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The Mechanism of Formation of Nickel(II) Complexes in Methanol

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The reaction of nickelII(II) ion with trithiocarbonate ion in methanol has been studies at 25°C. The kinetics of the reaction are first order at low ionic strength and second order at an ionic strength of 0.1 M. *This confirms the previously proposed ion pair mechanism for formation of* Ni^{II} *complexes and permits evaluation of the equilibrium constant for formation of an ion pair between* Ni^{II} *ion and trithiocarbonate ion in methanol. The radius of the ion pair is estimated to be between 5.0 and 5.5 angstroms.*

Introduction

Studies of rapid complexation reactions of nickel(II) in aqueous solution have led to the postulation of a two-step mechanism,[1]

$$\mathrm{Ni(Sol)_6{}^{2+} + L^{z-} \overset{K}{\rightleftarrows} [Ni(Sol)_5{}^{2+},L^{z-}]\ (ion\ pair)} \tag{1}$$

$$\mathrm{[Ni(Sol)_6{}^{2+},L^{z-}] \xrightarrow{k_s} Ni(Sol)_5L^{(2-z)+} + Sol} \tag{2}$$

Step (1) represents diffusion controlled formation of an ion pair or outer-sphere complex. The rate-limiing step (2) is a dissociative interchange process, I_d in the terminology of Langford and Gray.[2]

Since the rate of a dissociative process depends on on the leaving group, it has been expected (and apparently confirmed[3]) that the rate constant, k_s, will be nearly the same as the rate of solvent exchange on nickel(II). Rates of solvent exchange on nickel(II) ion have been measured in water ($k_{H_2O} = 3.0 \times 10^4$ sec^{-1} [4a]) and in methanol ($k_{CH_3OH} = 1.0 \times 10^3$ sec^{-1}-sec^{-1} [4a]).

The method of determining k_s from complexation reactions has been questionable, however. The rate law for equations (1) and (2) is:[3]

$$\frac{d[\mathrm{Ni(Sol)_5L^{(n-z)+}}]}{dt} = \frac{k_5K[\mathrm{L^{z-}}][\mathrm{Ni(Sol)_6{}^{2+}}]}{1+K[\mathrm{L^{z-}}]} \tag{3}$$

Under conditions of small ligand concentration the reaction should obey second order kinetics with the second order rate constant equal to k_sK. If the product $K[L^{Z-}]$ becomes large enough the rate law becomes first order and k_s can be determined directly. This latter situation has not been observed experimetally and the only two determinations of k_s for nickel(II) have been by means of sound absorption measurements[1] where $L^{Z-} = SO_4{}^{2-}$ and temperature-jump measurements[5] where L = methyl phosphate.

The usual way around this problem has been to calculate K using an equation originally derived by Fuoss[6] and Eigen.[1]

The equation has been modified by Pearson and Ellgen[3] to include the effect of ionic strength:[3]

$$K = \frac{4\pi Na^3}{3000}\exp\left(\frac{1}{kT}\cdot\left[\frac{z_1z_2e^2\chi}{D(1+\chi a)} - \frac{z_1z_2e^2}{aD}\right]\right) \tag{4}$$

$$\chi^2 = \frac{8\pi Ne^2}{1000\ DkT}$$

The calculetd K is then divided into the experimentally determined rate constant, k_sK. Values of k_s obtained in this way for aqueous solutions range from 0.3×10^4 to 2.0×10^4 sec^{-1}, supporting the conclusion that the water exchange process determines the over-all rate.[3] Unfortunately small errors in a, the distance of closest approach of the oppositely charge ions, can cause large errors in K. A careful examination of equations(4)shows that large values of K will be obtained in a medium of low dielectric constant, D, at a low ionic strength, μ. In fact for methanol Pearson and Ellgen[3] calculated K = 50,000 at zero ionic strength. Thus even at low concentrations of reagents in methanol one might expect to observe first order kinetics for complex formation reactions.

In an attempt to confirm kinetically the accepted mechanism of complexation of nickel(II) we undertook a study of trithiocarbonato complexes. This system was chosen because the complexes exhibit strong absorption in the UV-visible region, allowing very small concentrations to be used. Trithiocarbonate is relatively small for a dinegative ion so large values of K are expected and all species are readily

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(1) M. Eigen, *Z. Electrochem.*, *64*, 115(1960); M. Eigen and K. Tamm. *Z. Electrochem.*, *66*, 107(1962).

(2) C.H. Langford and H.B. Gray, « Ligand Substitution Processes », W.A. Benjamin, Inc., New York, 1965, Chapter 1.

(3) R.G. Pearson and P. Ellgen, *Inorg. Chem.*, *6*, 1379(1967), and references therein.

(4) a. R.E. Connick and D. Fiat, *J. Chem. Phys.*, *44*, 4103(1966).
b. Z. Luz and S. Meiboom, *J. Chem. Phys.*, *40*, 2686 (1964).

(5) H. Brintzinger and G.G. Hammes, *Inorg. Chem.*, *5*, 1286 (1966).

(6) R.M. Fuoss, *J. Amer. Chem. Soc.*, *80*, 5059 (1958).

soluble in methanol. The results of our study are reported here.

Experimental Section

Materials. Reagent grade methanol was dried over 3A molecular sieves and used without further purification. Hexamethanolnickel(II) perchlorate was prepared as described by Imhof and Drago,[7] except that the solution of $Ni(CH_3OH)_6(ClO_4)_2$ in methanol had to be exaporated under vacuum until first formation of crystals before treatment with dry ether would cause separation of a large yield of product. The pale yellow-green powder was characterized by means of its visible spectrum in methanol and was stored in a vacuum desiccator. Potassium trithiocarbonate was prepared as described by Yeoman.[8] The reaction was carried out in a glove bag under dry nitrogen which had been deoxygenated by means of quinone hyposulfite.[9] The crystals were dried and stored over P_2O_5 in a desiccator from which light was excluded. Application of vacuum promoted decomposition of the salt.

Kinetic runs. All kinetic runs were made using a Durrum-Gibson spectrophotometric stopped-flow apparatus thermostatted at 25°C. Results at several wavelengths were found to be in good agreement. In runs where high ionic strengths were desired weighed quantities of commercially available sodium perchlorate were added to both the Ni^{II} and trithiocarbonate solutions. At concentrations of sodium perchlorate above 0.2 *M* trithiocarbonate decomposes rapidly so ionic strength was limited to 0.1 *M*.

To prepare solutions for kinetic runs the desired quantities of reagents were weighed in a glove bag under nitrogen. The solids were transferred to dry volumetric flasks and methanol which had been flushed with dry, deoxygenated nitrogen was added. The flasks were sealed by means of serum caps. Aliquots could then the withdrawn using a hypodermic syringe and transferred to the stopped-flow apparatus without contacting the atmosphere. Since the trithiocarbonate solutions decomposed slowly ($t_{1/2}$ ~12 hours) even in the absence of perchlorate, all runs were made within one-half hour of preparation of the solutions.

Data obtained from Polaroid photographs of the oscilloscope traces were treated using the Sigma-2 computer of the Indiana University Chemistry Department. A program written by Mr. Dan Bacon converted the observed per cent transmittance values to concentrations and carried out a first or second order rate plot using the method of least squares to obtain the slope in each case. Examples of the plots which were obtained are shown in Figure 1. For the calculation of kt in the first order case equation (5) was used were c_o is the initial concentration

$$kt = \ln(c_o/c) \qquad (5)$$

of Ni^{2+} and c is the concentration at time t, obtained from equation (6).

$$c = c_o(A_\infty - A)/(A_\infty - A_o) \qquad (6)$$

A_o, A_∞, and A are respectively the absorbance of the solution at zero time, the final absorbance, and the absorbance at time t. For the second order case equation (7) was used to calculate kt, where B represents the difference in concentrations between trithiocarbonate and Ni^{2+} and the other symbols have already been defined.

$$kt = (1/B)\ln[c_o(B+c)/c(B+c_o)] \qquad (7)$$

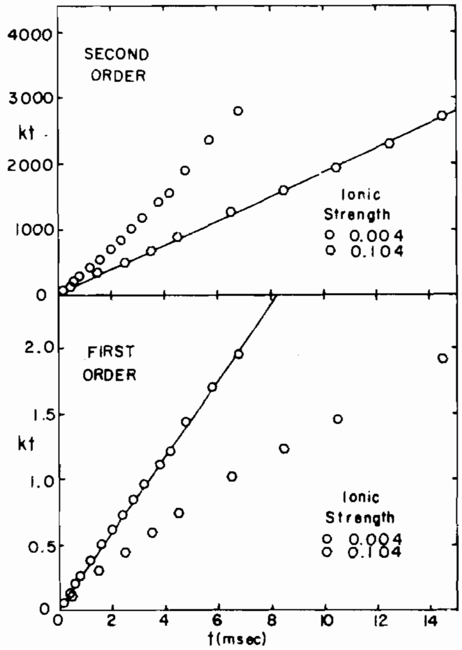

Figure 1. Second and first order plots for the formation of $NiCS_3$ at different ionic strengths. Initial concentrations in all cases: $Ni^{2+} = 5.0 \times 10^{-4} M$; $CS_3^{2-} = 1.0 \times 10^{-3} M$.

Results

Preliminary studies of the nickel(II)+trithiocarbonate reaction showed three separate changes in per cent transmittance. The first was complete within 20 milliseconds, the second required about 10 seconds, and the third required several minutes. Scrupulous exclusion of oxygen from the reaction mixture eliminated the third change in per cent transmittance. In the absence of oxygen the product spectrum, after correction for any residual CS_3^{2-}, coresponded to that of $Ni(CS_3)_2^{2-}$.[10]

Since no *tris-* complex of trithiocarbonate with Ni^{II} has been reported, it seems reasonable that the three observed changes in per cent transmittance correspond to the reactions:

$$Ni^{2+} + CS_3^{2-} \rightarrow NiCS_3 \qquad (8)$$

$$NiCS_3 + CS_3^{2-} \rightarrow Ni(CS_3)_2^{2-} \qquad (9)$$

$$Ni(CS_3)_2^{2-} + CS_3^{2-} + \tfrac{1}{2}O_2 \rightarrow Ni(CS_3)(CS_4)^{2-} + COS_2^{2-} \qquad (10)$$

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[7] V. Imhof and R.S. Drago, *Inorg. Chem.*, *4*, 427 (1965).
[8] E. Yeoman, *J. Chem. Soc.*, *119*, 46 (1921).
[9] D.F. Shriver, « The Manipulation of Air-sensitive Compounds », Mc Graw Hill, New York, 1969, p. 195.
[10] a. J.P. Fackler, Jr, and D. Coucouvanis, *J. Amer. Chem. Soc.*, *88*, 3913 (1966);
b. *ibid*, *89*, 1346 (1967).

In the presence of excess CS_3^{2-} and an oxidizing agent $Ni((CS_3)(CS_4)^{2-}$ is reported to be readily obtained.[10] Since this reaction could be suppressed by exclusion of oxygen it was not studied further. All data on reactions (8) and (9) were obtained from runs where oxygen was excluded.

Deskin[11] has reported an over-all formation constant for $Ni(CS_3)_2^{2-}$ in aqueous solution, $\beta_2 = 4.1\times10^8$, but formation constants for the stepwise reactions are not available. Nevertheless the formation of $Ni(CS_3)_2^{2-}$ is 80% complete under the least favorable conditions employed in our study. Thus it seems virtually certain that reaction (8) goes to completion in all runs. Kinetic data on reaction (9) were taken from runs with $Ni^{2+}:CS_3^{2-} = 1:10$. No corrections for reversibility of any of these reactions were made.

Kinetic runs were carefully made over a range of wavelengths from 4000 to 5600 Å in order to determine the spectrum of the intermediate formed during the first change in per cent transmittance. After subtracting the absorbance due to unreacted CS_3^{2-}, a spectrum was obtained with a maximum at 4250 Å. (23.5×10^3 cm^{-1}). Other regions of the spectrum were obscured either by extremely strong absorption due to CS_3^{2-} or by small differences between the spectrum of the intermediate and that of CS_3^{2-}. Although little can be said about the structure of the intermediate on the basis of one absorption maximum, it is clear that the spectrum differs from both CS_3^{2-} and $Ni(CS_3)_2^{2-}$. The possibility that the intermediate contains monodentate trithiocarbonate seems slight. The high effective concentration of the second «tooth» of the ligand usually makes ring closing reactions faster than the initial attachment of a bidentate ligand.[12] The most reasonable intermediate species is then $NiCS_3$.

Studies of reaction (5) were first carried out with no added $NaClO_4$ and at 2.5×10^{-4} *M* nickel(II). The excess of CS_3^{2-} ranged from two-fold to ten-fold, but the kinetics were always first order for both reaction (8) and (9). Rate constants for the two processes were different by a factor of 600 so there was no difficulty in separating them. Averaging values obtained from different solutions and at different wavelengths gave a value of $k_1' = (3.0\pm0.2)\times10^2$ sec^{-1} for reaction (8) and a value of $k_2' = 0.51\pm0.03$ sec^{-1} for reaction (9). The observed rate law fits equation (3) if $1 \ll K[CS_3^{2-}]$.

We attempted to attain the conditions ($1 \gg K[CS_3^{2-}]$) necessary for second order kinetics by decreasing trithiocarbonate concentration, but a point of diminishing returns is reached due to the magnitudes of the molar absorptivities involved at about 2×10^{-4} *M* CS_3^{2-}. The change in %T during the reaction becomes too small to measure accurately. However, it is clear from equation (4) (and from common sense reasoning) that increasing ionic strength should decrease K, the ion pair formation constant. The results of runs at high ionic strenght where $[Ni(CH_3OH)_6^{2+}]_0 = 5.0\times10^{-4}$, $[CS_3^{2-}]_0 = 1.0\times10^{-3}$, are shown in Table I. Each rate constant reported is the average of at least theree separate runs. In addition it should be noted (see Figure 1) that at high ionic strengths the kinetics are observed to be second order. This will be indicated by a double prime on the rate constant, k_1''.

Table I. Rate Constants and Ion Pair Formation Constants for Reaction $Ni^{2+}+CS_3^{2-}\rightarrow NiCS_3$.

μ	$k_1''\times10^{-5}(M^{-1}\ sec^{-1})$	$K\times10^{-3}(M^{-1})$
0.014	3.37±.12	1.12±0.8
0.054	3.06±.06	1.02±.07
0.104	1.83±.07	0.61±.05

Discussion

The observation of first order kinetics at low ionic strength for the reaction of trithiocarbonate with nickel(II) in methanol is strong confirmatory evidence for the ion pair interchange mechanism proposed earlier.[3] The variation of the order of the reaction confirms the rate law given in equation (3) and makes it possible to evaluate both k_s and K from the experimental data. The observed values of K, obtained by dividing the second order rate constants, k_1'', by the first order constant, k_1', appear in the third column of Table I.

The first order rate constant which we have observed is approximately one-third as great as the first order constant for the exchange of methanol on nickel(II).[4b] This confirms the previous suggestion[3] that a steric factor is necessary to take into account any solvent dissociation processes which occur at a site on the solvated metal ion remote from the location of the entering ligand. Assuming that solvent exchange rate is not affected by ion pairing, the steric factor in this case would be 0.30. This is in good agreement with the observation that when space-filling models of $Ni(CH_3OH)_6^{2+}$ and CS_3^{2-} are constructed the ligand can approach closest to the metal along an octahedral edge. In addition, Brady[13] has interpreted solution X-ray data to indicate that ligands in the outer sphere occupy positions on octahedral edges.

It is of interest to compare our experimental results with those predicred by the Fuoss equation.[6] Although an ion-pair radius of 6A has been used previously for Ni^{II} in methanol,[3] the use of space-filling models and direct measurement yielded a distance of closest approach of 5.0 to 5.5 A for $Ni(CH_3OH)_6^{2+}$ and CS_3^{2-}. Table II lists ion pair formation constants calculated from the theoretical equation (4). The best agreement with our experimental values occurs between 5.0 and 5.5 A if the second order rate constant at $\mu = 0.014$ is ignored. Although second order plots at this ionic strength appeared to be linear, it is clear by substituting K values from Table II into equation (3) that the region of mixed first and second order kinetics has been reached. Thus the second order constant determined at this ionic strength will be too small and the experimental K will be too small also.

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(11) W.A. Deskin, *J. Amer. Chem. Soc.*, **80**, 5680 (1958).

(12) F. Basolo and R.G. Pearson, « Mechanism of Inorganic Reactions », 2nd ed., John Wiley and Sons, Inc. New Yiork, 1967, p. 225.

(13) G.W. Brady, *J. Chem. Phys.*, **33**, 1079 (1960).

Table II. Ion Pair Constants from Fuoss Equation for 2–2 Electrolyte in Methanol at 25°C.

	$K\times10^{-3}$ (M^{-1})			
μ	a=4.5 A	a=5.0 A	a=5.5 A	a=6.0 A
0.100	1.4	0.58	0.29	0.17
0.050	4.9	1.8	0.83	0.45
0.010	49	16	6.4	3.1
0.005	98	31	12	5.9
0.001	290	89	35	16
0.000	800	240	94	44

Very few studies of formation constants of outer-sphere complexes have been made in cases where the inner-sphere complex is substitution labile.[14] Our work is the first such study in a non-aqueous medium. It seems evident that few reaction systems involving nickel(II) will permit the observation of first order kinetics at low ionic strengths unless the reactions are carried out below 25°C. For instance, the anions studied by Pearson and Ellgen[3] have either smaller charges or larger radii than trithiocarbonate. Both of these differences lead to smaller values of K. In order to reduce the ionic strength to the point where first order kinetics would be observed the concentrations of reactants would have to be so small as to make spectrophotometric observation very difficult. In aqueous solution the rate of water exchange on Ni^{II} is too large for k_1' to be measurable by stopped flow methods. The same is true of most solvents other than methanol at 25°C. Stopped flow studies of other nickel(II) systems at temperatures below 0°C, however, should be able to provide considerable data on the stabilities of outer-sphere complexes of nickel(II).

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[14] M.T. Beck, *Coordin. Chem. Rev.*, 3, 91 (1968).