order in hydroxide involves O–C bond breaking in the oxalato complex. The lack of such a path for the fumarato and maleato complexes is consistent with the previous statements on the bonding in these complexes. Both are proposed to have more charge delocation giving greater carbon–oxygen double-bond character and placing more negative charge on the carboxyl carbon. These effects will make O–C bond rupture and OH^- attack at the carboxyl carbon more difficult.

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Rates and Mechanism of Formation of Some Nickel(II) Complexes in Methanol

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Neutral ligands react with nickel(II) to form complexes at a slower rate in methanol than in water. Monovalent anions react at about the same rate in methanol as in water. Divalent anions react faster in methanol than in water. These results are in very good agreement with the ion-pair interchange mechanism for complex formation reactions. The agreement can be made reasonably quantitative. Small amounts of water added to methanol markedly accelerate the rates of complex formation.

Introduction

The development of techniques for kinetic study of rapid reactions has resulted in an extensive accumulation of rate data for reactions of the type

$$M(H_2O)_6^{n+} + L^{z-} \longrightarrow M(H_2O)_5L^{(n-z)+} + H_2O \qquad (1)$$

The results for these systems have been reviewed by several authors.[1-3] Because many of its reactions proceed at rates accessible to stopped-flow investigation, hexaaquonickel(II) has been a favorite substrate for these studies. The behavior which has been observed for nickel(II) is typical of that for a large class of aquometal ions. The characteristic kinetic features of these reactions can be summarized briefly. (i) The rate law for formation of $M(H_2O)_5L$ is second order over-all, first order in metal ion, and first order in ligand. (ii) For a given metal ion, large variation in formation rates can be observed with different ligands. In general, ligands bearing a large negative charge react rapidly, while those bearing a more positive charge react more slowly. Ligands having the same charge tend to react at about the same rate; such variations as are observed fail to correlate with expected relative nucleophilicities. (iii) For a range of metal ions, ligand-substitution rates parallel the rates of water exchange.

These observations are accounted for by a mechanism in which the ligand and the aquated metal ion are in rapid equilibrium with an outer-sphere complex in which the incoming group occupies a position in the second coordination sphere. The rate-determining step is the collapse of this outer-sphere complex to give the inner-sphere complex

$$M(H_2O)_6^{n+} + L^{z-} \overset{K_0}{\rightleftharpoons} [M(H_2O)_6,L]^{(n-z)+} \qquad (2)$$

$$[M(H_2O)_6,L]^{(n-z)+} \xrightarrow{k_0} M(H_2O)_5L^{(n-z)+} + H_2O \qquad (3)$$

The rate law predicted by this mechanism is, for excess metal ion

$$\frac{d[M(H_2O)_5L^{(n-z)+}]}{dt} = \frac{K_0k_0[M(H_2O)_6^{n+}][L^{z-}]}{1 + K_0[M(H_2O)_6^{n+}]} \qquad (4)$$

In the usual event that $1 >> K_0[M(H_2O)_6^{n+}]$, this becomes

$$\frac{d[M(H_2O)_5L^{(n-z)+}]}{dt} = K_0k_0[M(H_2O)_6^{n+}][L^{z-}] \qquad (5)$$

As pictured here, the rate step (3) is an interchange process characterized, in the classification scheme of Langford and Gray,[4] by "dissociative activation." In this scheme the mechanism for step 3 would be assigned the symbol I_d.

The rate of reaction 3 is expected to be close to the rate of solvent exchange. This has been repeatedly confirmed (see below), particularly for nickel(II). The rate at which $Ni(H_2O)_6^{2+}$ exchanges water molecules in the inner coordination sphere is known to be 3.0×10^4 sec^{-1}.[5] The rate for methanol exchange on

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[1] R. G. Wilkins and M. Eigen, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

[2] M. Eigen, IUPAC 7th International Conference on Coordination Chemistry, Butterworth and Co. Ltd., London, 1963.

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

[4] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.

[5] R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

$Ni(CH_3OH)_6^{2+}$ is 1.0×10^3 sec^{-1}.[6] Hence the rate of outer-sphere collapse to inner-sphere complex would be expected to be slower in methanol than in water. Since the bulk dielectric constant for methanol is much smaller than it is for water, charged ligands should form outer-sphere complexes (ion pairs) more extensively in methanol. The mechanism described above expresses the rate constant for complex formation as the product k_0K_0. Thus the change from an aqueous to a methanolic medium is expected to produce competing effects on the rate constant for substitution.

Moreover, the magnitude of the effect on the K_0 term can be varied by comparing ligands with different charges. Uncharged ligands would be expected to form outer-sphere complexes to approximately the same extent in either solvent. Charged ligands will not only form ion pairs more extensively, but the ratio $K_0(CH_3OH)/K_0(H_2O)$ is expected to increase rapidly with increasing negative charge on the ligand. Thus this study was undertaken in the expectation that uncharged ligands would react more slowly in methanol than in water. Singly charged ligands were expected to show markedly less slowing, while doubly charged ligands might well react more rapidly in methanol than in water.

Experimental Section

Materials.—CP grade methanol from Union Carbide was dried by reaction with magnesium and distilled. Anhydrous stock solutions of methanolic nickel perchlorate were prepared in the manner described by Luz and Meiboom.[6] Anhydrous nickel chloride from K & K Laboratories and 2 equiv of G. F. Smith anhydrous silver perchlorate were covered with anhydrous methanol and the mixture was vigorously stirred. Aliquots were tested with silver ion, and, if necessary, small increments of solid nickel chloride were added until a faint but definite cloudiness due to excess chloride indicated that no unprecipitated silver ion remained. The precipitated silver chloride was then removed by filtration through a glass frit. The resulting solution was standardized against EDTA. Potassium dithiooxalate from Eastman Kodak Co. was purified by repeated reprecipitation from a minimum volume of cold water. The aqueous solution was diluted with three volumes of cold methanol and the precipitation was effected by dropwise addition of two or three volumes of cold diethyl ether. Sodium maleonitrile dithiolate was prepared as described in the literature.[7] The purity of the dithiooxalate and maleonitrile dithiolate was confirmed by spectrophotometric titration of an aliquot of standard nickel solution. In both cases a plot of absorbance at a suitable wavelength *vs.* volume of ligand solution added breaks sharply when a mole ratio of 1:2 is reached. Anhydrous reagent grade sodium perchlorate for ionic strength control was obtained from G. F. Smith and Co. Potassium selenocyanate was prepared in this laboratory some years ago by Dr. John Burmeister. All other materials were reagent grade commercial products.

Instrumentation.—All kinetic runs were made on the stopped-flow device previously described.[8] This instrument was modified during the course of this work by the introduction of a more sensitive photomultiplier and stabilized power supplies for the photomultiplier and zero-suppression circuits. In addition, the tungsten lamp was stabilized by replacing the Beckman DU power supply with a bank of 12-v batteries maintained on trickle charge. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer. Spectra of reactant and product solutions were obtained. Wavelengths offering large absorbance changes were selected for kinetic studies.

Kinetic Runs.—All kinetic runs were made under pseudo-first-order conditions at 25°. The temperature was maintained constant to within ±0.1°. The ionic strength of reactant solutions was maintained constant using sodium perchlorate as the inert electrolyte. In most runs with charged ligands, ionic reactants made only a negligible contribution to the total ionic strength. Studies with phenanthroline and bipyridine were made with nickel ion in excess and at a relatively high concentration level. Consequently, nickel perchlorate frequently accounted for a large fraction of the total ionic strength. Fortunately, as has previously been observed in rate studies with these ligands in aqueous solution, the phenanthroline and bipyridine rates are quite insensitive to ionic strength.[9]

Stock ligand and sodium perchlorate solutions were prepared by dissolving weighed quantities of the pure solids. Methanolic solutions were prepared in volumetric flasks which had been dried at 110° for at least several hours. In all cases freshly dried and distilled methanol was used for the preparation of solutions. Stock solutions were stored in tightly stoppered volumetric flasks. Dithiooxalate and maleonitrile dithiolate solutions were observed to decompose upon standing for 1 or 2 days. Consequently, kinetic runs with these ligands were made within a few hours of the preparation of the solutions.

Solutions for kinetic runs in water–methanol mixtures were prepared by pipetting appropriate volumes of water, stock sodium perchlorate solution, and stock reactant solution into oven-dried volumetric flasks which were then filled to the mark with anhydrous methanol. The per cent by volume compositions reported for these cases are computed assuming zero volume change on mixing.

Results

Phenanthroline and Bipyridine.—The rates at which phenanthroline and bipyridine react with nickel(II) ion according to eq 1 were determined in anhydrous methanol solution. In addition, the rate of the bipyridine reaction was studied in water–methanol mixtures at several compositions. In all cases, nickel ion was present in at least 20-fold excess. While stability constants for these systems are well known in water, no data are available for methanol solution. In water the formation of successive complexes follows the "normal" order of decreasing stability with increasing extent of substitution.[10] This has also been observed to be the case in aqueous ethanol. Successive formation constants for nickel–2,2′-bipyridine complexes in an aqueous medium containing 41.5% ethanol by weight have been reported[11] to be: $\beta_1 = 8.4 \times 10^6$, $\beta_2 = 4.9 \times 10^{13}$, $\beta_3 = 3.8 \times 10^{19}$. In aqueous solution the formation constants for $Ni(bipy)^{2+}$ and $Ni(phen)^{2+}$ are 5×10^7 and 6×10^8, respectively.[10] The first formation constant appears to decrease slightly in a less polar medium, but the available evidence clearly indicates that the concentrations used (nickel ion in a minimum 20-fold excess and minimum concentration 8×10^{-4} *M*) are adequate to ensure that formation of mono complex is complete and that no significant

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[6] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964); R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, *Z. Elektrochem.*, **68**, 110 (1960); data at 25°.

[7] G. Bähr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955); **90**, 438 (1957).

[8] J. Moore and R. G. Pearson, *Inorg. Chem.*, **5**, 1523 (1966).

[9] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *ibid.*, **4**, 929 (1965).

[10] A. E. Martell and L. G. Sillén, "Stability Constants of Metal Ion Complexes," 2nd ed, Special Publication No. 17, The Chemical Society, London, 1964.

[11] S. Cabani and M. Landucci, *J. Chem. Soc.*, 278 (1962).

concentrations of bis or tris complexes are formed under the conditions employed in the kinetic studies. The kinetic data obtained are consistent with the thermodynamic evidence that these reactions go completely and exclusively to the mono complex.

Excellent pseudo-first-order kinetic plots were obtained. As in aqueous solution, the reaction is first order in nickel ion concentration as well as in the ligand concentration. In all cases rate studies were performed at several nickel ion concentrations and the second-order rate constants computed for different nickel concentrations are in good agreement.

The rate observed for the formation of a complex with a bidentate ligand is commonly assumed to be limited by the rate of replacement of the first solvent molecule; coordination at the second site is usually rapid.[3] This assumption has been examined in detail by Wilkins[9] for the case of $Ni(bipy)^{2+}$ formation in water and has been found to be in excellent agreement with a variety of experimental observations.[12]

Thiocyanate and Selenocyanate.—Thiocyanate complexes with nickel(II) are not very stable in aqueous solution. Various workers have reported values for the first formation constant of about 40.[10] While no data are available for methanolic solution, the equilibrium

$$NiS_6^{2+} + X^- \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} NiS_5X^+ + S \qquad (X^- = SCN^- \text{ or } SeCN^-) \tag{6}$$

would be expected to lie farther to the right in the less polar methanolic medium. Selenocyanate decomposes rapidly in water in the presence of nickel ion.[13] Overall formation constants for $Ni(SeCN)_x^{(x-2)-}$ of $\beta_1 = 5 \times 10^2$, $\beta_2 = 3 \times 10^4$, $\beta_3 = 5 \times 10^5$, and $\beta_4 = 6 \times 10^6$ have been reported for methanol solutions containing a small amount of water.[13] In view of the great similarity of selenocyanate and thiocyanate, these values probably represent a first-order approximation to the case for the methanolic nickel thiocyanate system.

Kinetic runs were made with nickel ion in a minimum of tenfold excess. The available evidence indicates that this is adequate to ensure that complex formation is limited to the mono species. On the other hand, if $\beta_1 \approx 10^3$ for these ligands, formation of the mono complex would not be expected to be complete under the conditions of most kinetic runs. This is equivalent to observation of a nonzero value for k_{1r} in eq 6. If nickel ion is present in a constant excess, the integrated rate equation corresponding to eq 6 is

$$\ln\left(\frac{x_\infty - x}{x_\infty}\right) = -(k_{1f}[NiS_6^{2+}] + k_{1r})t \tag{7}$$

where $x = [NiS_5X^+]$ and x_∞ denotes this concentration at equilibrium. Kinetic studies were made at several nickel ion concentrations. Good first-order kinetic plots were obtained. From (7), a plot of the observed pseudo-first-order rate constant *vs.* nickel ion concentration should be linear with a slope equal to k_{1f} and an intercept equal to k_{1r}. Figure 1 shows such plots for data obtained in this study for SCN^-. In anhydrous methanol the intercept is zero within experimental error for both SCN^- and $SeCN^-$. This implies that $NiSCN^+$ and $NiSeCN^+$ formation in anhydrous methanol is complete under the conditions employed here. However, the data from studies in media containing 1 and 3 vol. % water are best fitted by lines having small positive intercepts. While the estimates of k_{1r} from these plots are not particularly accurate, the value of β_1 computed from the kinetic data ($\beta_1 = k_{1f}/k_{1r}$) for selenocyanate in these cases is in order of magnitude agreement with the value reported by Golub.

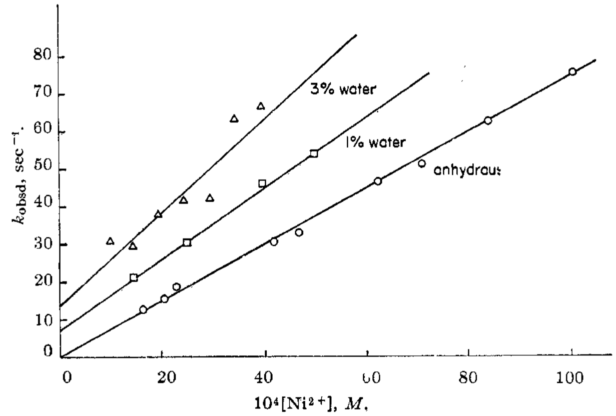

Figure 1.—Observed pseudo-first-order rate constant plotted against nickel ion concentration for the reaction $Ni^{2+} + SCN^- \rightarrow NiSCN^+$.

Dithiooxalate (DTO) and Maleonitriledithiolate (MNT).—Both bis(dithiooxalato)nickelate(II) and bis(maleonitriledithiolato)nickelate(II) are planar and diamagnetic.[14,15] In solution both complexes show the strong absorption in the visible region which is characteristic of nickel(II) in a planar environment. In both methanol and water, spectra of solutions containing nickel ion and MNT in widely varying ratios show no absorption bands which are not assignable to either free MNT or $Ni(MNT)_2^{2-}$. Similarly, aqueous solutions containing both DTO and Ni^{2+} exhibit only the characteristic spectrum of $Ni(DTO)_2^{2-}$ even at high $[Ni^{2+}]$:[DTO] ratios. In methanol, however, solutions containing an excess of nickel ion have markedly different spectra. Such solutions are an intense purple whereas solutions containing only $Ni(DTO)_2^{2-}$ are a dark red. As the excess of nickel is reduced, the spectrum changes to that of the bis complex. The spectrum of a solution containing the 1:2 stoichiometric ratio is that of the bis complex. It is not clear whether this behavior is due to stabilization of NiDTO in methanol or whether polymeric species are involved. In any case, kinetic runs with these ligands were made

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(12) However, see K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Am. Chem. Soc.*, **88**, 4610 (1966).

(13) A. M. Golub and V. V. Skopenko, *Russ. J. Inorg. Chem.*, **7**, 653 (1962).

(14) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

(15) R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964).

with the ligand present in at least tenfold excess. Since tris complexes are not formed in these systems, the product in the kinetic runs was exclusively the bis complex. The total formation constant, β_2, for $Ni(DTO)_2^{2-}$ has been estimated[16] to be 3×10^9 in aqueous solution. This value is consistent with the assumption that the reaction went to completion under the conditions of this work. Spectrophotometric examination gave no indication that $Ni(DTO)_2^{2-}$ is significantly less stable in methanol. While the corresponding stability constant for $Ni(MNT)_2^{2-}$ has not been reported, indications are that its stability is greater than that of the DTO complex. Thus Billig and co-workers have reported that displacement of MNT from $Ni(MNT)_2^{2-}$ does not occur with most common ligands. The displacement is effected by cyanide ion, but only when the cyanide ion is present in substantial excess.[17] While a large excess of cyanide ion is required to displace DTO from $Ni(DTO)_2^{2-}$, this displacement is also effected by an excess of MNT.

Excellent pseudo-first-order kinetics were observed for both ligands. Kinetic runs were made at several concentrations of excess ligand. With DTO in both methanol and water, the observed pseudo-first-order rate constants are directly proportional to the ligand concentration. That is, the observed rate law is

$$\frac{d[Ni(DTO)_2^{2-}]}{dt} = k[NiS_6^{2+}][DTO] \qquad (8)$$

Linear plots of observed first-order rate constants *vs.* [DTO] are shown in Figure 2. In both water and methanol, however, the reaction of MNT with nickel ion shows a dependence on ligand concentration which is somewhat greater than first order.

Reactions of both ligands were monitored at two wavelengths without effect on the observed rate. Within the experimental error, the absorbance changes observed in the kinetic runs were equal to the computed difference between reactants and products. These observations make it unlikely that the concentration of the intermediate mono(ligand)nickel(II) complex ever becomes significant in the course of these reactions. Where a second-order rate law is observed, as for DTO, this requires that the forward step in eq 9 be rate determining while $k_{2f} >> k_{1f}$ and k_{1r} is small.

$$NiS_6^{2+} + L^{2-} \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} NiS_4L + 2S \qquad (9)$$

$$NiS_4L + L^{2-} \xrightarrow{k_{2f}} NiL_2^{2-} + 4S \qquad (10)$$

The data for the MNT reactions are fitted well by the assumption that k_{1r} is relatively large so that Ni-MNT can return to reactants as well as go on to $Ni(MNT)_2^{2-}$. Assuming that the concentration of NiMNT reaches a steady state, the rate of appearance of $Ni(MNT)_2^{2-}$ becomes

$$\frac{d[Ni(MNT)_2^{2-}]}{dt} = \left(\frac{k_{1f}k_{2f}[MNT]^2}{k_{2f}[MNT] + k_{1r}}\right)[NiS_6^{2+}] \qquad (11)$$

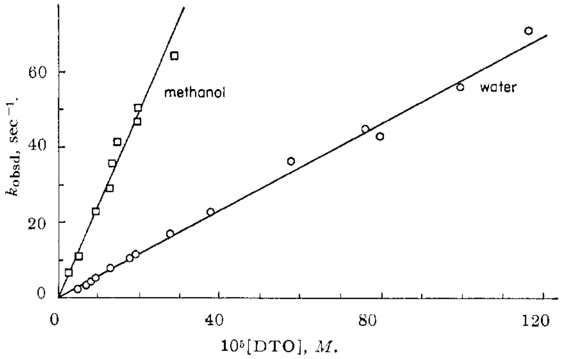

Figure 2.—Observed pseudo-first-order rate constant plotted against concentration of dithiooxalate ion for the reaction $Ni^{2+} + 2DTO^{2-} \rightarrow Ni(DTO)_2^{2-}$.

Hence

$$k_{obsd} = \frac{k_{1f}k_{2f}[MNT]^2}{k_{2f}[MNT] + k_{1r}} \qquad (12)$$

Since this can be rearranged to give

$$\frac{[MNT]}{k_{obsd}} = \frac{1}{k_{1f}} + \left(\frac{k_{1r}}{k_{1f}k_{2f}}\right)\frac{1}{[MNT]} \qquad (13)$$

a plot of $[MNT]/k_{obsd}$ *vs.* $1/[MNT]$ should be linear with an intercept equal to $1/k_{1f}$ and a slope equal to $k_{1r}/k_{1f}k_{2f}$. The data for the aqueous reaction are plotted in this manner in Figure 3. There is a very great scatter because of the method of handling the data. Nevertheless, values of $1/k_{1f}$ and k_{1r}/k_{2f} from such plots have been used to reconstitute k_{obsd} *vs.* [MNT] curves. The solid line in Figure 4 was computed in this way. The points are experimental. In the case of the aqueous reaction, the agreement is clearly better than that afforded by any possible straight line. However, the methanol reaction exhibits less curvature and is fitted almost as well by a straight line through the origin (corresponding to simple first-order dependence on [MNT]). This difference is readily rationalized on the basis of the interpretation presented here. The reverse reaction in eq 9 must involve charge separation in the transition state. Hence, k_{1r} would be expected to be smaller in methanol than in water. In the limit of $k_{1r} = 0$, relation 12 becomes $k_{obsd} = k_{1f}[MNT]$.

Discussion

This study was begun in the expectation that the mechanism for metal complex formation would be the same in methanol as in water. That the data obtained conform well to the general kinetic features of the aqueous reactions summarized in the Introduction indicates that this expectation has been realized. Moreover, comparison of aqueous and methanolic rates provides additional support for the ion-pair interchange mechanism described by eq 2 and 3.

This mechanism expresses the second-order rate constant, k_{1f}, as the product K_0k_0. If the ion-pair equilibrium constant, K_0, can be estimated, the rate of ligand interchange between first and second coordination spheres, k_0, is readily calculated. Since k_0 should be insensitive to the nature of the incoming ligand and should be similar to the rate of solvent exchange on the

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(16) W. A. Deskin, *J. Am. Chem. Soc.*, **80**, 5680 (1958).

(17) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

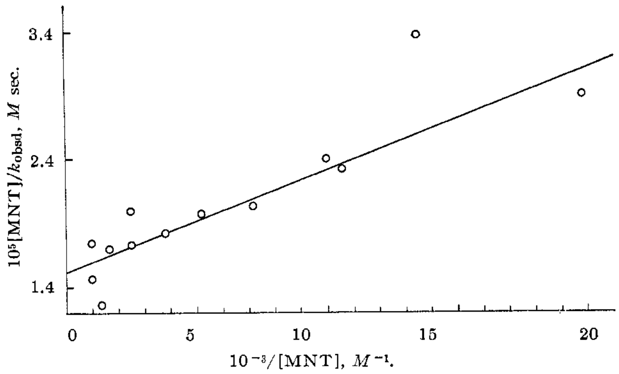

Figure 3.—Plot of concentration of maleonitriledithiolate ion divided by observed first-order rate constant *vs.* the reciprocal of the maleonitriledithiolate concentration (aqueous solution).

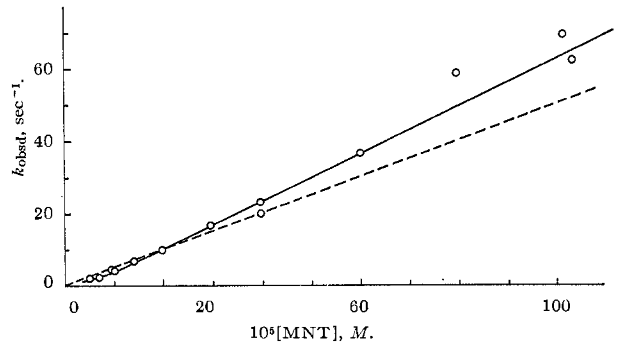

Figure 4.—Observed pseudo-first-order rate constant plotted against maleonitriledithiolate ion concentration for the reaction $Ni^{2+} + 2MNT^{2-} \rightarrow Ni(MNT)_2^{2-}$. The circles are experimental points; the solid line is calculated from eq 12; the dashed line is a straight line (aqueous solution).

free nickel(II) ion, this procedure constitutes a test of the mechanism. Unfortunately, experimental K_0 values are not available for the systems of interest. Consequently, it is necessary to rely on estimates computed from a theoretical equation. Reasonable values are obtained from the equation

$$K_0 = \frac{4\pi N a^3}{3000} e^{-U(a)/kT} \tag{14}$$

where

$$U(a) = \frac{z_1 z_2 e^2}{aD} - \frac{z_1 z_2 e^2 \kappa}{D(1 + \kappa a)}$$

and

$$\kappa^2 = \frac{8\pi N e^2 \mu}{1000DkT}$$

In this equation N is Avogadro's number, a is the distance of closest approach of the two ions, k is Boltzmann's constant, T is the absolute temperature, e is the charge of an electron, D is the bulk dielectric constant, μ is the ionic strength, z_1 and z_2 are the charges on ions 1 and 2, respectively. This result has been derived independently by Fuoss and Eigen.[18,19]

Previous workers have taken the distance of closest approach, a, to be 5 A in aqueous solution. The van der Waals radius of a methyl group is 0.8 A greater than for a hydrogen atom. For methanol, therefore, a distance of 6 A seems reasonable. Table I shows values of K_0 computed from eq 14 for methanol and water solutions at various ionic strengths. While the justification for using this equation at the higher ionic strengths is tenuous, the values obtained are reasonable in all cases. Nevertheless, they cannot be regarded as accurate to better than a factor of 3 or 4.

TABLE I

ION-PAIR CONSTANTS FROM THE FUOSS RELATION AT 25°

$K_0 = [NiS_6,L^{(2-z)+}]/[NiS_6^{2+}][L^{z-}]$

μ	$z = 1$	$z = 2$
	Methanol (a = 6 A)	
0.500	3.3	20
0.300	4.6	40
0.100	10	130
0.050	16	500
0.000	170	50,000
	Water (a = 5 A)	
0.500	1.2	4.5
0.300	1.4	6.5
0.100	2.0	14
0.050	2.5	21
0.000	5.6	100

Table II presents some representative rate constants from the literature for reactions of negatively charged ligands with nickel ion in aqueous solution. Column two lists observed second-order rate constants, k_{1f}, and column three shows k_0 values computed ($k_0 = k_{1f}/K_0$) using K_0 values obtained from eq 14. This study has obtained these rate constants for the aqueous reactions of MNT and DTO. These values are presented in columns five and six of Table III. Inspection of the tables shows that the k_0 values obtained vary over approximately a factor of 6. When the uncertainty in the evaluation of K_0 and the large variation in second-order rate constants are considered, the constancy of k_0 for various ligands is remarkable. This is in complete accord with the requirements of the ion-pair interchange mechanism and further indicates that

TABLE II

$Ni(H_2O)_5L$ FORMATION RATES IN AQUEOUS SOLUTION AT 25°

Ligand	k_{1f}, M^{-1} sec^{-1}	k_0, sec^{-1}
$HP_2O_7^{3-}$ [a]	2.1×10^6	2×10^4
tiron^{3-} [b]	2.9×10^5	0.3×10^4
$C_2O_4^{2-}$ [c]	7.5×10^4	0.5×10^4
SO_4^{2-} [d]	...	1.5×10^4
$HC_2O_4^-$ [c]	5×10^3	0.3×10^4
digly$^-$ [e]	2.1×10^4	1×10^4
SCN^- [f]	6×10^3	0.5×10^4

[a] G. G. Hammes and M. L. Morrell, *J. Am. Chem. Soc.*, **86**, 1497 (1964). [b] K. Kustin and K. O. Watkins, *Inorg. Chem.*, **3**, 1706 (1964) [rate measured at 20°]. [c] G. H. Nancollas and N. Sutin, *ibid.*, **3**, 360 (1964). [d] M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962) [20°, measurement by sound absorption]. [e] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962); digly$^-$ is the diglycinate anion. [f] A. G. Davis and W. M. Smith, *Proc. Chem. Soc.*, 380 (1961).

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(18) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(19) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

Table III

Comparison of Rates at 25°

$$\mathrm{NiS_6}^{2+} + \mathrm{L}^{z-} \xrightarrow{k_{1f}} \mathrm{NiS_5L}^{(2-z)+} + \mathrm{S}$$

Ligand	μ	$k_{1f}(CH_3OH)$, M^{-1} sec^{-1}	$k_0(CH_3OH)$, sec^{-1}	$k_{1f}(H_2O)$, M^{-1} sec^{-1}	$k_0(H_2O)$, sec^{-1}
phen	0.200	3.5×10^2	...	3.2×10^3 [a]	...
bipy	0.200	1.4×10^2	...	1.6×10^3 [a]	...
	0.100	1.2×10^2	...	...	...
	0.060	1.0×10^2	...	...	...
SCN^-	0.50	(3.6×10^3)[c]	...	6×10^3 [b]	5.0×10^3
	0.300	4.5×10^3	1.0×10^3	...	...
	0.100	7.4×10^3	0.74×10^3	...	...
	0.050	1.2×10^4	0.75×10^3	...	...
$SeCN^-$	0.100	5.3×10^3	0.53×10^3	...	...
MNT^{2-}	0.100	2.0×10^5	1.5×10^3	6.6×10^4	4.7×10^3
DTO^{2-}	0.100	2.5×10^5	1.9×10^3	5.8×10^4	4.1×10^3
	0.050	5.4×10^5	1.1×10^3	8.0×10^4	3.8×10^3

[a] See ref 9. [b] A. G. Davis and W. M. Smith, *Proc. Chem. Soc.*, 380 (1961). This value is an extrapolation from a log k *vs.* $1/T$ plot of lower temperature data given in this reference. [c] Estimated from data at the lower ionic strengths by means of a plot of k_{1f} *vs.* $K_0(\mu)$.

ligand participation in the transition state of reaction 3 has a negligible effect on the energetics. A median value for k_0 would be 10^4 sec^{-1}. This compares to an exchange rate for $Ni(H_2O)_6^{2+}$ of 3.0×10^4 sec^{-1}, again in good agreement with the requirements of the mechanism. If the ligand partner in the ion pair has a negligible effect on the water-exchange rate, k_0 would be expected to be equal to the product of a steric factor, f, and the solvent exchange rate, k_{ex}: $k_0 = fk_{ex}$. The factor $(1 - f)$ represents the fraction of the time that solvent exchange occurs at a site remote from L and hence does not lead to substitution by the ligand. This steric factor, f, must be less than 1 and hence k_0 should be somewhat smaller than k_{ex}, as is observed.

The Introduction discussed qualitatively the rate effects predicted by the ion-pair interchange mechanism for changing the solvent from water to methanol. Comparison of columns three and five in Table III shows that these expectations have been borne out. Calculating k_0 values from the methanolic rates in column three using the appropriate K_0 values from Table I gives the results in column four of Table III. As in the aqueous case, the values are remarkably constant. Here a median value of k_0 is about the same as the rate for methanol exchange on $Ni(CH_3OH)_6^{2+}$, implying that the steric factor, f, is unity. Probably, this is a reflection of the uncertainty in the computation of K_0 and has no mechanistic significance.

The effect of added water on the rate of the reactions is also readily interpreted on the basis of the ion-pair interchange mechanism. Luz and Meiboom[20] have reported that the rate of methanol exchange on nickel ion is accelerated by addition of water. This is reasonable since addition of even small amounts of water will lead to the formation of mixed methanol–aquo complexes, $Ni(CH_3OH)_{6-x}(H_2O)_x^{2+}$. These would be reasonably expected to undergo solvent exchange at a rate intermediate between that for $Ni(CH_3OH)_6^{2+}$ and that for $Ni(H_2O)_6^{2+}$. Hence, the k_0 term is expected to become larger with increasing water content although the bulk of the effect would probably occur with only small amounts of water. Addition of water will affect the K_0 term only through the effect of the bulk dielectric constant. Relatively large amounts of water would be required to produce a substantial decrease in K_0.

These considerations lead to the conclusion that small amounts of water should increase the second-order rate irrespective of the charge on the incoming group. Uncharged ligands are expected to form ion–dipole pairs to an extent relatively independent of the dielectric constant. Thus the effect on k_0 should be of predominant importance. The substitution rate should rise smoothly but progressively less rapidly with increasing water content. The results for bipyridine presented in Table IV conform to this expectation.[21] For charged ligands, on the other hand, small amounts of water should again increase the rate, but eventually the increasing dielectric constant must cause K_0 to decrease. The rate is therefore expected to go through a maximum.

This expectation is partially fulfilled by the available data. The rates of both the thiocyanate and selenocyanate reactions increase with small amounts of added water (Table IV) in a medium of ionic strength 0.1 M. Unfortunately, experimental aqueous rates at this ionic strength are not available for comparison. If, however, the aqueous rate for SCN^- substitution at ionic strength 0.5 M is corrected to 0.1 M using the appropriate ratio of K_0 values (see below), one obtains $k_{1f} = 1.0 \times 10^4\ M^{-1}$ sec^{-1}. This value is slightly less than that ($k_{1f} = 1.5 \times 10^4\ M^{-1}$ sec^{-1}) observed in a medium containing 97% methanol and 3% water. These values should require the anticipated maximum. In view of the approximations involved in obtaining the aqueous value, however, the difference between the aqueous and methanolic values is not large enough to be conclusive.

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[20] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1066 (1964).

[21] E. F. Caldin, private communication, has observed that the rate of formation of $Ni(py)^{2+}$ is the same in pure H_2O and in 99% CH_3OH–1% H_2O.

TABLE IV

EFFECT OF ADDED WATER ON THE RATE OF THE REACTION

$$\mathrm{NiS_6}^{2+} + \mathrm{L}^{z-} \xrightarrow{k_{1f}} \mathrm{NiS_5L}^{(2-z)+} + \mathrm{S}$$

Ligand	μ	Vol. % H_2O	k_{1f}, M^{-1} sec^{-1}
bipy	0.200	0	1.4×10^2
	0.200	1	2.1×10^2
	0.200	3	4.3×10^2
	0.200	5	5.7×10^2
	0.200	10	8.0×10^2
	0.200	25	11×10^2
		100	16×10^2 [a]
SCN^-	0.100	0	7.4×10^3
	0.100	1	9.4×10^3
	0.100	3	13×10^3
	0.100	100	10×10^3 [b]
$SeCN^-$	0.100	0	5.3×10^3
	0.100	1	10×10^3
	0.100	3	16×10^3

[a] See ref 9. [b] See text.

The effect of ionic strength on the reaction rate is also well explained by the ion-pair interchange mechanism. Ionic strength is expected to affect the rate only through the K_0 term. Consequently, for a given ligand, the ratio of rates at two ionic strengths should be equal to the corresponding ratios of K_0 values. Equivalently, computed k_0 values should be independent of ionic strength. Data are available for the thiocyanate reaction in methanol and for the dithiooxalate reaction in both water and methanol. As can be seen from Table III, constant k_0 values are obtained for thiocyanate and the aqueous dithiooxalate reaction. The results for the dithiooxalate reaction in methanol are in less satisfactory agreement. Inspection of the data reveals that agreement is least satisfactory under conditions of high ionic strength, large ligand charge, and low dielectric constant. These are precisely the conditions under which theoretical treatment of ionic strength effects is expected to become inadequate.

Substitution in octahedral complexes has often been discussed in terms of a "five-coordinate intermediate" arising from an SN1 dissociative mechanism. Such an intermediate can be considered in either of two roles. Within the framework of the ion-pair interchange mechanism, the reaction of eq 3 could be considered to proceed through such an intermediate. It has been seen, however, that ion-pair collapse to inner-sphere product proceeds at a rate which is independent of the nature of the ligand. Therefore, such an intermediate could have little ability to discriminate among nucleophiles. However, an ability to discriminate among nucleophiles is usually taken as the minimum requirement which must be demonstrated to support the postulate of a five-coordinate intermediate.

Alternatively, one can consider the following mechanism in which ion pairs play no role. The five-coordinate intermediate is produced to a small extent in a rapid-equilibrium step (15).

$$\mathrm{NiS_6}^{2+} \underset{}{\overset{K_5}{\rightleftharpoons}} \mathrm{NiS_5}^{2+} + \mathrm{S} \tag{15}$$

$$\mathrm{NiS_5}^{2+} + \mathrm{L}^{z-} \xrightarrow{k_5} \mathrm{NiS_5L}^{(2-z)+} \tag{16}$$

It then reacts with L in the rate-determining step to produce the inner-sphere complex. One obtains the rate law

$$\frac{\mathrm{d}[\mathrm{NiS_5L}^{(2-z)+}]}{\mathrm{d}t} = K_5k_5[\mathrm{NiS_6}^{2+}][\mathrm{L}^{z-}] \tag{17}$$

The rate of the slow step (16) would be expected to be unaffected by dielectric constant for an uncharged ligand and to increase faster in methanol than in water for ligands bearing progressively more negative charges. To rationalize the observed solvent effect on the basis of this mechanism, one must then assume that K_5 is smaller in methanol than in water.

The explanation afforded by this mechanism is inferior to that provided by the ion-pair interchange mechanism in two respects. First, since ligands bearing the same charge are observed to react at about the same rate, the postulated five-coordinate intermediate cannot be discriminating among incoming groups of the same charge on the basis of relative nucleophilicities. Second, the assumption that K_5 would be smaller in methanol than in water is without independent support.

In fact, one can reasonably argue that K_5 should be larger in methanol than in water. Available evidence on mixed alcohol–water metal solvates indicates that water is more tightly bound to metal ions than are alcohols.[22] If water is more tightly bound in these systems, one would expect that dissociation of a water molecule to give a five-coordinate species would be more difficult than dissociation of a methanol molecule. Steric considerations would suggest the same conclusion. This, of course, is exactly the opposite of the assumption required to make the mechanism of (15) and (16) fit the kinetic observations.

In conclusion, the results of this study are in excellent semiquantitative agreement with the predictions of the ion-pair interchange mechanism. It would be very desirable to obtain directly measured values of the ion-pair equilibrium constant. However, the high rate of formation of the inner-sphere complexes makes this virtually impossible. As a result one must rely on values of K_0 estimated by eq 14. While these values are open to some criticism, it should be borne in mind that studies in aqueous solution have invariably involved the use of eq 14 also.[23] It is the consistency of the kinetic results found in methanol with those found in water that offers the best evidence for the mechanism.

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(22) R. G. Pasternack and R. A. Plane, *Inorg. Chem.*, **4,** 1171 (1965).

(23) See the references of Table II.