

Ligand Substitution Kinetics of Nickel(II) Ion in a Solvent of Low Donor Strength. Propylene Carbonate

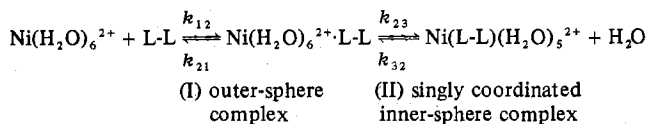
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As part of an investigation of the influence of the donor strength and other properties of the solvent on the substitution kinetics of labile metal complexes, we have studied the reactions of nickel(II) ion with 4-phenylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine in the very weak donor propylene carbonate as solvent. Reaction rates at 25 °C are the highest and activation enthalpies are among the lowest found so far for nickel(II) ion in any solvent. The weak donor ability of the solvent made it necessary to devote particular attention to purification of the solvent and assessment of the influence of impurities; the effect of propylene glycol was found to be unusual.

In aqueous solution, the rate constants and activation parameters for many ligand substitution reactions at metal ions are similar to the corresponding quantities for solvent exchange and depend only slightly on the nature of the ligand. In such cases, the reaction is best represented by a dissociative interchange (I_d) mechanism,^{2,3} which can be illustrated as in eq 1 for the reaction of nickel(II) ion with an uncharged,



(III) doubly coordinated (chelated) inner-sphere complex

bidentate ligand. Process I is rapid (diffusion controlled) and, with few exceptions,^{3,4} process III is also rapid. Process II is therefore the rate-determining step for most ligands reacting by an I_d mechanism, irrespective of their dentate numbers. The complete rate equations can be found elsewhere,^{3,5} only the simplest but most common case will be considered here. Provided (i) a large excess of nickel(II) ion is present, (ii) both intermediates are present at steady-state concentrations, and (iii) the concentration of the outer-sphere complex is much smaller than that of free ligand, the rate equation reduces to

$$d[\text{NiL}_2^{2+}]/dt = k_{1,f}[\text{Ni}^{2+}][\text{L-L}] - k_{1,d}[\text{NiL}_2^{2+}] \quad (2)$$

where

$$k_{1,f} = K_{12}k_{23} \quad (3)$$

$$k_{1,d} = k_{32}(k_{43}/k_{34}) = k_{32}/K_{34} \quad (4)$$

Here $k_{1,f}$ and $k_{1,d}$ are the overall second-order and first-order rate constants for ligand substitution resulting in formation and dissociation, respectively, of the inner-sphere complex. The equilibrium constant, K_{12} , applies to the formation of the outer-sphere complex. For a unidentate ligand, eq 3 also applies, but eq 4 simplifies to $k_{1,d} = k_{32}$. It is convenient to write eq 2 in the form

$$k_{\text{obsd}} = k_{1,f}[\text{Ni}^{2+}] + k_{1,d} \quad (5)$$

where k_{obsd} is the experimentally observed pseudo-first-order rate constant, showing that a plot of k_{obsd} vs. $[\text{Ni}^{2+}]$ should be linear with a slope and intercept equal to $k_{1,f}$ and $k_{1,d}$, respectively.

Since the rate-determining step of reaction 1 (process II) involves loss of a solvent molecule from the inner-coordination sphere of the metal ion, its rate constant, k_{23} , should be related to that for solvent exchange, k_s , as $k_{23} = fk_s$, where f represents

the probability that the ligand will enter a particular coordination site vacated by a solvent molecule. Hence, for an I_d mechanism the following relationship should apply

$$k_{1,f} = fK_{12}k_s \quad (6)$$

However, assignment of a mechanism is complicated by the fact that evaluation of both f and K_{12} is uncertain; difficulties have been discussed recently.⁵⁻⁷ For f , we will use a value of $3/4$, recommended by Neely and Connick,⁸ and for K_{12} , values calculated from the Eigen-Fuoss expression

$$K_{12} = 4\pi Na^3/(3 \times 10^3) \quad (7)$$

where a is the center-to-center distance of closest approach of the solvated metal ion and the reaction site on the ligand. In testing for an I_d mechanism, it is convenient to consider a dimensionless ratio R_1 given by

$$R_1 = (4/3)k_{1,f}/K_{12}k_s \quad (8)$$

which should have a value near unity. Furthermore, the activation parameters for ligand substitution should be similar to those for solvent exchange. These criteria for an I_d mechanism are met reasonably well by a large number of labile complexes in aqueous solution.^{2,3,9,10}

In reaction 1, the solvent is assigned a direct and crucial role. Consequently, variation of the solvent would be highly desirable. Pioneering work in which this was done was carried out by Pearson and Ellgen¹¹ and Bennetto and Caldin.¹² During the last few years considerable additional information has accumulated on the solvent dependence of ligand substitution kinetics of labile metal complexes, and it has been reviewed recently.⁵ The principal finding has been that *the apparently straightforward behavior of aqueous solutions is not general*. The solvent influences all three steps in reaction 1, often in a complex manner. The entire spectrum of solvent effects has not yet been resolved. However, in our opinion, two solvent properties may prove to be of particular importance; these are the donor strength of the solvent toward the metal ion and, in the case of bulky solvent molecules, steric crowding in the inner sphere of the solvated metal ion. These two properties are the subjects of this and the following paper.

The solvent under consideration here, propylene carbonate, is an important member of the class of dipolar aprotic solvents. It is often the solvent of choice when it is desirable to minimize solvation of both cations and anions without sacrificing a high dielectric constant. It shares with other dipolar aprotic solvents the property of being a poor proton and hydrogen-bond donor. It is also a relatively weak electron donor, similar to acetonitrile with respect to hydrogen ion¹³ and antimony pentachloride¹⁴ as acceptors and much weaker than acetonitrile toward nickel(II) ion as acceptor. As a result of its relative chemical inertness, the liquid exhibits little specific association.

Table I. Impurity Levels in Propylene Carbonate Obtained by Different Methods

| | Method | | |
|----------------------------------|-----------|----------|-----------|
| | A | B | C |
| Water | 2-3 mM | 4 mM | 4 mM |
| 1,2-Propanediol | 0.7 mM | <0.03 mM | <0.03 mM |
| Allyl alcohol | 0.02 mM | Trace | Absent |
| Propylene oxide | 0.02 mM | Trace | Absent |
| Optical absorbance ($l = 1$ cm) | | | |
| At 340 nm | 0.04 | 0.04 | 0.04 |
| At 240 nm | 0.38-0.43 | 0.30 | 0.43-0.46 |

However, its high polarity results in some nonspecific order and a high dielectric constant of 64.

It is important to obtain kinetic information in a solvent possessing low donor strength and weak specific order if the highly complex solvent dependence of ligand substitution kinetics is ever to be understood. The donor strength of the solvent is expected to be important because it should influence the relative stabilities of the transition state and the ground state of the metal ion. Stabilization of the ligand is expected to be less important if the transition state involves a dissociative mode of activation, which seems to be the case for octahedral nickel complexes in all solvents studied so far. An equally important reason for the choice of propylene carbonate for studies of this kind is that the composition of the inner sphere of the metal ion can be changed by adding low concentrations of stronger donor solvents, such as dimethyl sulfoxide, without introducing major complications caused by changes in bulk solvent structure.

Experimental Section

Solvent. Since propylene carbonate is a very weak ligand toward nickel(II) ion, it was necessary to devote particular attention to its purification and tests for impurities. Previous work¹⁵ had shown that principal impurities are water, propylene oxide, allyl alcohol, and both 1,2- and 1,3-propanediol (propylene glycol), and it was to be expected that all of these would be stronger ligands than propylene carbonate. Commercial propylene carbonate (Eastman) was purified by shaking with Molecular Sieves (Linde 4A) for at least 1 day, followed by two preliminary vacuum distillations from anhydrous calcium sulfate under nitrogen at a pressure of 1 Torr through a 25-in. vacuum-jacketed and silvered column packed with glass helices. A third and final distillation was carried out under nitrogen at a pressure of 1 Torr, a pot temperature near 110 °C, and a head temperature near 70 °C, in three different ways: (A) as for the preliminary distillations, at a distillation rate of 60 ml/h; (B) as for (A), but with the calcium sulfate omitted; and (C) as for (B), but in a Perkin-Elmer Model 251 Auto Annular Still with a Teflon spinning band, at a reflux ratio of 5:1 to 10:1 and a distillation rate of 10 ml/h. During each distillation, the purity of the product was monitored through the ultraviolet spectrum of each 100-200-ml cut, using as a criterion of purity the absence of appreciable absorption in the region just below 340 nm.¹³ The middle two-thirds fraction of the solvent was collected for further tests, mainly by gas chromatography using a Hewlett-Packard Model 5750 instrument. Our conditions for satisfactory gas chromatographic analysis differed somewhat from those employed by Jasinski¹⁵ and were as follows: column, 10 ft 3% OV-17; column temperature, 70-140 °C at 4 °C/min; injector temperature, 140 °C; sample size, 10 μ l; detector, flame ionization; carrier gas, air (34 ml/min) + hydrogen (57 ml/min) + nitrogen (50 ml/min). Finally, water was determined with a Photovolt Aquatest II Karl Fischer titrator. Results are presented in Table I. It appears that final distillation from calcium sulfate (method A) has the disadvantage that it produces solvent containing significant amounts of propylene glycol (for the effect of this impurity, see Results and Discussion) without offering any offsetting advantage of reducing the water content significantly. Method C was used for subsequent measurements.

Reagents. Nickel was introduced as $\text{Ni}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n \approx 2$), prepared as described before.¹⁶ Its solutions and also those of the ligands were dried overnight with molecular sieves (Linde 4A, $1/16$ -in. pellets, heated in vacuo at 350 °C), after which Karl Fischer titration detected no water (less than a few tenths of 1 mM). The nickel

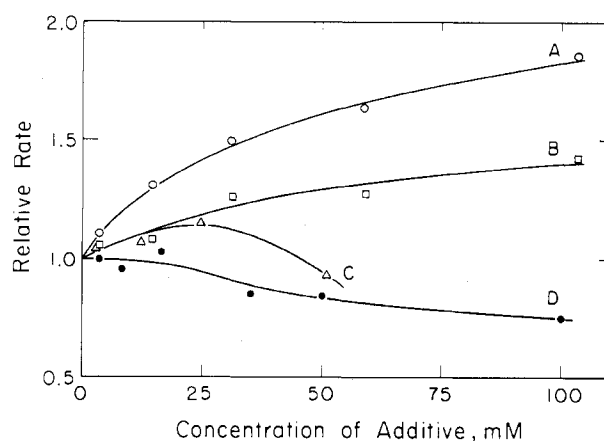


Figure 1. Effect of impurities (X) on rates of reaction of nickel(II) ion with incoming ligands (Y) in propylene carbonate at 25 °C: (A) $C_{\text{Ni}} = 4 \times 10^{-4}$ M, X = water, Y = 2,2'-bipyridine; (B) $C_{\text{Ni}} = 1 \times 10^{-3}$ M, X = water, Y = 4-phenylpyridine; (C) $C_{\text{Ni}} = 2 \times 10^{-3}$ M, X = propylene oxide, Y = 4-phenylpyridine; (D) $C_{\text{Ni}} = 1 \times 10^{-3}$ M, X = 1-propanol, Y = 2,2'-bipyridine.

solutions were then standardized by EDTA titration.¹⁶ Other details have been given before.¹⁶

Instrumentation and Experimental Procedure. Kinetic measurements were made with a Durrum Instrument Co. (Palo Alto, Calif.) Model D-110 stopped-flow spectrophotometer equipped with a Kel-F flow system, following the precautions necessary for adequate temperature control.¹⁶ Reactions were monitored at wavelengths where the complex and free ligand show the largest difference in absorptivity, viz., at 275, 307, 271, and 334 nm for 4-phenylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine, respectively. Pseudo-first-order conditions were maintained, with (phenanthroline excepted) the total ligand concentration (C_l) held constant at 2.5×10^{-5} M (after mixing) and the total nickel concentration (C_{Ni}) varied through three or four values from 0.5 to 2.0 mM. In the case of phenanthroline, the reaction is so fast that it was necessary to reduce C_{Ni} to 0.3-1.0 mM and C_l to 5×10^{-6} M. Reproducibility of second-order rate constants was $\pm 20\%$ for phenanthroline and $\pm 5\%$ for other ligands.

Results and Discussion

The influence of the known impurities, water, propylene oxide, and propylene glycol (X), on the kinetics of the reactions of nickel(II) ion with 4-phenylpyridine and 2,2'-bipyridine (Y) was determined. These impurities are much stronger ligands than propylene carbonate (S) toward nickel(II) ion, so that it may be expected that, even at quite low concentrations of X, mixed complexes of the type $\text{NiX}_a\text{S}_b^{2+}$ will be present. It also may be expected that S will be more labile in these mixed complexes than in NiS_6^{2+} , so that, if a dissociative mechanism applies, the mixed complexes will react faster with Y than NiS_6^{2+} does. As far as the fully substituted complex MiX_6^{2+} is concerned, evidence obtained so far for several types of X in a variety of weak-donor solvents indicates that it generally reacts more slowly with Y than NiS_6^{2+} does.¹⁷ Consequently, when increasing amounts of X are added to NiS_6^{2+} , the rate of the reaction with Y generally passes through a maximum.

Some of the results obtained at relatively low concentrations of X are shown in Figure 1. The effects of the known impurities, water and propylene oxide, as well as of 1-propanol, which was added for purposes of comparison with propylene glycol, are relatively modest. The effect of water was expected to be larger, because the ease with which water is removed from propylene carbonate by molecular sieves (see Experimental Section) indicates that water is only weakly hydrogen bonded to propylene carbonate and that it therefore should have a high activity toward nickel.

The influence of the remaining known impurity, propylene glycol, is much more drastic than that of 1-propanol and is shown in Figure 2. The shape of the curve is consistent with

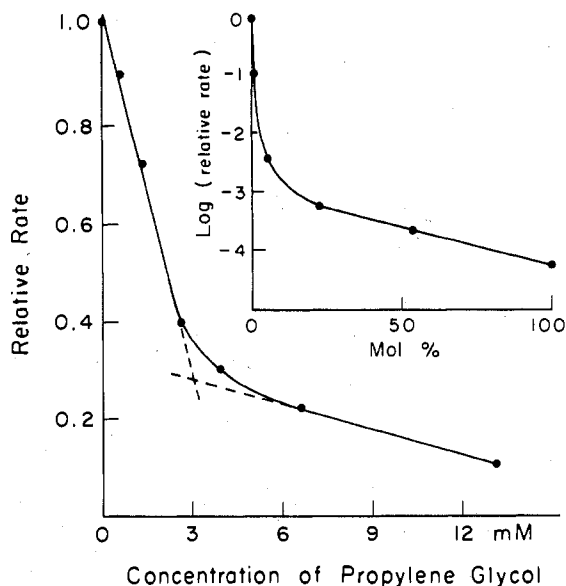


Figure 2. Effect of propylene glycol on rate of reaction of nickel(II) ion with 2,2'-bipyridine in propylene carbonate at 25 °C: large curve, plot of relative values of k_{obsd} for $C_{\text{Ni}} = 1.0 \times 10^{-3}$ M; inset, plot of relative values of $k_{1,f}$, the second-order rate constant, determined over a range of C_{Ni} values from 0.5 to 2 mM.

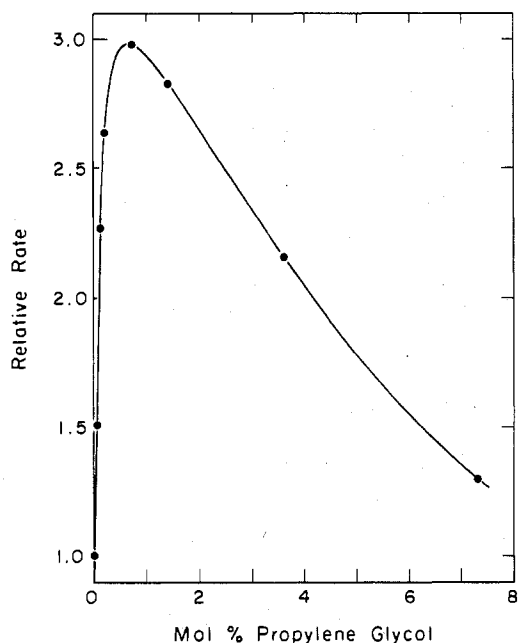


Figure 3. Effect of propylene glycol on rate of reaction of nickel(II) ion with 4-phenylpyridine in acetonitrile at 25 °C; $C_{\text{Ni}} = 1 \times 10^{-3}$ M.

virtual completion of the reaction of nickel(II) ion with propylene glycol acting as a bidentate ligand. The same conclusion was reached for C_{Ni} values of 0.5 and 2.0 mM. However, the shape of the curve is surprising in that it does not exhibit the expected maximum, such as is shown in Figure 3 for acetonitrile as solvent. If it were not for the effectiveness of molecular sieves, which reduces the water content to below a few tenths of 1 mM, the possibility would have arisen that the major nickel species initially present was a mixed solvate, such as $\text{Ni}(\text{H}_2\text{O})_4\text{S}_2^{2+}$, which could have accounted for the shape of Figure 2, for the only modest acceleration of reactions with Y when further water is added (Figure 1), and for the very high rates in general (see Table II). The possibility also had to be considered that, instead of water, an unidentified impurity is initially present in the inner sphere. However, the

Table II. Rate Constants and Activation Parameters for Ligand Substitution at Nickel(II) Ion in Propylene Carbonate as Solvent

| Ligand | $\log k_{1,f}^a$ | | | ΔH^\ddagger ^b | ΔS^\ddagger ^c |
|------------------|------------------|------------------|------------------|----------------------------------|----------------------------------|
| | 10 °C | 15 °C | 25 °C | | |
| 4-Phenylpyridine | 4.9 ₆ | 5.2 ₀ | 5.3 ₁ | 8 | ~-6 |
| Phenanthroline | 6.3 | 6.5 | ~7 | | |
| Bipyridine | 5.2 ₉ | 5.3 ₆ | 5.4 ₅ | 4 | ~-20 |
| Terpyridine | 5.0 ₅ | 5.1 ₄ | 5.3 ₂ | 6 | ~-13 |

^a Units: $\text{l. mol}^{-1} \text{s}^{-1}$. ^b Units: kcal mol^{-1} (1 cal = 4.18 J).

^c Units: $\text{cal K}^{-1} \text{mol}^{-1}$.

electronic spectrum of nickel provides no evidence for this. The unexpected shape of Figure 2 therefore remains unexplained, although it is conceivable that, for some reason, the mono and bis complexes of nickel(II) ion with propylene glycol are much less stable than the tris complex.

Rate constants and activation parameters for the reaction of nickel(II) ion with 4-phenylpyridine, 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine are reported in Table II. The data will be compared to those obtained in other solvents in the following paper.¹⁸ Only three features will be noted here. First, rate constants generally parallel those in acetonitrile, which is also a relatively weak donor toward nickel(II) ion, but here they are some two powers of 10 higher. In fact, rate constants in propylene carbonate are the highest found so far in any solvent. The fact is beginning to emerge that there is some correlation between ligand substitution rates and donor strength of the solvent, although the correlation is perturbed by steric and other effects. Second, in propylene carbonate, nickel(II) ion exhibits little discrimination among ligands, with the exception of phenanthroline, which appears to exhibit atypical behavior in all nonaqueous solvents studied so far.¹⁸ Third, the kinetic parameters for solvent exchange in propylene carbonate are not yet available. However, in a variety of solvents previously studied, the kinetic parameters for substitution by 4-phenylpyridine are consistent with those for solvent exchange within the framework of a dissociative interchange mechanism. For 4-phenylpyridine the value of R_1 calculated from eq 7 and 8 typically falls in the range 0.3–1.0. By analogy, we estimate that for the solvent-exchange parameters of nickel(II) ion in propylene carbonate, $\log k_s(25^\circ\text{C}) \approx 5.7$ and $\Delta H_s^\ddagger \approx 8 \text{ kcal mol}^{-1}$.

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Registry No. Ni²⁺, 14701-22-5; 4-phenylpyridine, 939-23-1; phenanthroline, 66-71-7; bipyridine, 366-18-7; terpyridine, 1148-79-4.

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