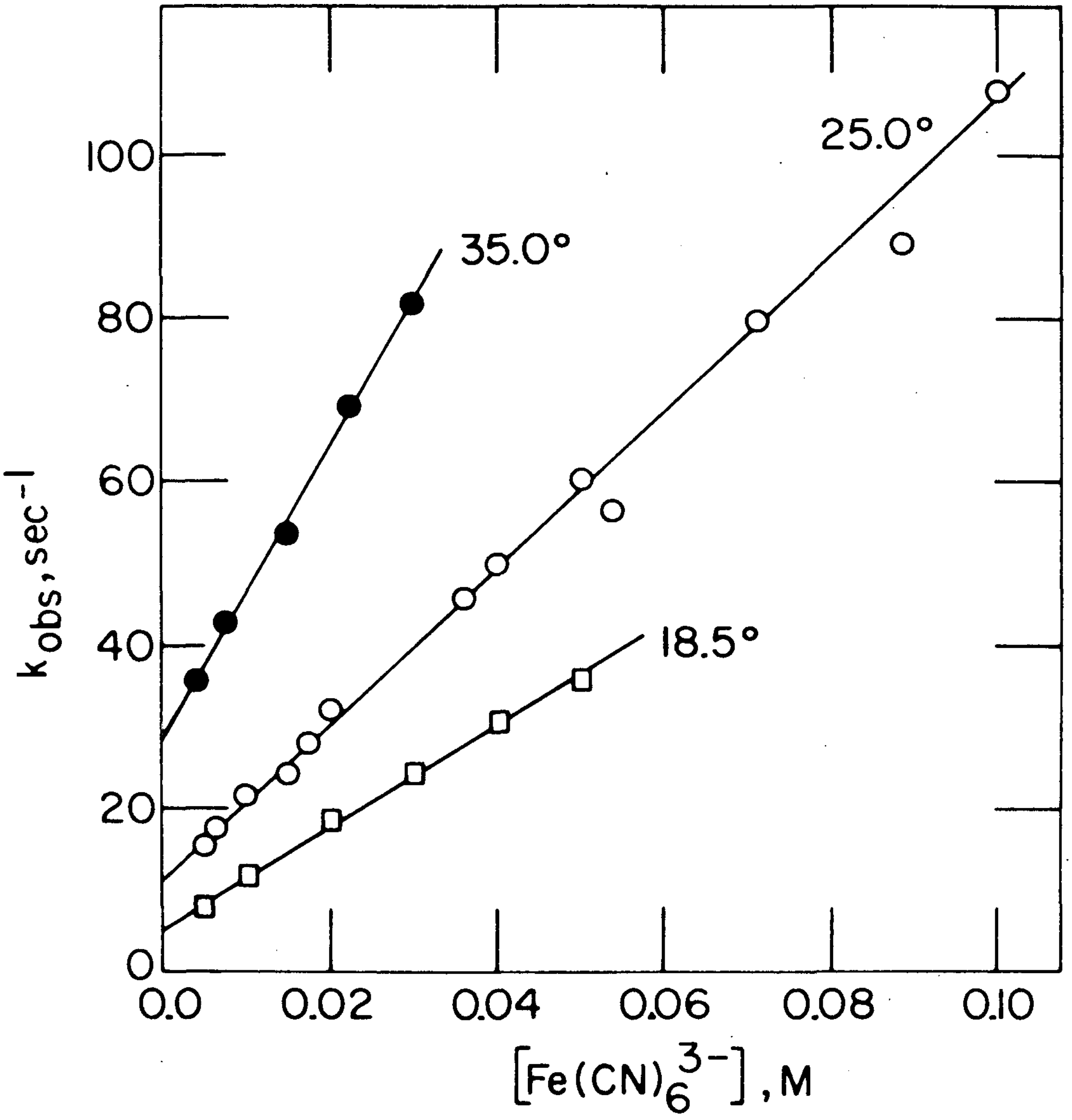

Figure 12. The dependence of k_{obs} on ligand concentration for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$

Table 13. Kinetic and equilibrium constants for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$

Temp	k_f $(M^{-1}sec^{-1})$	k_f^{calc} $(M^{-1}sec^{-1})$[a]	$k_r(sec^{-1})$	k_r^{calc} (sec^{-1})[a]	K_{kin}[b]	K_{kin}^{calc}[a]	K_{spec}[c]
18.5°	621±16	624	5.5±0.5	5.5	112±13	114	106±7
25.0°	926±24	943	11.9±1.2	11.0	78±10	86.1	99.9±11.6
35.0°	1770±52	1727	28.5±1.0	29.7	62±4	58.2	96.8±7.9

[a] Calculated from computer fit of Eq 21.

[b] $K_{kin} = k_f/k_r$.

[c] K_{spec} determined from Eq 18.

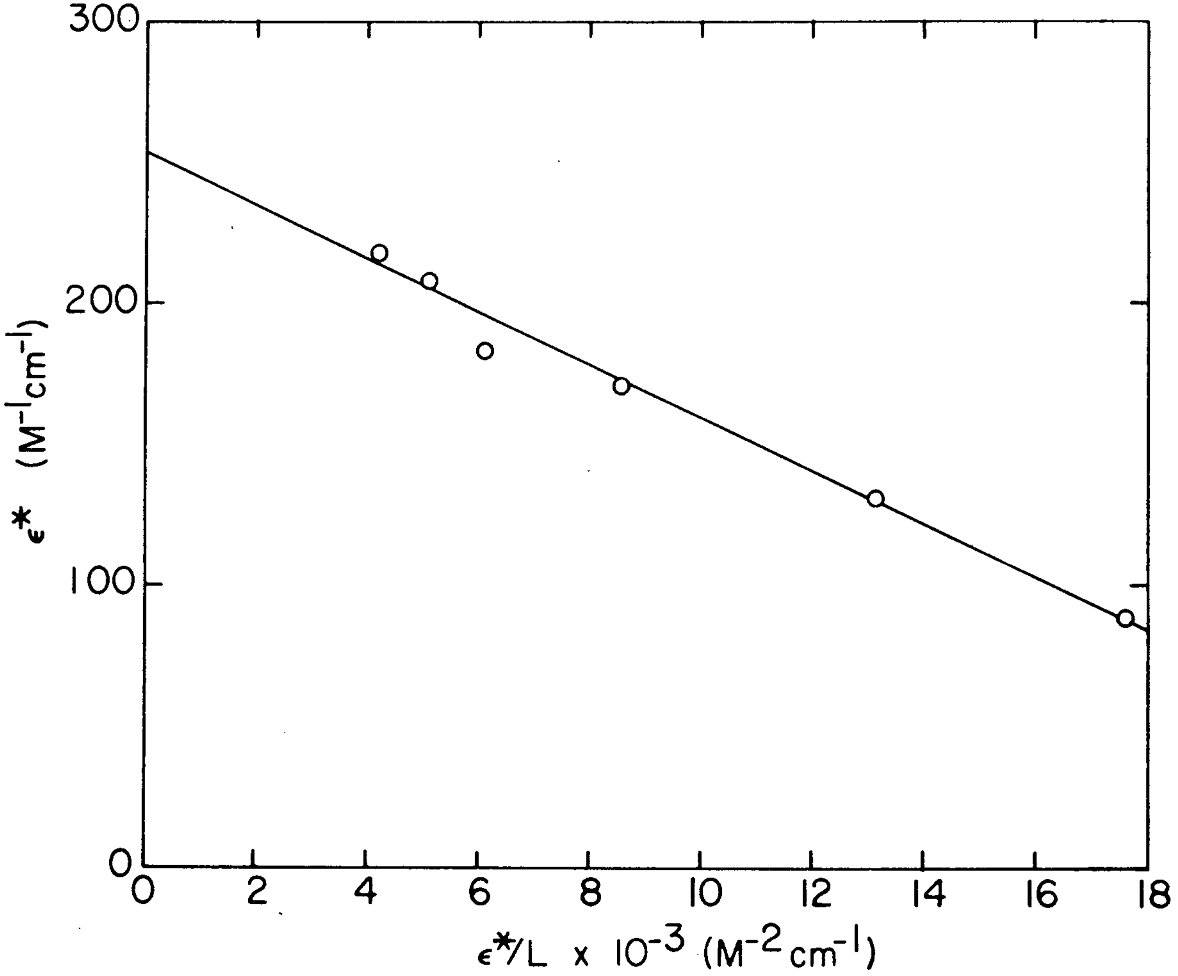

Figure 13. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$ at 18.5°C yielding $K_{eq} = 106\pm7\ M^{-1}$ and $\varepsilon_1 = 253\pm7\ M^{-1}cm^{-1}$

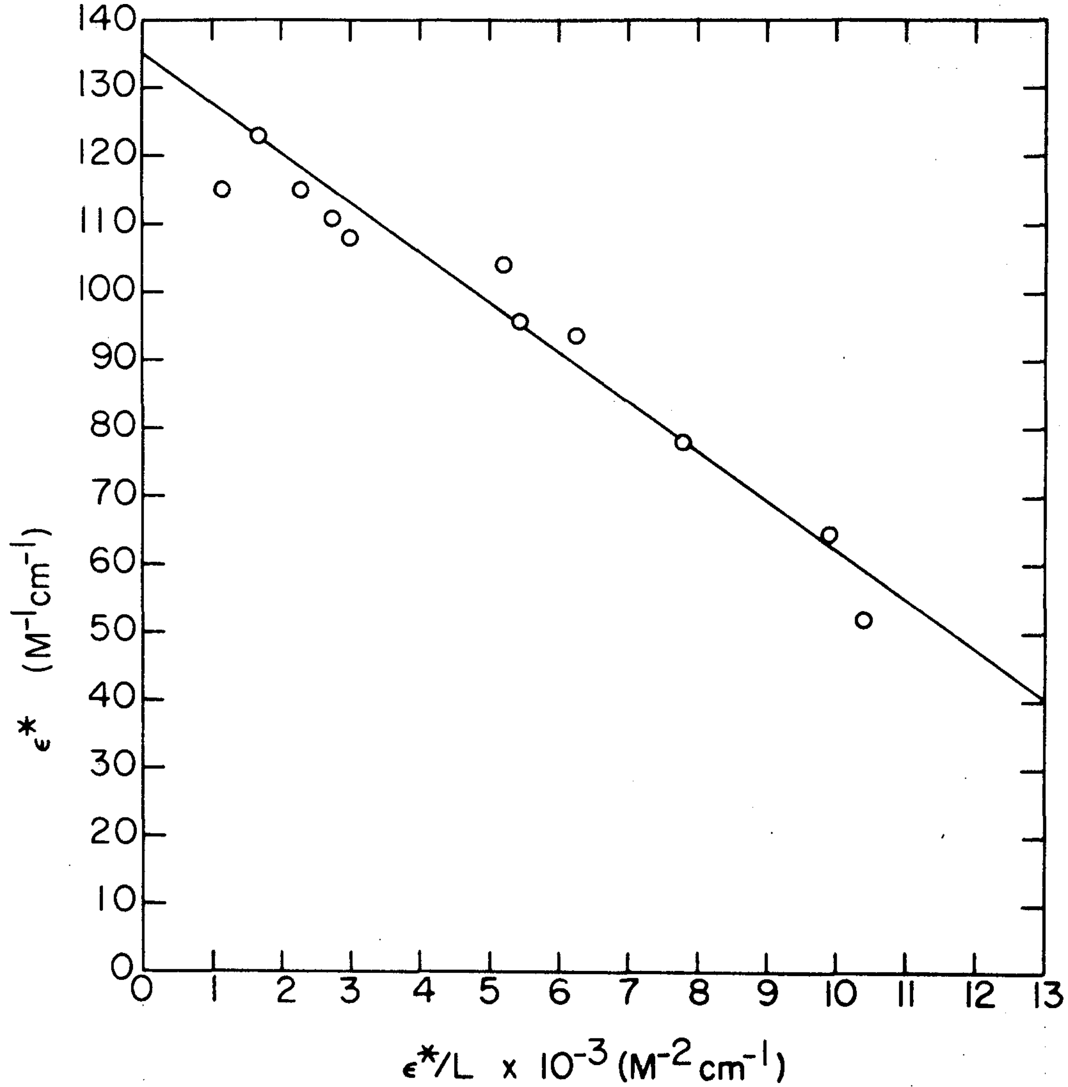

Figure 14. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$ at 25.0°C yielding $K_{eq} = 99.9 \pm 11.6$ M^{-1} and $\varepsilon_1 = 156 \pm 3$ $M^{-1}cm^{-1}$

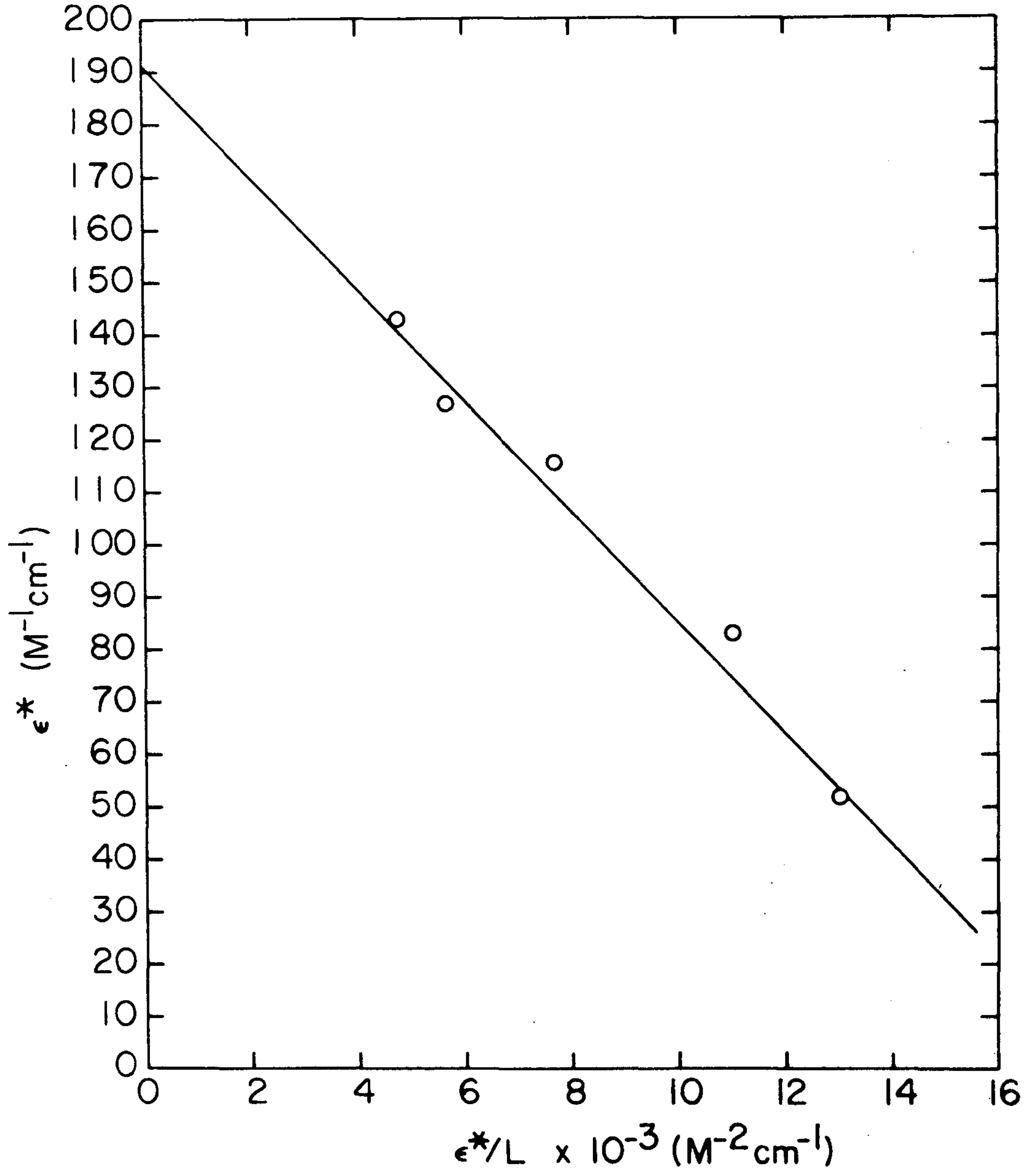

Figure 15. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{3-}$ at 35.0°C yielding $K_{eq} = 96.8 \pm 7.9$ M^{-1} and $\varepsilon_1 = 191 \pm 8$ $M^{-1}cm^{-1}$

$\Delta H_r^{\ddagger} = 17.7 \pm 0.9$ kcal mol^{-1} and $\Delta S_r^{\ddagger} = 5.4 \pm 2.8$ e.u.

The Reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$

The reaction of $Cr(CN)_6^{3-}$ with $C_2H_5Co(dmgH)_2H_2O$ was observed to proceed by two stages. The first stage of the reaction was fast and of stopped-flow speed. The second stage was slower and observable by conventional methods. The first step was assumed to be the reaction representing the cyano-bridged complex formation. The second step had a spectroscopically determined $K_{eq}(25.0°) > 10^4M^{-1}$ and may possibly be the formation of $C_2H_5Co(dmgH)_2CN^-$ (4).

The first stage of the reaction was studied as a function of concentration and temperature. The $Cr(CN)_6^{3-}$ concentration range studied was $5.0x10^{-3}M$ to $5.0x10^{-2}M$ with $C_2H_5Co(dmgH)_2H_2O$ in the range $2.5\text{-}5.7x10^{-4}M$. The observed kinetic results are given in Table 14 for 18.5°, Table 15 for 25.0°, and Table 16 for 35.0°. The data showed no deviation from Eq 16, $k_{obs} = k_f[L] + k_r$. This is shown in Figure 16 for the temperatures 18.5°, 25.0°, and 35.0°. The values for the individual rate constants for the three temperatures are given in Table 17.

The pH dependence of the reaction was not studied since the aquation of $Cr(CN)_6^{3-}$ is acid dependent (22). Any increase of acid concentration would cause decomposition of the $Cr(CN)_6^{3-}$ and lead to the presence of lower cyanochromate species.

Table 14. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$ at 18.5°[a]

$[Cr(CN)_6^{3-}]$(M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	142	11.6	11.8
0.0100	201	15.7	14.9
0.0200	238	21.4	21.2
0.0300	247	27.5	27.5
0.0400	-	32.6	33.8
0.0500	-	35.3	40.1

[a] μ=1.0M, λ=450nm, first stage of reaction only, 5.7×10^{-4}M $C_2H_5Co(dmgH)_2H_2O$.

[b] Computer fit of Eq 21.

Table 15. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$ at 25.0°[a]

$[Cr(CN)_6^{3-}]$(M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	343	20.0	19.7
0.0100	617	23.4	25.6
0.0200	768	41.0	37.6
0.0300	822	55.8	49.5
0.0400	918	73.7	61.5

[a] μ=1.0M, λ=450nm, first stage of reaction, 3.8×10^{-4}M $C_2H_5Co(dmgH)_2H_2O$.

[b] Computer fit of Eq 21.

Table 16. Kinetic data for reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$ at 35.0°[a]

$[Cr(CN)_6^{3-}]$(M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	131	43.4	44.4
0.0100	177	60.9	55.9
0.0200	219	75.3	79.0
0.0300	234	105.8	102.1
0.0400	234	112.5	125.2

[a] μ=1.0M, λ=450nm, first stage of reaction, 2.5×10^{-4}M $C_2H_5Co(dmgH)_2H_2O$.

[b] Computer fit of Eq 21.

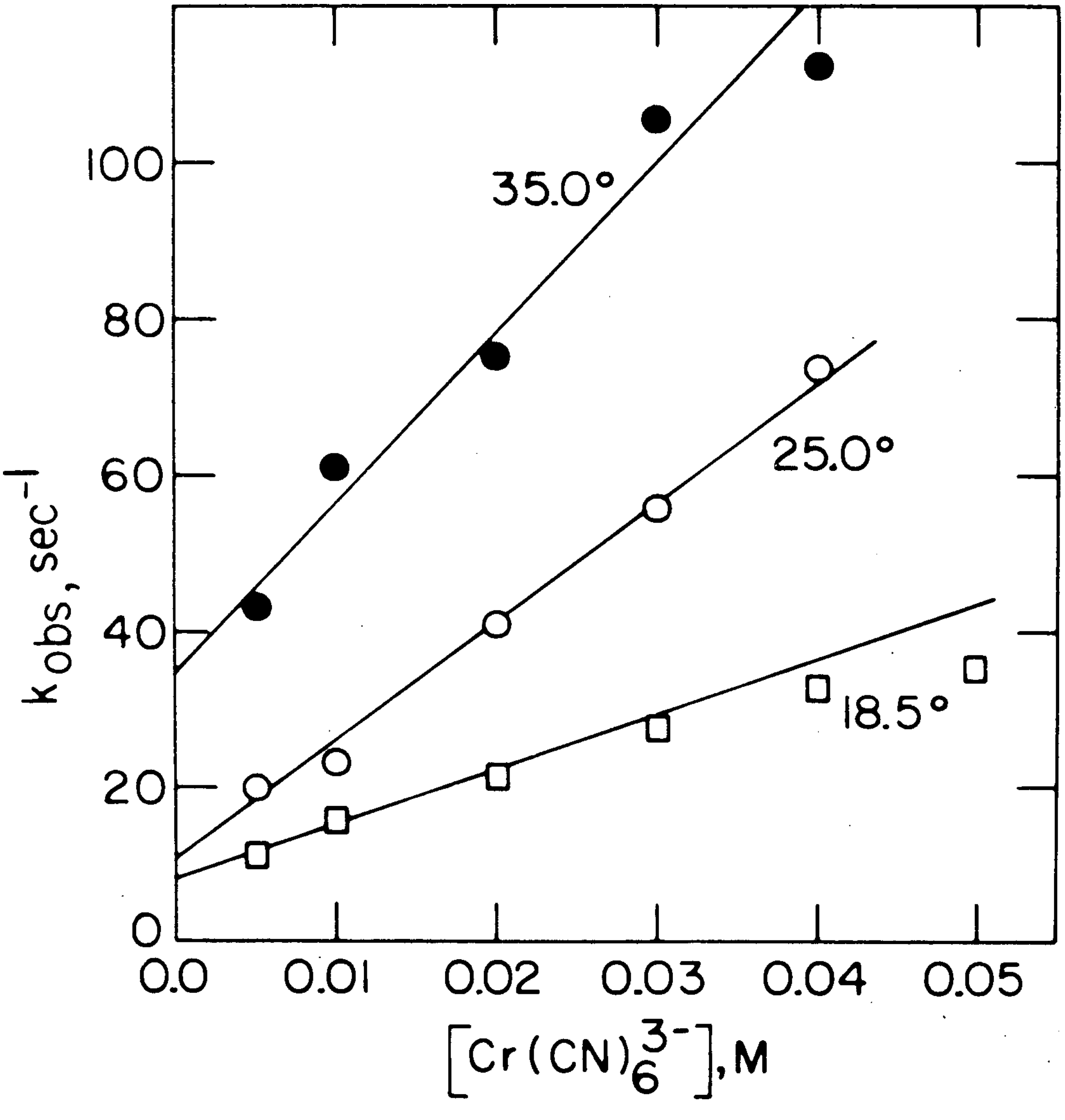

Figure 16. The dependence of k_{obs} on ligand concentration for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$

Table 17. Kinetic and equilibrium constants for $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$[a]

Temp	k_f ($M^{-1}sec^{-1}$)	k_f^{calc} ($M^{-1}sec^{-1}$)[b]	k_r (sec^{-1})	k_r^{calc} (sec^{-1})[b]	K_{kin}^{c} (M^{-1})[b]	K_{kin}^{calc} (M^{-1})[b]	K_{spec} (M^{-1})[d]
18.5°	624±27	754	8.9±0.5	7.7	70±7	98.6	190±23
25.0°	1566±70	1194	9.9±1.7	13.7	158±34	87.0	97±20
35.0°	2013±227	2309	37.3±5.6	32.8	54±14	70.3	177±4

[a] μ=1.00M, λ=450nm, first stage of reaction only.

[b] Calculated from computer fit of Eq 21.

[c] $K_{kin} = k_f/k_r$.

[d] K_{spec} obtained from Eq 18.

The spectroscopic equilibrium constant was determined from the kinetic runs. For 18.5° the spectroscopic determination from Figure 17 gave $K_{eq} = 190 \pm 23\ M^{-1}$ as compared to the kinetic value of $K_{eq} = 70 \pm 7\ M^{-1}$. For 25.0° the spectroscopic determination from Figure 18 gave $K_{eq} = 97 \pm 20\ M^{-1}$ as compared to the kinetic value of $K_{eq} = 158 \pm 34\ M^{-1}$. For 35.0° the spectroscopic determination gave $K_{eq} = 177 \pm 4\ M^{-1}$ from Figure 19 while the kinetic value was $K_{eq} = 54 \pm 14\ M^{-1}$. These values are given in Table 17.

The activation parameters fit to Eq 16, $k_{obs} = k_f[L] + k_r$, were calculated using Eq 21. The forward rate, k_f, was calculated to have $\Delta H_f^{\ddagger} = 11.5 \pm 1.9$ kcal mol^{-1} and $\Delta S_f^{\ddagger} = -6.1 \pm 6.3$ e.u. The reverse rate, k_r, had $\Delta H_r^{\ddagger} = 15.3 \pm 2.4$ kcal mol^{-1} and $\Delta S_r^{\ddagger} = -2.0 \pm 7.8$ e.u.

The Reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$

The kinetics of the reaction were studied as a function of concentration, pH, and temperature. The concentration range of $Fe(CN)_6^{4-}$ was $5.0 \times 10^{-3}M$ to $7.5 \times 10^{-2}M$ with the $C_2H_5Co(dmgH)_2H_2O$ $1.5\text{-}2.6 \times 10^{-4}M$. The observed kinetic data is given in Table 18 for 18.5°, Table 19 for 25.0°, and Table 20 for 35.0°. The data were not consistent with Eq 16, $k_{obs} = k_f[L] + k_r$, as evident from Figure 20. The data were consistent with Eq 17 as evident from the plots of $1/(k_{obs}-B)$ vs $1/[L]$ in Figure 21 for 18.5°, Figure 22 for 25.0°, and Figure 23 for 35.0°. The value of B was obtained from plots of k_{obs} vs [L], Figure 20.

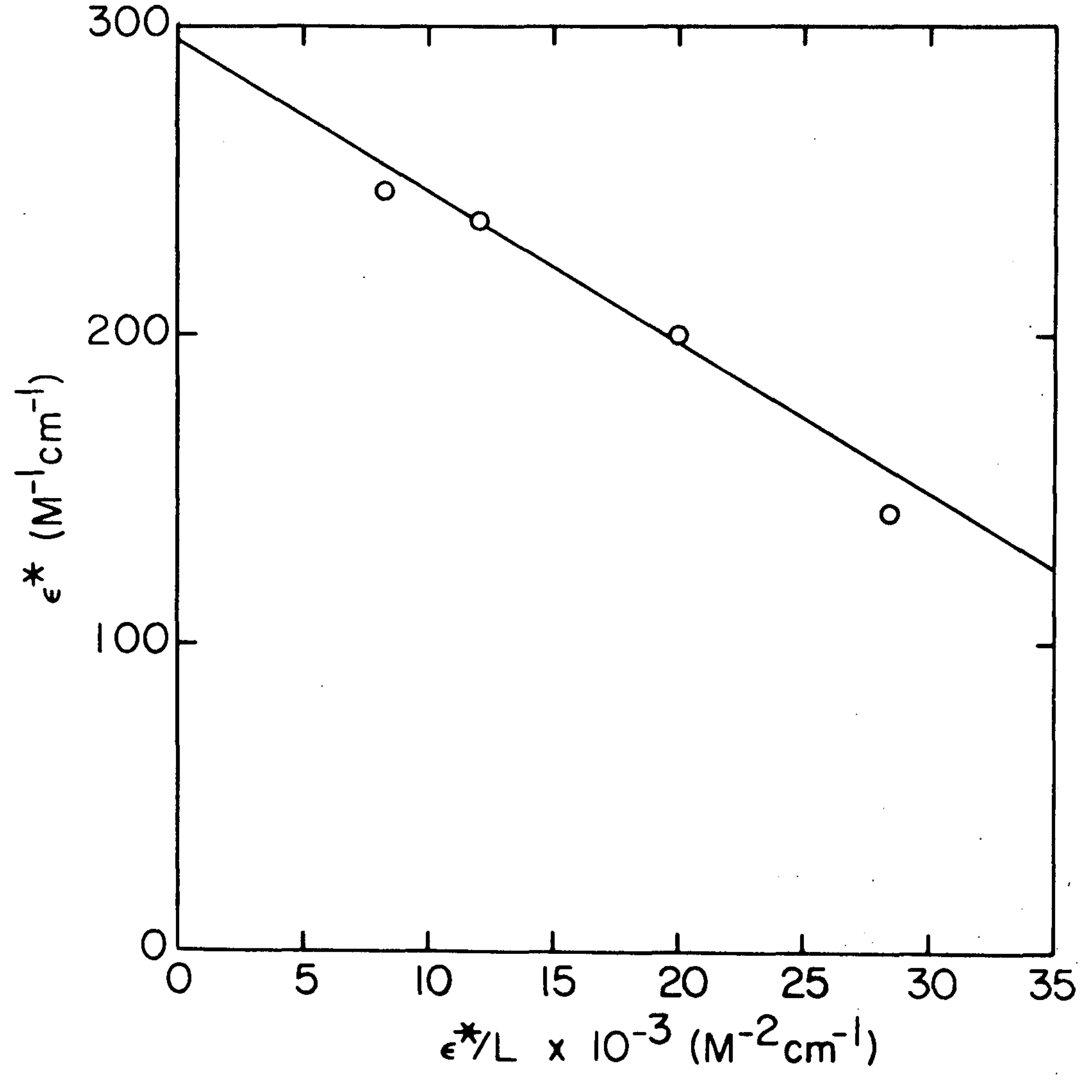

Figure 17. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$ at 18.5°C yielding K_{eq} = 190±23 M^{-1} and ε_1 = 1194±12 $M^{-1}cm^{-1}$

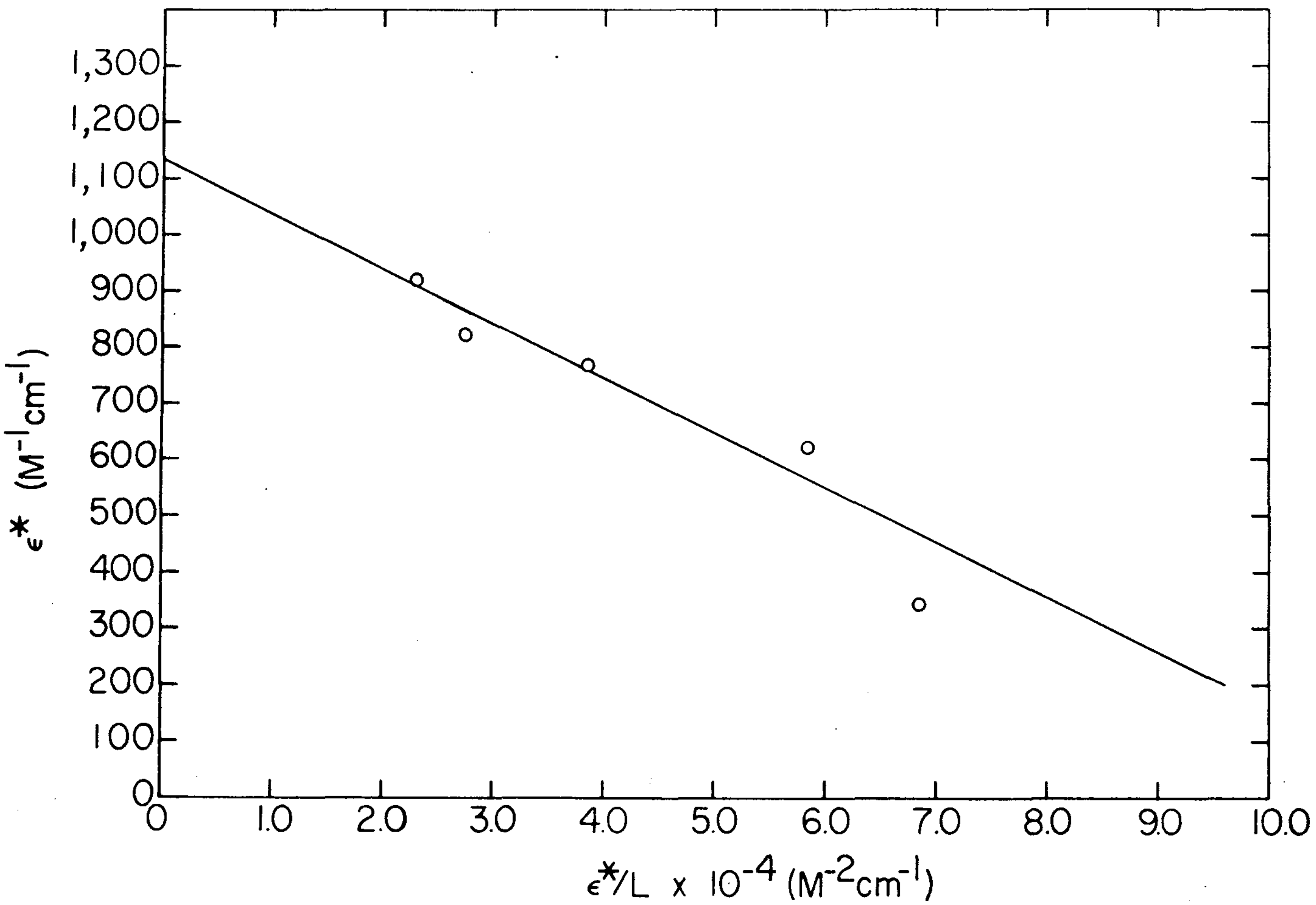

Figure 18. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$ at 25.0°C yielding K_{eq} = 97±20 M^{-1} and ε_1 = 312±101 $M^{-1}cm^{-1}$.

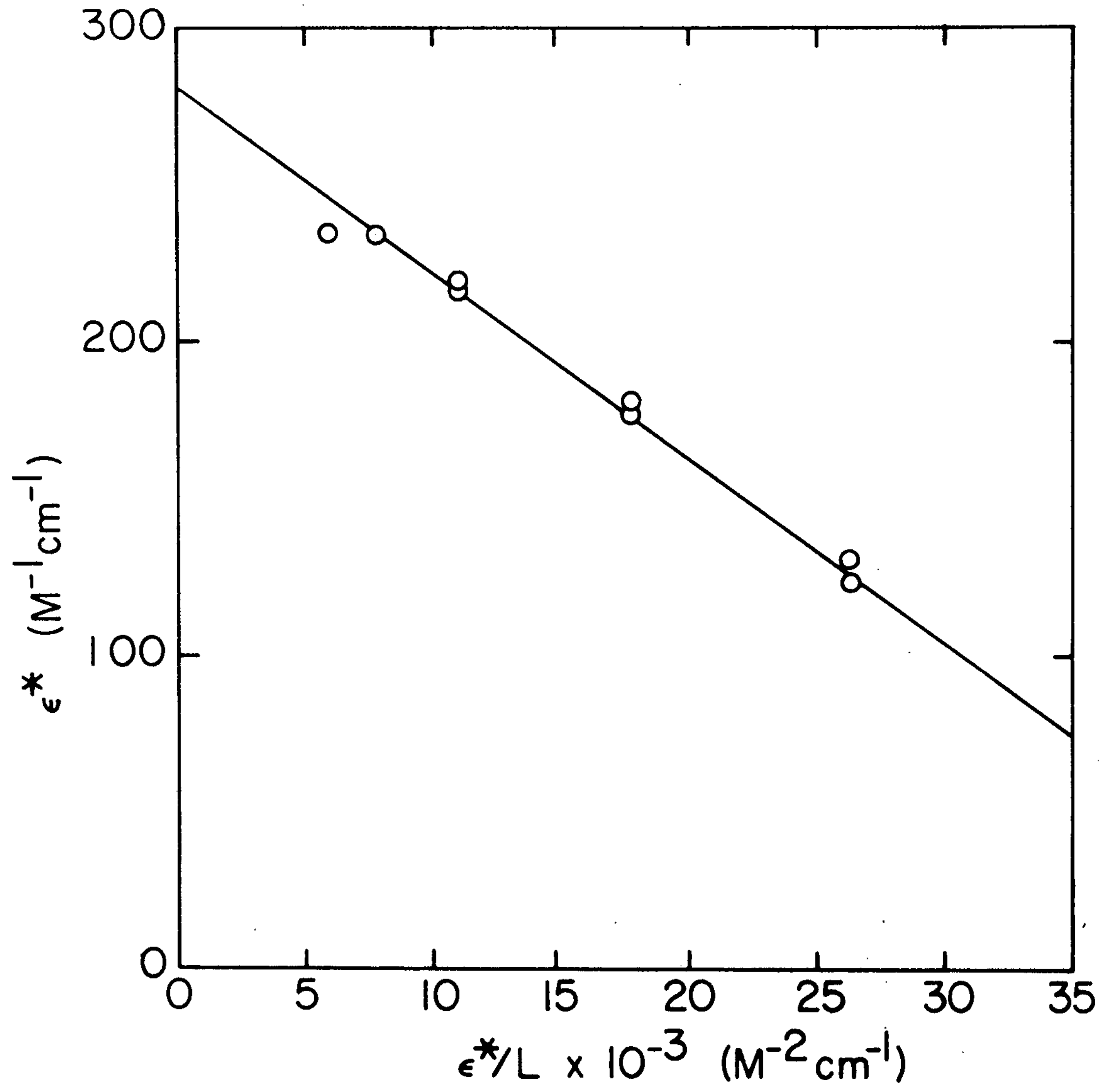

Figure 19. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Cr(CN)_6^{3-}$ at 35.0°C yielding $K_{eq} = 177 \pm 4$ M^{-1} and $\varepsilon_1 = 1211 \pm 3$ $M^{-1}cm^{-1}$

Table 18. Kinetic data for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 18.5°[a]

$[Fe(CN)_6^{4-}]$(M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0055	52	0.65	0.66
0.0110	108	1.15	1.11
0.0220	172	1.73	1.78
0.0330	216	2.20	2.24
0.0440	248	2.63	2.58
0.0550	280	2.86	2.84
0.1100[c]		6.59	

[a] μ=1.00M, λ=450nm, 2.6×10^{-4}M $C_2H_5Co(dmgH)_2H_2O$.

[b] Computer fit of Eq 8.

[c] $\mu>1.0$M.

Table 19. Kinetic data for the reaction $C_2H_5(Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 25.0°[a]

$[Fe(CN)_6^{4-}]$(M)	ε*$(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	-	1.45	1.42
0.0100	149	1.77	1.83
0.0150	188	2.31	2.24
0.0250	271	2.90	2.99
0.0350	285	3.78	3.70
0.0450	333	4.39	4.36
0.0500	326	4.77	4.67
0.0723	368	5.85	5.95

[a] μ=1.00M, λ=450nm, 1.5×10^{-4}M $C_2H_5Co(dmgH)_2H_2O$.

[b] Calculated from Eq 8.

Table 20. Kinetic data for reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 35.0°[a]

$[Fe(CN)_6^{4-}]$ (M)	$\varepsilon^*(M^{-1}cm^{-1})$	$k_{obs}(sec^{-1})$	$k_{obs}^{calc}(sec^{-1})$[b]
0.0050	54	4.1	4.1
0.0100	115	4.8	4.8
0.0200	217	6.0	6.1
0.0300	267	7.3	7.3
0.0400	298	8.4	8.3
0.0500	323	9.2	9.2
0.0750	-	11.8	11.2

[a] μ=1.00M, λ=450nm, $2.5x10^{-4}M$ $C_2H_5Co(dmgH)_2H_2O$.

[b] Computer fit of Eq 8.

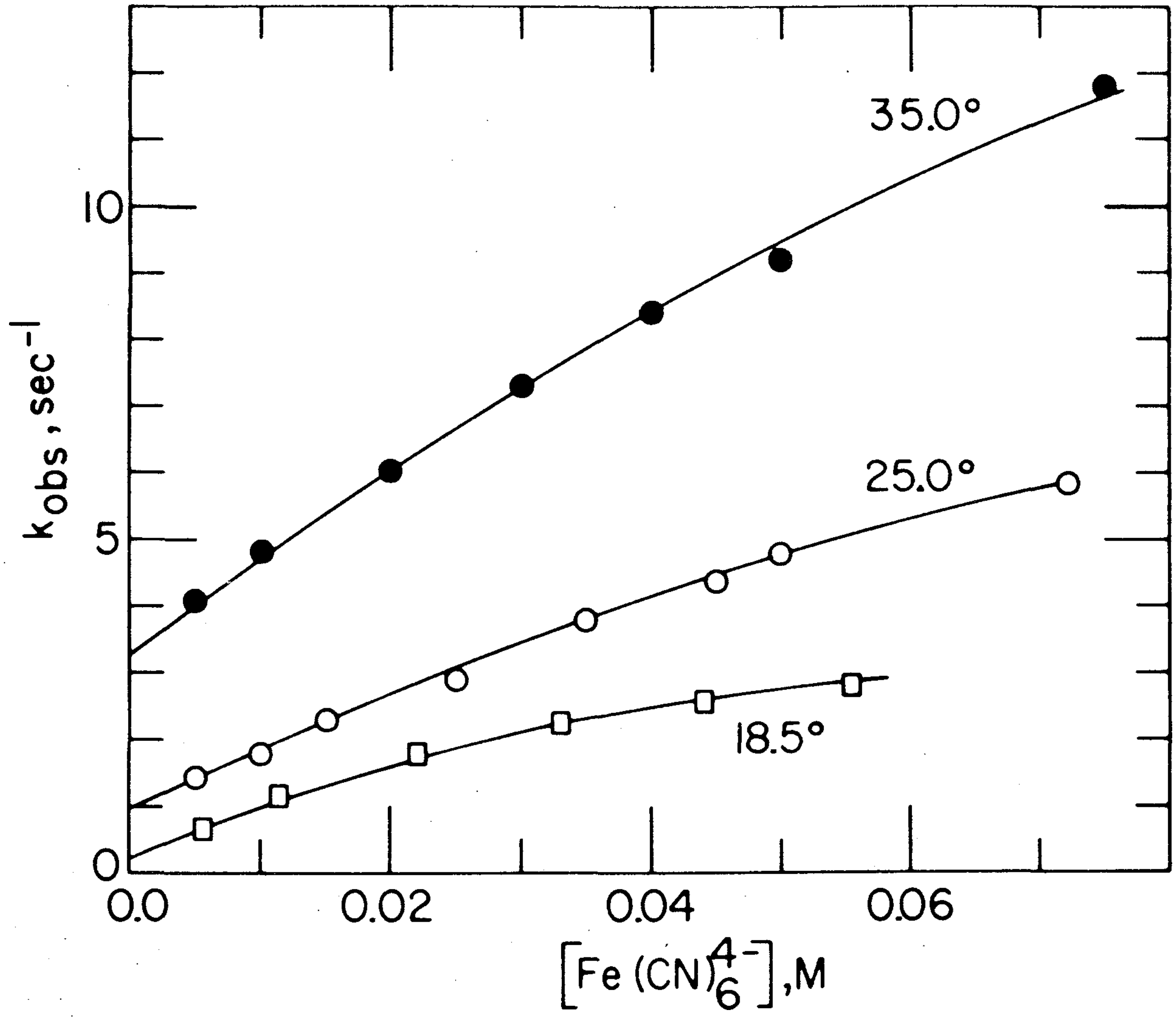

Figure 20. Plot illustrating the non-linear dependence of k_{obs} on ligand concentration for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6{}^{4-}$

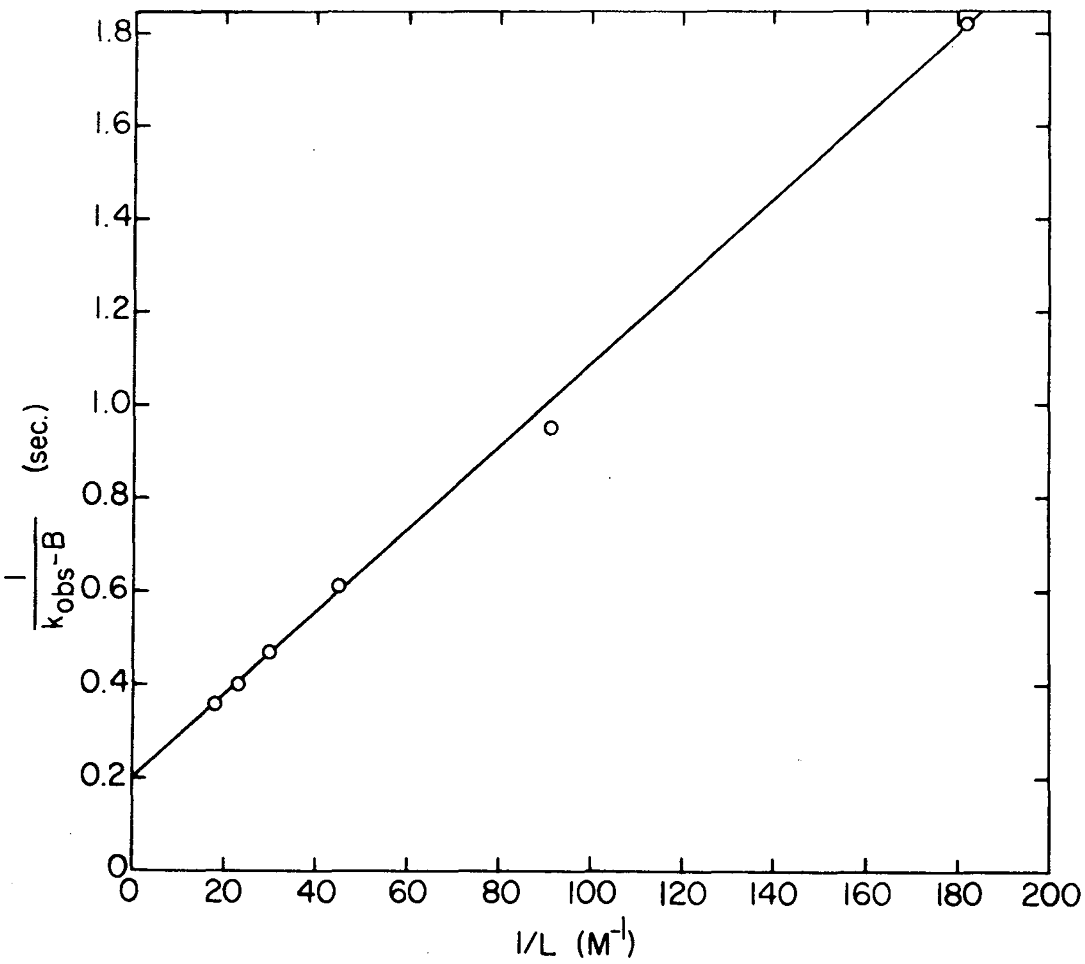

Figure 21. Plot illustrating the fit of Eq 17 to the data of the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 18.5°C

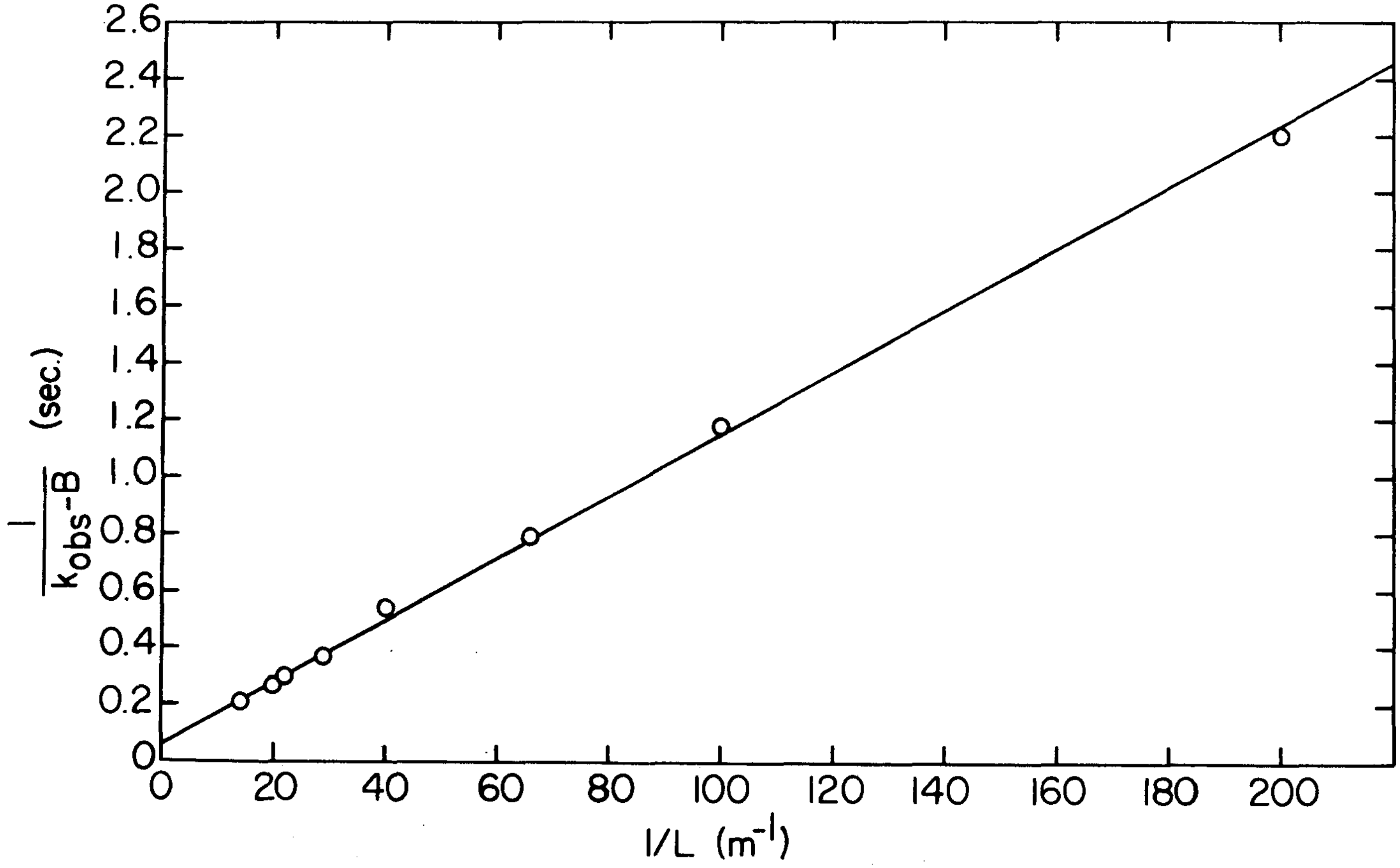

Figure 22. Plot illustrating the fit of Eq 17 to the data of the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 25.0°C

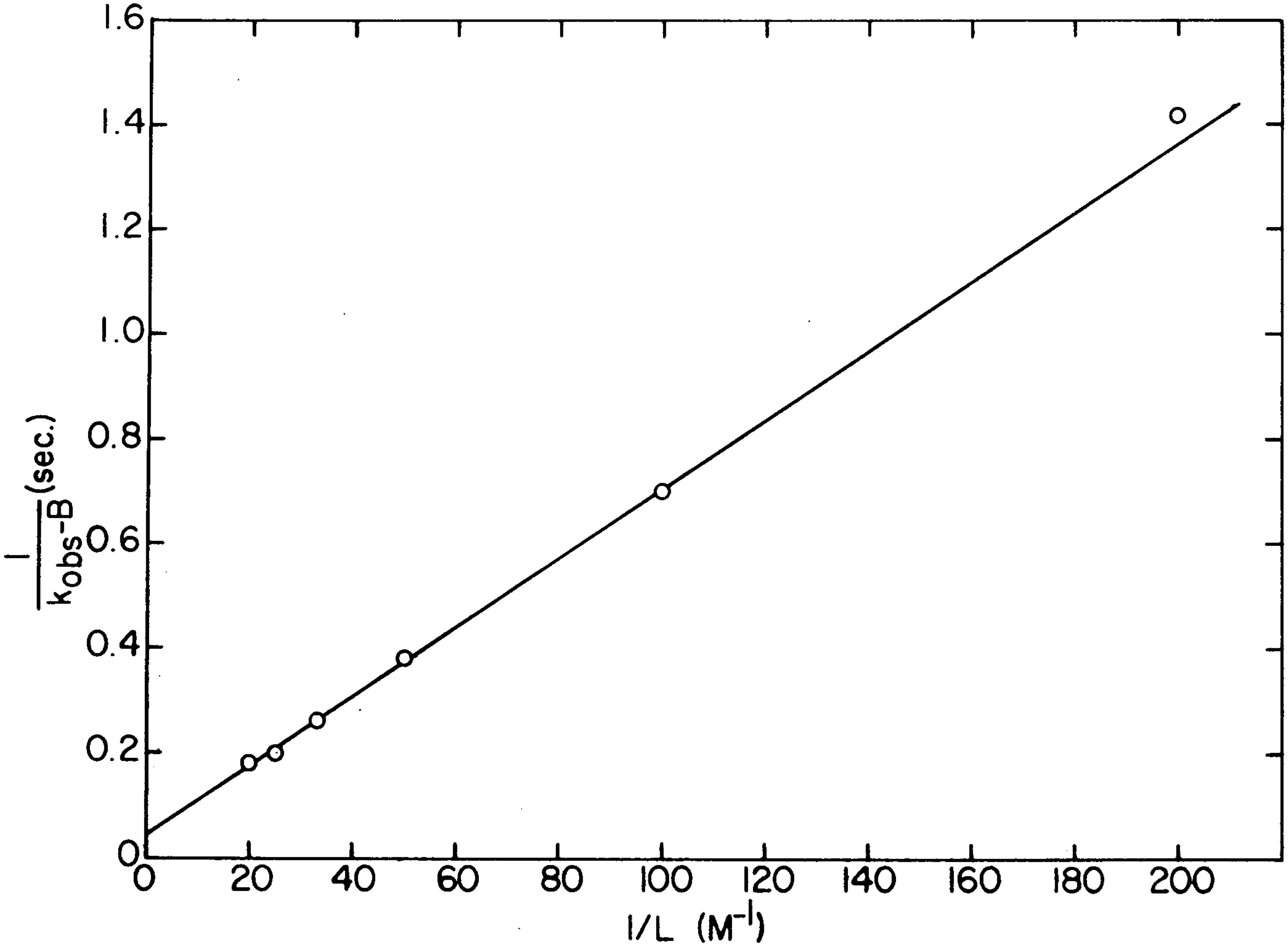

Figure 23. Plot illustrating the fit of Eq 17 to the data of the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6{}^{4-}$ at 35.0°C

At zero ligand concentrations Eq 16 and 17 simplify to $k_{obs} = k_r$ for Eq 16 and $k_{obs} = B$ for Eq 17. Therefore the intercept of the k_{obs} vs [L] plot was used as the value of B. The values obtained at the three temperatures are given in Table 21.

The pH dependence of the reaction was studied in the range pH 5.9 to pH 10.4. In this pH range the only ligand species present was $Fe(CN)_6^{4-}$ (30). There was no pH dependence as shown in Table 9.

The spectroscopic equilibrium constant was determined at the three temperatures from the absorbance change in the kinetic runs according to Eq 18. The value for 18.5°, $K_{eq} = 23.6 \pm 3.3\ M^{-1}$, was obtained from Figure 24. The value for 25.0°, $K_{eq} = 44.9 \pm 4.0\ M^{-1}$, was obtained from Figure 25. The value for 35.0°, $K_{eq} = 41.6 \pm 6.6\ M^{-1}$, was calculated from Figure 26. The equilibrium constant was also calculated from Eq 19. This resulted in a $K_{eq}(25.0°) = 28.1 \pm 2.6\ M^{-1}$ determined at four wavelengths: λ = 460 nm, 450 nm, 430 nm, and 420 nm. A representative plot is shown in Figure 27 for λ = 450 nm. The equilibrium results are given in Table 21.

Table 21. Kinetic and equilibrium constants for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$

Temp	$A(M^{-1}sec^{-1})^a$	$B(sec^{-1})^a$	$C(M^{-1})^a$	$\frac{A}{C}(sec^{-1})$	K_{eq}^b
18.5°	111±5	0.10±.04	22.5±2.5	4.9±1.6	23.6±3 3
25.0°	85±3	1.00±.04	6.0±3.1	14.1±1.0	44.9±4.0[c]
35.0°	130±3	3.40±0.06	3.7±1.3	34.9±2.3	41.6±6.6

[a] Parameters for the equation $k_{obs} = \frac{A[L]+B}{1+C[L]}$ fit graphically.

[b] Spectrophotometric determination of K_{eq} by Eq 18.

[c] Spectrophotometric determination by Eq 19 yields K_{eq} at 25.0° = 28.1±2.6.

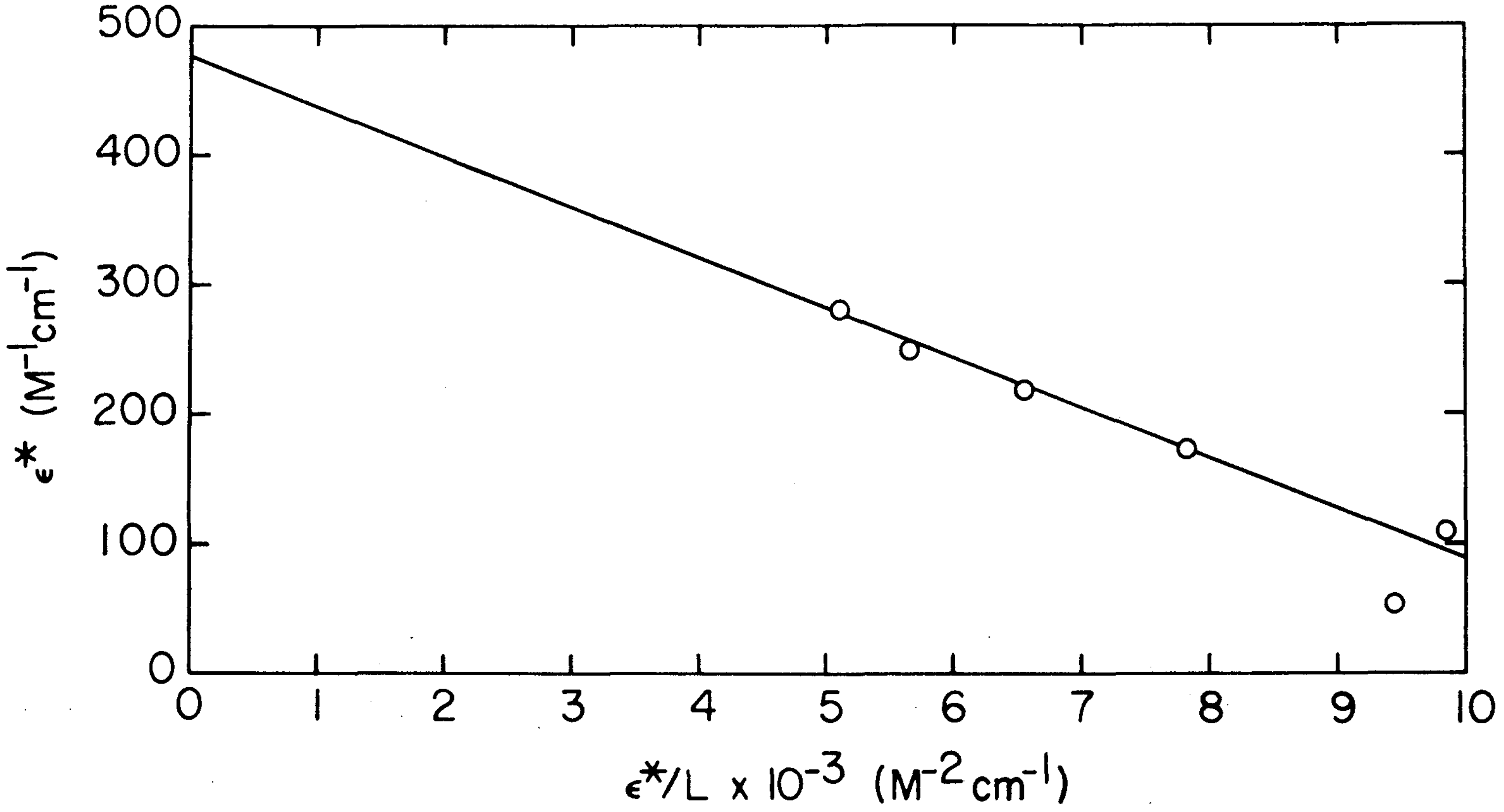

Figure 24. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 18.5°C yielding a $K_{eq} = 23.6 \pm 3.3\ M^{-1}$ and $\varepsilon_1 = 997 \pm 45\ M^{-1}cm^{-1}$

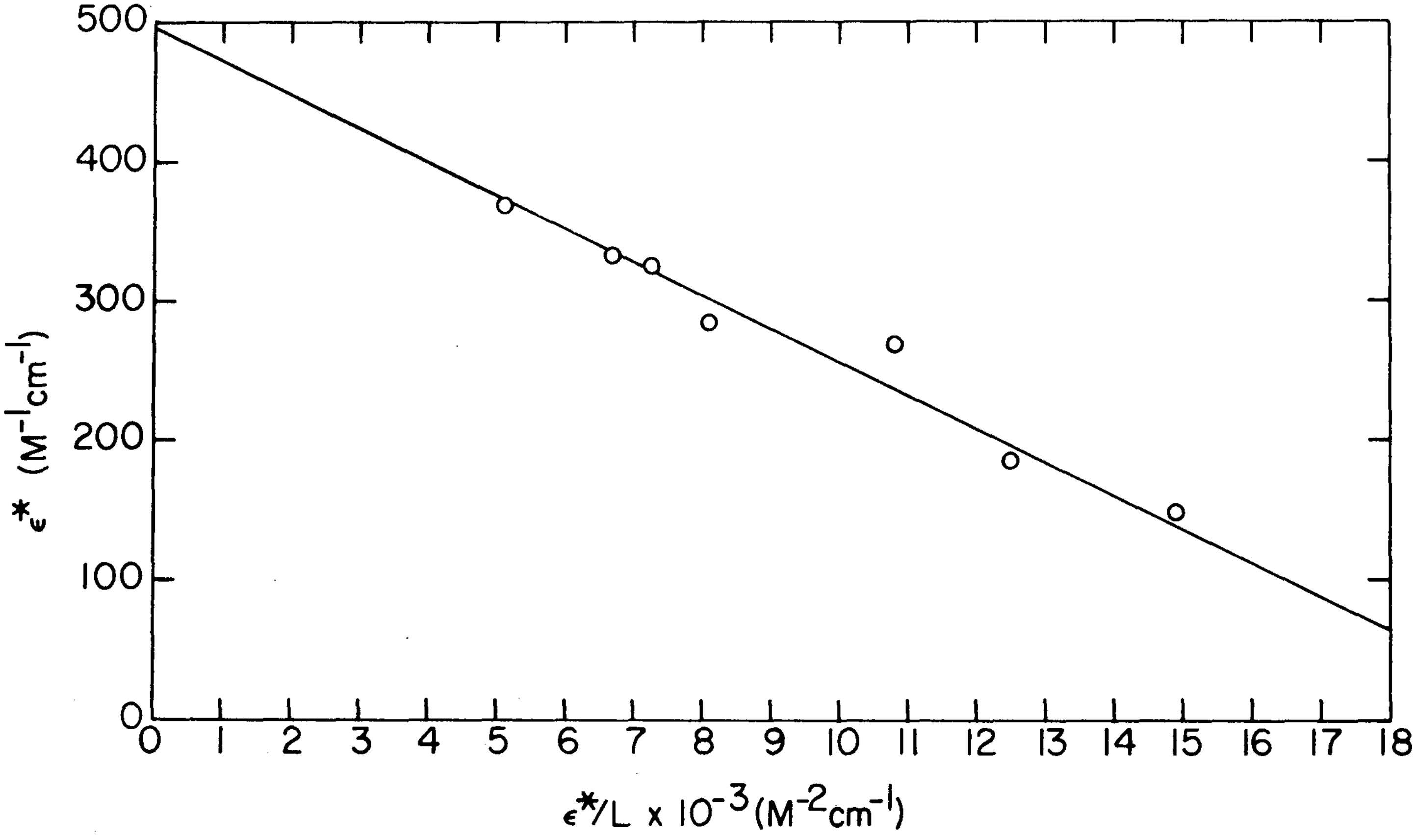

Figure 25. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 25°C yielding K_{eq} = 44.9 ± 4.0 M^{-1} and $\varepsilon_1 = 1008 \pm 20$ $M^{-1}cm^{-1}$

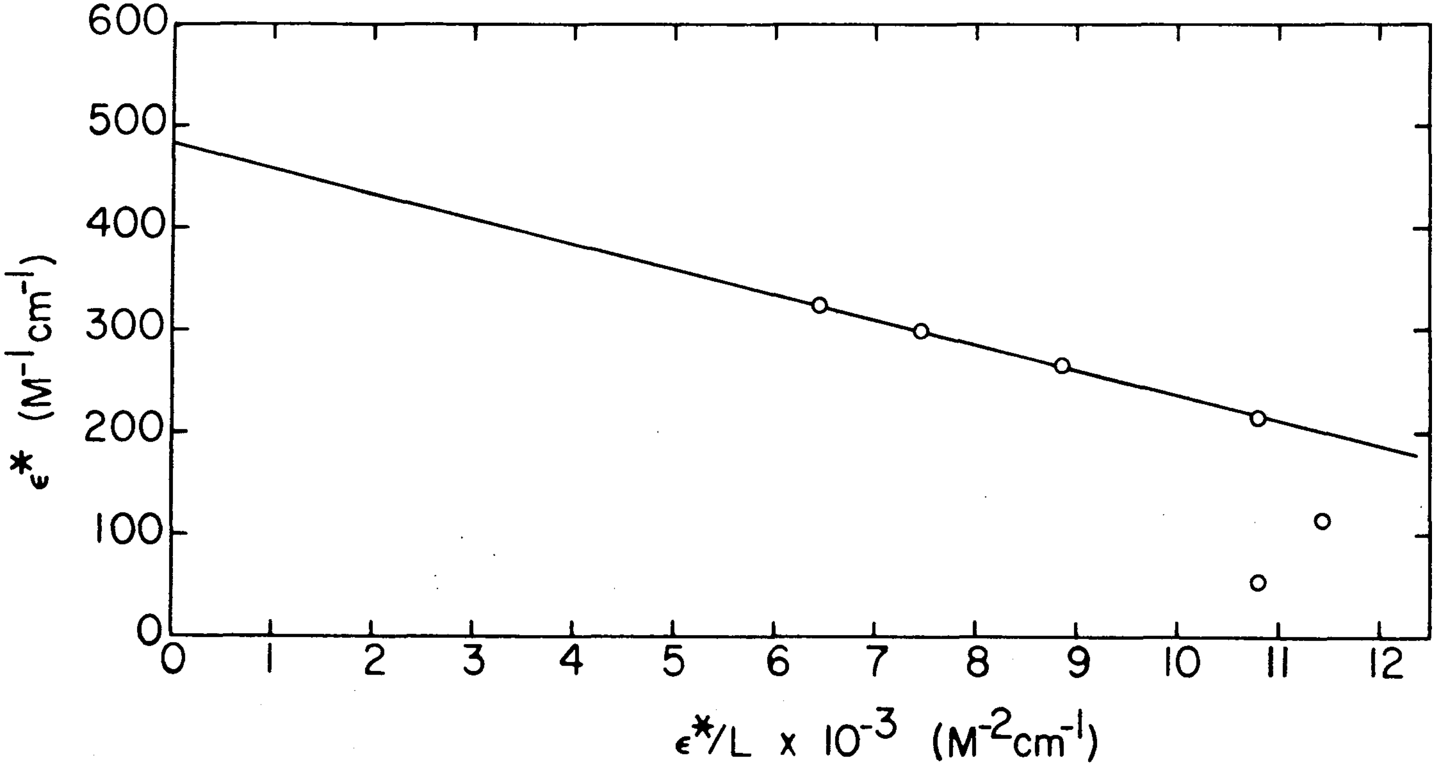

Figure 26. Plot for the calculation of K_{eq} from the ΔD's of the kinetic runs for the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 35.0°C yielding K_{eq} = $41.6 \pm 6.6\ M^{-1}$ and $\varepsilon_1 = 1012 \pm 5\ M^{-1}cm^{-1}$

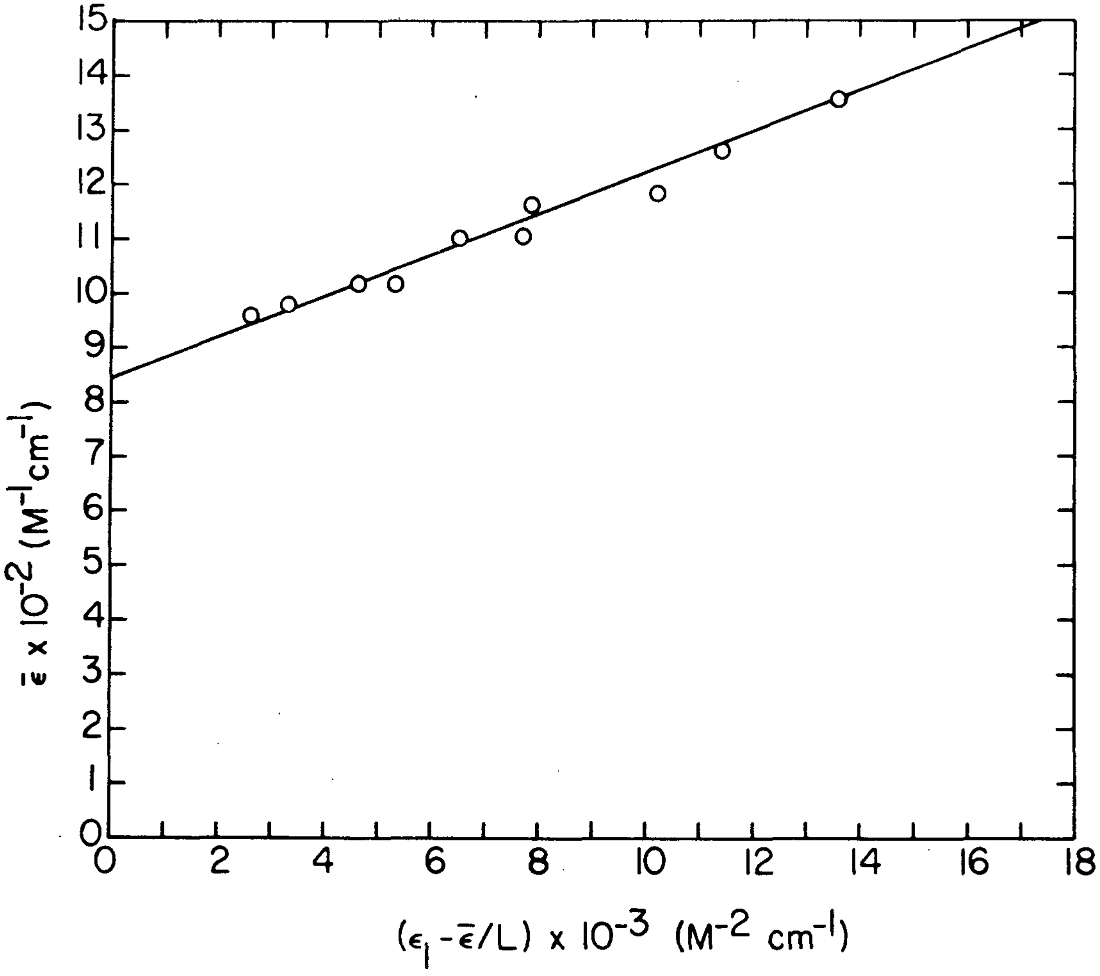

Figure 27. Plot for the calculation of K_{eq} from $\bar{\varepsilon}$ values from the equilibrium study of the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ at 25.0°C yielding $K_{eq} = 28.1 \pm 2.6$ M^{-1} and $\varepsilon_1 = 848 \pm 26$ $M^{-1}cm^{-1}$

DISCUSSION

The equilibrium between the alkylcobaloxime and the hexacyanide ligands corresponds to the formation of a cyano-bridged complex. This is evident from the calculation for the equilibrium constant which is constructed such that there is only one absorbing product in solution. The spectrum of this product, Figures 5 and 6, is markedly dissimilar to the C-bonded spectrum of the $C_2H_5Co(dmgH)_2CN^-$ as observed in Figure 7. The products formed are analogous to the hexacyano-cobalamin species observed by George _et al_. (20).

The kinetic results for $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, and $Cr(CN)_6^{3-}$ do not in themselves distinguish between Eq 12 or Eq 13. For these ligands the data can be rationalized by Eq 5, a bimolecular rate expression. For the $Fe(CN)_6^{4-}$ reaction, where Eq 17 must be employed, a non-linear dependence of the rate upon ligand concentration is observed. This dependence would occur for both the limiting S_N1 mechanism or the outer-sphere mechanism. For the $Fe(CN)_6^{4-}$ reaction, the limiting S_N1 mechanism would be

$$C_2H_5Co(dmgH)_2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_2H_5Co(dmgH)_2 + H_2O \qquad (22)$$

$$C_2H_5Co(dmgH)_2 + Fe(CN)_6^{4-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_2H_5Co(dmgH)_2\{NCFe(CN)_5\}^{4-} \qquad (23)$$

where the observed rate constant in the form of Eq 17 would be (see Appendix):

$$k_{obs} = \frac{\frac{k_1k_2}{k_{-1}}[Fe(CN)_6{}^{4-}] + k_{-2}}{1 + \frac{k_2}{k_{-1}}[Fe(CN)_6{}^{4-}]} \qquad (24)$$

with A = $(k_1k_2)/k_{-1}$, B = k_{-2}, and C = k_2/k_{-1}. For the other ligands studied, $M(CN)_6{}^{3-}$, Eq 25 is in the form

$$k_{obs} = \frac{k_1k_2}{k_{-1}}[M(CN)_6{}^{3-}] + k_{-2} \qquad (25)$$

with $k_f = (k_1k_2)/k_{-1}$ and $k_r = k_{-2}$. The limitations on Eq 24 simplifying to Eq 25 is that $k_2/k_{-1}[M(CN)_6{}^{3-}] << 1$ for the limiting S_N1 mechanism. As seen in Eq 22, the first step in the limiting S_N1 mechanism is not dependent of the ligand. Therefore values of k_1 for all the ligands are identical and the values for the remaining constants can be calculated. The values for 25.0° for the limiting S_N1 mechanisms are given in Table 22. The values of k_2/k_{-1} multiplied by typical concentrations of $M(CN)_6{}^{3-}$ give products which are greater than one instead of being much smaller. The results are not consistent with a limiting S_N1 mechanism for the $M(CN)_6{}^{3-}$ ligands. Although it is not mandatory for all four ligands, both $M(CN)_6{}^{3-}$ and $M(CN)_6{}^{4-}$, to react by the same mechanism, it appears most likely that all the ligands would react alike.

The other mechanism discussed which also fits Eq 17 and therefore the kinetic data of $Fe(CN)_6{}^{4-}$ is a mechanism in which rapid preassociation of the cobaloxime with $Fe(CN)_6{}^{4-}$

Table 22. Treatment of the kinetic results at 25.0° as a limiting S_N1 mechanism[a]

Ligand	$\frac{k_1k_2}{k_{-1}}(M^{-1}sec^{-1})$	$k_{-2}(sec^{-1})$	$\frac{k_2}{k_{-1}}(M^{-1})$	$k_1(sec^{-1})$
$Fe(CN)_6^{4-}$	85	1.0	6.0	14.1
$Co(CN)_6^{3-}$	896	12.3	63.5	14.1
$Fe(CN)_6^{3-}$	926	11.9	65.7	14.1
$Cr(CN)_6^{3-}$	1566	9.9	111	14.1

[a] Treatment of data according to Eq 24 by computer.

occurs. The reaction scheme with $Fe(CN)_6{}^{4-}$ for this would be

$$C_2H_5Co(dmgH)_2H_2O + Fe(CN)_6{}^{4-} \underset{}{\overset{K_{O.S.}}{\rightleftarrows}} \{C_2H_5Co(dmgH)_2H_2O - Fe(CN)_6\}^{4-} \qquad (26)$$

$$\{C_2H_5Co(dmgH)_2H_2O - Fe(CN)_6\}^{4-} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} C_2H_5(dmgH)_2NCFe(CN)_5{}^{4-} + H_2O \qquad (27)$$

in which no specific orientation of the intermediate is implied. The observed rate constant for this would be (see Appendix)

$$k_{obs} = \frac{(k_3+k_{-3})K_{O.S.}[Fe(CN)_6{}^{4-}] + k_{-3}}{1 + K_{O.S.}[Fe(CN)_6{}^{4-}]} \qquad (28)$$

which is expressed in the form of Eq 17. For Eq 28 to simplify

$$k_{obs} = (k_3+k_{-3})K_{O.S.}[M(CN)_6{}^{3-}] + k_{-3} \qquad (29)$$

to the form of Eq 29 for the $M(CN)_6{}^{3-}$ ligands $K_{O.S.}[L] << 1$. Since all constants for this mechanism are unique for each ligand, only limits for $K_{O.S.}$ and k_3 can be calculated for the $M(CN)_6{}^{3-}$ ligands. Assuming that the outer-sphere association would depend largely on charge, $K_{O.S.}$ would have a similar value for the $M(CN)_6{}^{3-}$ ligands. For the restriction $K_{O.S.}[L] << 1$ to be true, $K_{O.S.}$ must be less than 1.0. The fit of the kinetic data at 25.0° for the outer-sphere mechanism using the value $K_{O.S.} < 1$ for $M(CN)_6{}^{3-}$ is given in Table 23. This mech-

Table 23. Treatment of the kinetic results at 25.0° according to an outer-sphere mechanism[a]

Ligand	$K(k_3+k_{-3})(M^{-1}s^{-1})$	$k_{-3}(s^{-1})$	$K_{O.S.}(M^{-1})$[b]	$(k_3+k_{-3})(s^{-1})$	$k_3(s^{-1})$
$Fe(CN)_6^{4-}$	85	1.0	6.0	15.1	14.1
$Co(CN)_6^{3-}$	896	12.3	$K < 1.0$	>896	>884
$Fe(CN)_6^{3-}$	926	11.9	$K < 1.0$	>926	>914
$Cr(CN)_6^{3-}$	1566	9.9	$K < 1.0$	>1566	>1556

[a] For Eq 16 $K_f = K_{O.S.}(k_3+k_{-3})$, $k_r = k_{-3}$.

For Eq 17 $A = K_{O.S.}(k_3+k_{-3})$, $B = k_{-3}$, and $C = K_{O.S.}$.

[b] The value for $K_{O.S.}$ was computed such that at the highest ligand concentrations used $K_{O.S.}[L] \ll 1$ for $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, and $Cr(CN)_6^{3-}$.

anism is consistent with the kinetic results for all the ligands studied. Results of $Fe(CN)_6^{4-}$ data computer fit to Eq 28 are given in Table 24.

From the results in Table 23 it is evident that the $K_{O.S.}$ value for $Fe(CN)_6^{4-}$ is larger than the $M(CN)_6^{3-}$ ligands. This would be indicative of a larger binding constant of the greater negative charge. The exact nature of the outer-sphere complex which is formed cannot be determined from kinetic data. The various possibilities include a reorientation of the ligand's hydration sphere or hydrogen bonding between the cobaloxime water molecule and the nitrogen of a cyanide.

The values of k_{-3} from Table 23 are also indicative of the similarities between the ligands and their charge. The $M(CN)_6^{3-}$ ligands are approximately constant and approximately ten times larger than the $Fe(CN)_6^{4-}$. This correlates with the electrostatic arguments for $K_{O.S.}$.

The approximate constancy of the quantity $(k_3+k_{-3})K_{O.S.}$ for the $M(CN)_6^{3-}$ reactions implies approximately constant values of k_3 for $M(CN)_6^{3-}$. To obtain the constancy requires a step similar in the reactions. This step would reflect cobalt-water bond breaking. The dissociative controlled reaction rate is well known in octahedral substitution. The deviation of k_3 for $Fe(CN)_6^{4-}$ from the other ligands does not contradict the mechanism. It is possible that the $Fe(CN)_6^{4-}$ would experience more association with the bound water,

Table 24. Computer fit of the reaction $C_2H_5Co(dmgH)_2H_2O$ and $Fe(CN)_6^{4-}$ to the associative mechanism[a]

Temp	$k_3(sec^{-1})$	$k_{-3}(sec^{-1})$	$K(M^{-1})$	$(k_3+k_{-3})K$
18.5°	4.8 ± 0.4	0.07 ± 0.07	25.3 ± 5.1	122 ± 14
25.0°	22.4 ± 8.4	0.99 ± 0.07	3.9 ± 1.8	92 ± 10
35.0°	24.6 ± 2.6	3.34 ± 0.06	6.3 ± 1.0	176 ± 10

[a] Fit to equation $k_{obs} = \frac{(k_3+k_{-3})K[L] + k_{-3}}{1 + K[L]}$ by computer (28).

possibly reflected by the $K_{O.S.}$, and thus impede the dissociation of the water.

The $Fe(CN)_6^{4-}$ reaction has been the only alkylcobaloxime reaction studied that has experienced deviation from Eq 29. For this to occur, the assumption $K_{O.S.}[L] << 1$ is no longer valid. In this study only the ligand of greatest negative charge had a sufficiently large value of $K_{O.S.}$ to exhibit deviation from Eq 29. If the mechanism in Eq 26-27 is operative for all the alkylcobaloxime substitutions, the systems of lower negatively charged ligands will not deviate from Eq 29 while it is possible for the more highly charged ligand to deviate. This assumes that $K_{O.S.}$ is predominantly electrostatic and k_3 is predominantly controlled by the dissociation of water.

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APPENDIX

For the following derivations, the symbols are defined as:

$[\ ]^{\circ}$ = initial concentration

$[\ ]^{t}$ or $[\ ]$ = concentration at time t

$[\ ]^{eq}$ = equilibrium concentration

$[(Co)]_{tot} = [C_2H_5Co(dmgH)_2H_2O] + (C_2H_5Co(dmgH)_2H_2O\cdot L]$

I. The limiting S_N1 mechanism (Eqs 1 and 2)

The rate of formation of the product is

$$\frac{d[EtCo(dmgH)_2L]}{dt} = k_2\ [L]\ [EtCo(dmgH)_2] - k_{-2}(EtCo(dmgH)_2L] \quad (1A)$$

Where $C_2H_5Co(dmgH)_2$ is defined as a steady-state intermediate

$$\frac{d[EtCo(dmgH)_2]_{ss}}{dt} = 0 = k_1[Et(Co)H_2O] + k_2(EtCoL] - k_{-1}[Et(Co)]_{22} - k_{-2}[Et(Co)]_{ss}[L] \quad (2A)$$

The steady-state concentration is therefore

$$[Et(Co)]_{ss} = \frac{k_1[EtCoH_2O] + k_{-2}[EtCoL]}{k_{-1} + k_2[L]} \quad (3A)$$

Substitution of Eq 3A into Eq 1A yields Eq 4A

$$\frac{d[EtCoL]}{dt} = k_2L\ \frac{k_1[EtCoH_2O] + k_{-2}[EtCoL]}{k_{-1} + k_2L} - k_{-2}[EtCoL] \quad (4A)$$

or

$$\frac{d[EtCoL]}{dt} = \frac{k_1k_2[L][EtCoH_2O] - k_{-1}k_{-2}[EtCoL]}{k_{-1} + k_2[L]} \qquad (5A)$$

The conservation of mass and the stoichiometry of the reaction require that

$$[EtCoH_2O]^o + [EtCoL]^o = [EtCoH_2O]^t + [EtCoL]^t = [EtCoH_2O]^{eq} + [EtCoL]^{eq} \qquad (6A)$$

By substituting Eq 6A into Eq 5A, the rate law becomes

$$-\frac{d\{[EtCoH_2O] - [EtCoH_2O]^{eq}\}}{dt} = \frac{k_1k_2[L] + k_{-1}k_{-2}}{k_{-1} + k_2[L]}\{[EtCoH_2O]^t - [EtCoH_2O]^{eq}\} \qquad (7A)$$

Integration of Eq 7A yields an equation identical in form to equation

$$\ln\{[EtCoH_2O]^t - [EtCoH_2O]^{eq}\} = \ln\{[EtCoH_2O]^o + [EtCoH_2O]^{eq}\} - \left(\frac{k_1k_2[L] + k_{-1}k_{-2}}{k_{-1} + K_2[L]}\right)t \qquad (8A)$$

When under conditions of excess [L] the observed rate constant would be

$$k_{obs} = \frac{k_1k_2[L] + k_{-1}k_{-2}}{k_{-1} + k_2[L]} \qquad (9A)$$

II. The associative mechanism (Eqs 6 and 7)

The rate of formation of product is

$$\frac{d[\mathrm{EtCoL}]}{dt} = -\frac{d[\mathrm{EtCoH_2O}]_{tot}}{dt} = k_3[\mathrm{EtCoH_2O{\cdot}L}] - k_{-3}[\mathrm{EtCoL}] \tag{10A}$$

The concentration of $\mathrm{EtCoH_2O{\cdot}L}$ is known to be

$$[\mathrm{EtCoH_2O{\cdot}L}] = \frac{K[L]}{1+K[L]}[\mathrm{EtCoH_2O}]_{tot} \tag{11A}$$

$$\text{and } [\mathrm{EtCoL}]^t = [\mathrm{EtCoH_2O}]_{tot}^{o} - [\mathrm{EtCoH_2O}]_{tot}^{t} \tag{12A}$$

Substituting Eqs 11A and 12A into Eq 10A yields

$$-\frac{d[\mathrm{EtCoH_2O}]_{tot}}{dt} = \{\frac{k_3K[L]}{1+KL} + k_{-3}\}\ [\mathrm{EtCoH_2O}]_{tot} - k_{-3}[\mathrm{EtCoH_2O}]_{tot}^{o} \tag{13A}$$

The state of equilibrium is defined as

$$k_{-3}[\mathrm{EtCoL}]^{eq} = k_{+3}[\mathrm{EtCoH_2O{\cdot}L}]^{eq} \tag{14A}$$

Substituting Eq 11A into Eq 14A yields Eq 15A

$$k_{-3}[\mathrm{EtCoL}]^{eq} = k_3\{\frac{K[L]}{1+K[L]}\}[\mathrm{EtCoH_2O}]_{tot}^{eq} \tag{15A}$$

which is substituted into Eq 13A yielding

$$-\frac{d[\mathrm{EtCoH_2O}]_{tot}}{dt} = \{\frac{k_3K[L]}{1+K[L]} + k_{-3}\}([\mathrm{EtCoH_2O}]_{tot} - [\mathrm{EtCoH_2O}]_{tot}^{eq}) \tag{16A}$$

At equilibrium $[\mathrm{EtCoH_2O}]_{tot}^{eq}$ is constant. Therefore

$$-\frac{d[\mathrm{EtCoH_2O}]_{tot}^{eq}}{dt} = 0 \tag{17A}$$

Combining Eqs 16A and 17A yields Eq 18A

$$-\frac{d([EtCoH_2O]_{tot}-[EtCoH_2O]^{eq}_{tot})}{dt} = \{\frac{(k_3+k_{-3})KL+k_{-3}}{1+KL}\}([EtCoH_2O]_{tot} - [EtCoH_2O]^{eq}_{tot}) \tag{18A}$$

which can be integrated to yield

$$\ln\{[EtCoH_2O]_{tot} - [EtCoH_2O]^{eq}_{tot}\} = \ln\{[EtCoH_2O]-[EtCoH_2O]\} - (\frac{(k_3+k_{-3})KL+k_{-3}}{1+KL})t \tag{19A}$$

Under pseudo-first order conditions with L in large excess Eq 19A has an observed rate constant of

$$k_{obs} = \{\frac{(k_3+k_{-3})KL+k_{-3}}{1+KL}\} \tag{20A}$$

III. The bimolecular mechanism (Eq 5)

The rate of formation of product is

$$\frac{d[EtCoL]}{dt} = k_f[L][CoH_2O] - k_r[EtCoL] \tag{21A}$$

The conservation of mass and the stoichiometry of the reaction require

$$[EtCoH_2O]^o + [EtCoL]^o = [EtCoH_2O]^t + [EtCoL]^t = [EtCoH_2O]^{eq} + [EtCoL]^{eq} \tag{22A}$$

At equilibrium

$$k_f[L][EtCoH_2O]^{eq} = k_r[EtCoL]^{eq} \tag{23A}$$

Equations 22A and 23A are substituted into Eq 21A yielding

$$\frac{d[\mathrm{EtCoL}]}{dt} = \frac{-d[\mathrm{EtCoH_2O}]}{dt} = (k_f[L]+k_r)([\mathrm{EtCoH_2O}]-[\mathrm{EtCoH_2O}]^{eq}) \tag{24A}$$

Applying Eq 17a to Eq 24A and integrating yields

$$\ln\{[\mathrm{EtCoH_2O}]-[\mathrm{EtCoH_2O}]^{eq}\} = \ln\{[\mathrm{EtCoH_2O}]-[\mathrm{EtCoH_2O}]^{eq}\} - (k_f[L]+k_r)t \tag{25A}$$

The observed rate constant under conditions of excess [L] is

$$k_{obs} = k_f[L] + k_r \tag{26A}$$