This apparent anomaly could likely be due to several factors among which are strong hydrogen bonding between the free amine and coordinated amines, greater solvation of the amine relative to the ester carbonyl function, steric considerations, etc.

In other solvent systems *cis*-$Co(en)_2(enH)Cl^{3+}$ behaves differently under basic conditions. For example in dimethyl sulfoxide, using piperidine to deprotonate the ammonium function, $Co(en)_3^{3+}$ is the sole product identified *via* its visible adsorption spectrum ($\epsilon_{469}^{\max}$ 86 for product; $\epsilon_{469}^{\max}$ 87 for $[Co(en)_3]Cl_3$[23]).

Acknowledgment.—We are indebted to the National Science Foundation for its support under Grant GP-6813. We also wish to thank Dr. E. R. Birnbaum and Dr. D. W. Darnall for their helpful discussions.

[23] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **28**, 572 (1955).

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On the Rates of Complex Formation Reactions of Hexa(dimethyl sulfoxide)nickel(II). The Five-Coordinate Intermediate Problem

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Rates of complex formation reactions of $Ni(DMSO)_6^{2+}$ ion with SCN^- and the murexide anion in DMSO are reported and compared with the rate of the corresponding reaction with bipyridine. All three complex formation rates appear to be significantly less than might be predicted from the solvent exchange rate. The rates are not related as are complex formation and solvent exchange rates of $Ni(OH_2)_6^{2+}$. It is suggested that the discrepancy could be explained by postulation of $Ni(DMSO)_5^{2+}$ as a kinetically detectable intermediate. Complex formation rates are related to other evidence for this intermediate. In support of the attempt to understand the mechanisms in DMSO, some complex formation rates in CH_3NO_2–DMSO mixtures are reported and the reaction of $Ni(OH_2)_6^{2+}$ with the murexide anion in water is described.

Introduction

There have been several studies of the rate at which solvent molecules exchange between the bulk solvent and the coordination sphere of hexa(dimethyl sulfoxide)nickel(II) ion in dimethyl sulfoxide (DMSO) as solvent.[1,2] Recently, Frankel[3] has reported a study in the mixed-solvent system DMSO–CH_3NO_2. The system has the simplifying feature that CH_3NO_2 fails to compete with DMSO for coordination sites (within the sensitivity of the nmr integration method for determining solvation numbers).[3] The surprising feature of Frankel's result is that the first-order experimental rate constant for solvent exchange is *not* a function of the bulk concentration of CH_3NO_2 (the inert solvent) in the solvent mixtures. There are only two straightforward interpretations of Frankel's observation. Either there is an intermediate formed in the substitution process so that the overall rate of exchange is independent of the probability of encounter between the $Ni(DMSO)_6^{2+}$ ion and DMSO, or the probability of encounter is independent of the bulk composition (the complex is strongly preferentially solvated by DMSO). Frankel preferred the first interpretation and the second is subject to test using the nmr relaxation time method for the study of preferential solvation recently proposed.[4-6]

If a labile intermediate is formed in the mixed solvent which reacts rapidly with DMSO to complete the exchange, there are two possible structures which deserve careful consideration since they imply quite distinct forms of behavior for Ni (II). One would be a labile CH_3NO_2-containing complex, $Ni(DMSO)_5(CH_3NO_2)^{2+}$, and the other, the elusive five-coordinate intermediate of octahedral substitution, $Ni(DMSO)_5^{2+}$. The decision between these two cannot be made on the basis of data obtained in mixed solvents unless the species $Ni(DMSO)_5(CH_3NO)^{2+}$ can be prepared and shown to be insufficiently labile for the requirements of the exchange kinetics. However, careful analysis of the details of the kinetics of complex formation reactions of $Ni(DMSO)_6^{2+}$ in DMSO with nonsolvent ligands can shed light on the problem.

In particular, it is of interest to explore the possibility of imperfect fitting of the complex formation data to the dissociative interchange model (discussed by Eigen[7])

$$\mathrm{Ni(DMSO)_6^{2+} + L \overset{K_E}{\rightleftharpoons} Ni(DMSO)_6^{2+},L}$$

$$\mathrm{Ni(DMSO)_6^{2+},L \xrightarrow{k} Ni(DMSO)_5L^{n+} + DMSO} \qquad (1)$$

In eq 1, $Ni(DMSO)_6^{2+}$,L represents the encounter complex or outer-sphere complex which is formed

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* To whom correspondence should be addressed.

(1) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **46**, 4164 (1967).

(2) S. Blackstaffe and R. A. Dwek, *Mol. Phys.*, **15**, 279 (1968).

(3) L. S. Frankel, *Chem. Commun.*, 1254 (1969).

(4) L. S. Frankel, T. R. Stengle, and C. H. Langford, *ibid.*, 373 (1965).

(5) L. S. Frankel, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1966.

(6) S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, **91**, 2236 (1969).

(7) M. Eigen, "Proceedings of the VIIth International Conference on Coordination Chemistry," Butterworths, London, 1962, p 97.

rapidly enough so that its formation and dissociation may be characterized by an equilibrium constant, K_E. The conversion to the product is governed by the rate of loss of a solvent molecule from the inner coordination sphere of Ni(II) so that the rate constant k is related to the solvent exchange rate constant. (According to Langford and Muir[8] it should be about a factor of approximately 5 less for essentially statistical reasons.)

The value of K_E in eq 1 may be estimated from an equation derived by Fuoss[9] from consideration of an electrostatic model of ion pairing (alternately derived by Eigen from consideration of the rates of diffusional encounter and dissociation where the only important potential prejudicing diffusion is electrostatic[10]). This equation is

$$K_E = \frac{4\pi N_0 a^3}{3000} \exp\left\{\left\langle \frac{z_1 z_2 e^2}{\epsilon a} - \frac{z_1 z_2 e^2 \beta}{\epsilon(1 + \beta a)}\right\rangle \Big/ kT\right\} \qquad (2)$$

where k is Boltzmann's constant, a is the distance of closest approach between the two encounter partners, ϵ is the dielectric constant, z_1 and z_2 are the signed numbers of electronic charges on the particles, β is the function of ionic strength arising in Debye–Hückel theory, and other symbols have their conventional significance.[9]

This paper is concerned with the interpretation of the complex formation reactions of the ion $Ni(DMSO)_6{}^{2+}$ with the ligands SCN^-, the murexide anion, and (drawing on the data of Bennetto and Caldin[11]) bipyridine. We will attempt to use the solvent exchange kinetic data and eq 2 to examine critically the applicability of eq 1 and the significance of Frankel's results. In this latter enterprise, some preferential solvation data will be reported.

Experimental Section

Materials.—$Ni(DMSO)_6(NO_3)_2$ was prepared following the recipe of Cotton and Francis.[12] DMSO was spectroscopic grade dried over 4-Å molecular sieves. Nitromethane was Spectrograde and $NaClO_4$, NaSCN, and ammonium mureoxide were the best available commercial materials used without further purification.

Kinetic Studies.—Fast complex formation kinetics were studied with the aid of a Durrum–Gibson stopped-flow spectrophotometer. This instrument may be thermostated easily to better than 0.1° and all measurements reported are at 25.0°. In the case of reactions with murexide, the wavelength chosen for kinetic study was 540 nm, corresponding to the disappearance of the absorption due to the uncoordinated ligand. In the case of reactions with thiocyanate, the wavelength of maximum difference in absorbance between the thiocyanato and entirely solvo complexes turned out to be 414 nm. This wavelength was used for kinetic studies. Stopped-flow photographs for reaction with murexide were recorded with 0–100 or 90–100% T full-scale amplification settings on the oscilloscope (100 or 10 mV full scale) but reactions with thiocyanate had to be recorded at 2 mV (2% T) full scale. The reaction of $Ni(DMSO)_6{}^{2+}$ with SCN^- in mixed DMSO–CH_3NO_2 was followed by the same method as those applied to reactions in DMSO. The lower limit of DMSO concentration was fixed by solubility of the thiocyanate salt.

Both reactions were studied under pseudo-first-order conditions. Ideally, an excess of metal complex over ligand should be chosen in order to avoid complication from the formation of higher than 1:1 complexes. However, the small equilibrium constant for formation of the thiocyanate complex rendered this procedure unattractive and the reaction with thiocyanate was studied in the presence of excess thiocyanate. This necessitated a high overall ionic strength. The measurements were at 0.3 M maintained with $NaClO_4$. In general, pseudo-first-order rates of approach to equilibrium are obtained. These may be factored into complex formation and dissociation rates by the device of plotting the observed pseudo-first-order rate constants against the concentration of the species in excess and evaluating the slope to obtain the second-order formation rate constant and the intercept to obtain the first-order dissociation (solvolysis) rate constant.[13] This procedure was followed except that the small spectral change in the thiocyanate case suggested that it would be wise to evaluate the equilibrium constant for the complex formation reaction independently using a more accurate spectrophotometer. The experiment was carried out using a Gilford manual spectrophotometer. The 414-nm data were analyzed by the Newton–Arcand[14] procedure and gave an equilibrium constant in excellent agreement with the value obtained from the ratio of the rate constants. From the equilibrium data, separate rate constants for *each* run are calculable

Since the rate of reaction of murexide with $Ni(OH_2)_6{}^{2+}$ was not readily available for comparison with the DMSO result, this reaction was also studied. The procedure was the same as that employed in the study of the reaction in DMSO.

Nmr Measurements.—The line shapes of CH_3NO_2 proton resonance were recorded at 25° on a JEOL C-60 spectrometer. Mixed solvents containing 0.1, 0.3, 0.5, and 0.7 mole fraction CH_3NO_2 in DMSO were studied with and without a 0.1 M concentration of $Ni(DMSO)_6(NO_3)_2$. Width at half-height of the line in the absence of paramagnetic solute was less than 0.8 Hz and line widths could be reproduced to 0.03 Hz. Reported broadenings are the average of three determinations.

Results

Table I presents a summary of the rate constants for complex formation reactions of $Ni(DMSO)_6{}^{2+}$ with NCS^- and the murexide monoanion at an ionic strength of 0.300 and at 25.0°. The formation rate constants are 29 and 77 M^{-1} sec^{-1} for thiocyanate and murexide, respectively. These are to be compared with the value

TABLE I

EXPERIMENTS SHOWING ANALYSIS OF RATE OF APPROACH TO EQUILIBRIUM FOR $Ni(DMSO)_6{}^{2+} + SCN^-$ AND $Ni(DMSO)_6{}^{2+}$ + MUREXIDE$^-$

(1) $[Ni(DMSO)_6{}^{2+}] = 0.01$ M; 25.0°; $\mu = 0.30$ Maintained with $NaClO_4$ ($K_{eq} = 2_2$ M^{-1})

$[SCN^-]$, M	k_{eq}(obsd), sec^{-1}	k_f, M^{-1} sec^{-1}	k_d, sec^{-1}
0.10	4.0_0	$27._1$	1.3
0.15	5.6_0	$28._3$	1.3
0.20	6.9_5	$28._1$	1.3
0.27	$10._0$	$31._4$	1.5
		Av 29 ± 1	1.3

(2) [Ammonium Murexide] = 2.0×10^{-5} M; 25.0°; $\mu = 0.30$ Maintained with $NaClO_4$ ($K_{eq} \simeq 5 \times 10^3$ M^{-1})

$[Ni^{2+}]$, M	k_{eq}(obsd), sec^{-1}	k_f, M^{-1} sec^{-1}	k_d, sec^{-1}
0.00080	0.076	76	0.015
0.0015	0.135	80	0.015
0.0020	0.165	75	0.015
		Av 77 ± 2	0.015

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[8] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, **89**, 3141 (1967).

[9] R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

[10] M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, **1**, 176 (1954).

[11] H. P. Bennetto and E. F. Caldin, *Chem. Commun.*, 599 (1969).

[12] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, **82**, 2986 (1960).

[13] R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).

[14] T. W. Newton and G. M. Arcand, *J. Amer. Chem. Soc.*, **75**, 2449 (1953).

of 69 M^{-1} sec^{-1} reported by Bennetto and Caldin[11] for the neutral ligand 2,2′-bipyridine. The dissociation rate constants are 0.3 and less than 0.005 sec^{-1} for the two ligands of this study. The equilibrium constant for the formation of $Ni(DMSO)_5NCS^+$ is found to be 21 ± 1 M^{-1} from both the rate constant ratio and the independent study.

Figures 1 and 2 show plots of the observed pseudo-first-order rate constants for formation of the murexide complex at low (and variable) ionic strength in DMSO and water. Figure 3 shows the rate of formation of the complex $Ni(DMSO)_5NCS^+$ in DMSO–CH_3NO_2 mixtures. The rationale for this experiment is explained in the Discussion. The points in Figures 1 and 2 are satisfactorily represented by a straight-line plot giving the following second-order rate constants for complex formation: 5.6 × 10^3 M^{-1} (H_2O) and 9.2 × 10^3 M^{-1} sec^{-1} (DMSO). The dissociation rate constants are small. They seem to be no larger than approximately 0.01 sec^{-1}. No similar low ionic strength study of reactions with SCN^- was possible because of the low formation constant and small spectral change.

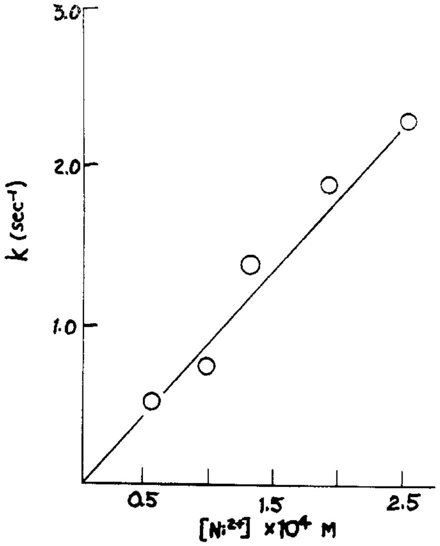

Figure 1.—Pseudo-first-order rate constants for the reaction of ammonium murexide with $Ni(DMSO)_6{}^{2+}$ in DMSO at 25°. The ionic strength is determined by the Ni^{2+} concentration. The murexide concentration is 1.0 × 10^{-5} M.

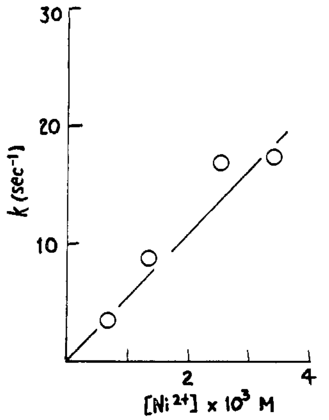

Figure 2.—Analog of Figure 1 for the reaction in aqueous solution.

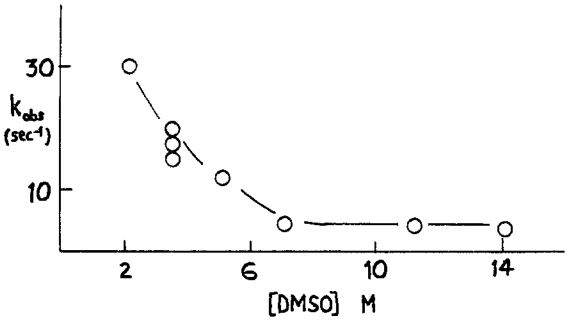

Figure 3.—Rate constant for approach to equilibrium as a function of DMSO concentration in DMSO–CH_3NO_2 mixtures. The concentration of the Ni(II) complex is 0.005 M and the concentration of NaNCS is 0.075 M. The ionic strength was maintained at 0.15 with $NaClO_4$ and the temperature was 25°. Changes in total absorbance change in a run move qualitatively in concert with the rate constants confirming that it is not the dissociation rate which is enhanced (an unlikely case in any event).

The increase in the half-width of the CH_3NO_2 proton line in mixtures of CH_3NO_2–DMSO containing 0.1 M $Ni(DMSO)_6(NO_3)_2$ was found as follows: 1.45, 1.37, 1.29, and 1.31 Hz for CH_3NO_2 mole fractions 0.10, 0.30, 0.50, and 0.70. In the fast-exchange case (applicable here),[4,15] the line width is proportional to the reciprocal of the relaxation time in the paramagnetic environment (outer coordination sphere) and to the probability that the molecule is present in the paramagnetic environment. Since the probability for a fixed concentration of paramagnetic solute depends on the ratio of the number of molecules in the paramagnetic sites and the number in the bulk solvent, a nearly constant line width suggests no great preferential solvation but instead a simple response of the population of the solvation sphere to the bulk population.[5] The slight decrease in CH_3NO_2 widths suggests a small preference for DMSO but no extreme exclusion of nitromethane. The conclusion that nitromethane *does* have access to the outer sphere of $Ni(DMSO)_6{}^{2+}$ is further supported by the magnitude of the line widths. They are between 5 and 10% of the values for DMSO protons in the same solutions which were approximately 28, 22, 18, and 16 Hz, respectively. The DMSO molecules have access to the first coordination sphere in a rapid (on the nmr time scale) exchange. In agreement with earlier workers, a recent critical analysis by Blackstaffe and Dweck[2] concludes that second-sphere broadening should be no more than 10% of the first sphere.

In the discussion to follow, the possibility that Frankel's result is a consequence of strong preferential solvation by DMSO will receive no further consideration. The nmr results render it sufficiently unlikely.

Discussion

(1) **Aqueous Solution.**—It has been generally accepted that the mechanism expressed in eq 1 is applicable to the second-order complex formation reactions

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[15] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 156.

of $Ni(OH_2)_6^{2+}$ observed in aqueous solution.[15] The model may be tested again against the results for the reactions of bipyridine, SCN^-, and murexide anion. The water exchange rate is 2.7×10^4 sec^{-1}.[15] It is expected that the second-order complex formation rate constants divided by estimated values of K_E from eq 2 will lie below that value by an amount appropriately ascribable to the statistical factor of 5–10.[8] The value of K_E is about 0.3 for a neutral ligand if a is 5 Å and between 2 and 10 for a monoanionic ligand.[15] Literature values then suggest values of the second-order rate constant divided by K_E of 0.2×10^4 sec^{-1} for bipyridine[16] and 0.6×10^4 sec^{-1} for SCN^-.[15] For the murexide reaction at an average ionic strength of 0.006 *M*, eq 2 suggests a choice of K_E equal to about 2–3. Since we find a second-order rate constant of 5.6×10^3 M^{-1} sec^{-1}, this suggests a value of about 0.25×10^4 sec^{-1} for the required quotient in good agreement with the results for the other two ligands. All three results are adequately consistent with the expected statistical factor required in relating complex formation by eq 1 to the solvent exchange process.

(2) **DMSO Solution.**—Turning now to the results for reactions in DMSO, it is only the experiments on murexide reactions at extremely low ionic strength that superficially appear to exhibit the same relationship to the solvent exchange rate constant as is observed for reactions in aqueous solution. According to the most critical analysis of nmr data,[2] the minimum value of the solvent exchange rate constant (maximal allowance being made for outer-sphere contributions to the nmr relaxation process) is 9.2×10^3 sec^{-1}. Only the very low ionic strength rate constant for the reaction with murexide anion approaches this value. The others are significantly smaller. However, it must be recognized that DMSO is a solvent of lower dielectric constant than water. The value of K_E will be large at low ionic strength.[17] In fact, direct application of eq 2 requires a value *greater than* 20. If K_E is taken as 20, the resulting first-order rate constant for DMSO replacement by murexide is a factor of 20 lower than the solvent exchange rate constant or less than the statistical factor can explain.

Actually, the data at high ionic strength are more reliably interpretable. For the ion $Ni(DMSO)_6^{2+}$, which is larger than $Ni(OH_2)_6^{2+}$, it seems reasonable to change the ion size parameter from 5 Å to at least 6 Å (as was done for methanol in ref 13). With this change, the value of K_E for neutral ligands obtained from eq 2 becomes 0.54. This value should represent a minimum at reasonable ionic strength for ions of opposite charge so that the high ionic strength second-order rate constants should be compared more or less directly with the solvent exchange rate constant (K_E lying near unity). Increasing ionic strength simply eliminates the electrostatic contribution to the probability of outer-sphere encounter and leaves the residual "steric" factor of the order of unity. From this point of view, the second-order rate constants—29, 77, and 69 M^{-1} sec^{-1}—are seen to present a real problem of interpretation according to the mechanism in eq 1. They lead to the suggestion that the solvent replacement rate (when a ligand enters the inner coordination sphere from the outer coordination sphere) is a factor of 50 or more below the solvent exchange rate. Fitting of the results to the suggested mechanism is much less attractive than for reactions of octahedral Ni(II) in water or methanol.[12] The difficulty is similar to one arising in analysis of reactions of $Cr(OH_2)_6^{3+}$ and related ions. The explanation proposed will be similar to one recently suggested for Cr(III) on other grounds.[18]

Actually, there is an alternate mechanism which could account for the discrepancy. It is the pathway through the five-coordinate intermediate (of lifetime sufficient for discrimination in reaction) $Ni(DMSO)_5^{2+}$ which has been suggested by Frankel. This mechanism is shown in eq 3.

$$\begin{tikzcd} \text{Ni(DMSO)}_6^{2+} \arrow[r, shift left, "k_1"] & \text{Ni(DMSO)}_5^{2+} + \text{DMSO} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"', "+\text{L}"] \\ & \text{Ni(DMSO)}_5\text{L} \end{tikzcd} \tag{3}$$

The mechanism in eq 3 interprets the second-order complex formation rate constants as the product of the first-order rate constant for solvent loss to form the intermediate (equal to the solvent exchange rate constant) multiplied by the ratio of k_2/k_{-1}. The factor k_2/k_{-1} is simply the competition ratio between DMSO and the entering ligand, L. If recombination of the intermediate with DMSO is more favorable than reaction with L, the second-order rate constants will come out low. (This will be true whether or not L is ion paired.) Also, they will have an ionic strength dependence similar to that for eq 1 by virtue of the fact that the competition ratio will reflect the probability of encounter of *the intermediate* with L.

(3) **Mixed Solvents.**—Equation 3 does suggest one additional experiment. If an intermediate is formed, it should be possible to increase the rate of formation of the complex with L by diluting out DMSO with an unreactive solvent. Further, if that unreactive solvent is similar in dielectric constant to DMSO, it can be expected that there would be little effect on a reaction proceeding according to mechanism 1. Frankel's experiments suggest CH_3NO_2 as the appropriate solvent. Figure 3 shows the effect of CH_3NO_2 on the rate of formation of $Ni(DMSO)_5NCS^+$ up to the solubility limit of the thiocyanate salt. It can be seen that the rate is enhanced by more than a factor of 10 at the lowest DMSO concentrations. This is entirely in accord with eq 3 but would be difficult to explain under eq 1. Unfortunately, it is not possible to give a detailed analysis of the relative rate constants in the mixed-solvent system because the nmr results show that there is the possibility of some small preferential solvation. However, it is true that a plot of the complex formation rate constant against the concentration of DMSO in the

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(16) P. Ellis, R. Hogg, and R. G. Wilkins, *J. Chem. Soc.*, 3308 (1959).

(17) For experimental proof of this point see various references reviewed in C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, **19**, 193 (1968). Especially, consult the papers by D. W. Watts and his collaborators.

(18) S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, **92**, 1215 (1970).

mixture is nearly linear (for large DMSO concentration) as would be required by the mechanism in eq 3 when it is recognized that k_{-1} is a second-order rate constant.

It has recently been unfashionable to suggest that the intermediate of five-coordination might be energetically favored in the absence of electronically esoteric ligands to stabilize it.[19] However, we would rest our case for giving serious consideration to the possibility that the intermediate is "relatively stable" in this system on the convergence of three lines of evidence which are probably worth recapitulating. First, the nmr exchange studies in mixed solvents require some sort of intermediate. Second, the complex formation rates in pure DMSO cannot be readily fitted into the scheme that works for aqueous systems. Third, the effect of adding CH_3NO_2 affects complex formation rates as would be predicted if there were a five-coordinate intermediate. No one of these lines of evidence is convincing alone. Together, they add up to sufficient circumstantial evidence to warrent serious consideration of the pathway in eq 3. Perhaps, the reason that the intermediate arises in DMSO is steric. Hindrance has been shown to favor five-coordination.[20]

With respect to the energetic objection to the intermediate, Tobe's warning is relevant:[21] ". . . attacking (the intermediate) on energetic grounds (is) . . .harking back to the arguments used against Dr. Ingold in the thirties when he proposed the now accepted unimolecular mechanism for certain substitution reactions at tetrahedral carbon."

Acknowledgment.—We are indebted to the National Research Council of Canada for financial support. C. H. L. acknowledges an Alfred P. Sloan research fellowship for 1968–1970.

[19] See ref 15, pp 132–135.

[20] P. Paoletti and M. Ciampolini, *Inorg. Chem.*, **6**, 64 (1967).

[21] M. L. Tobe, *Advan. Chem. Ser.*, **No. 49**, 29 (1965).

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A New Three-Coordinate Complex of Nickel(0). Tris(tri-*o*-tolyl phosphite)nickel

BY L. W. GOSSER AND C. A. TOLMAN

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The preparation and properties of coordinatively unsaturated tris(tri-*o*-tolyl phosphite)nickel(0) and coordinatively saturated tetrakis(tri-*o*-tolyl phosphite)nickel(0) are described. Spectrophotometric measurements give a ligand-association equilibrium constant of $15 \pm 2\ M^{-1}$ in benzene at 28°. The temperature dependence of the equilibrium gives $\Delta H^\circ = -13 \pm 1.5$ kcal/mol and $\Delta S^\circ = -37 \pm 4$ eu. Facile reactions of the three-coordinate complex with tri-*o*-tolyl phosphite, CO, and C_2H_4 are described.

Introduction

Since the discovery of $Ni[PCl_3]_4$ in 1951 by Irvine and Wilkinson,[1] a variety of zerovalent nickel complexes with phosphorus ligands have been described.[2] In most cases the complexes have been four-coordinate.[3] Two- and three-coordinate phosphine complexes $Ni[P(C_6H_{11})_3]_2$[4] and $Ni[P(C_6H_5)_3]_3$[5] have been reported. A two-coordinate phosphite complex, $Ni[P(O\text{-}o\text{-}C_6H_4CH_5)_3]_2$, has been claimed in a recent patent.[6] Claims of three-coordinate phosphite complexes $Ni[P(OC_2H_5)_3]_3$ based on molecular weights[7] and $Ni[P(OC_6H_5)_3]_3$ based on elemental analysis[8] have been made but are probably erroneous, as shown by recent spectrophotometric and ^{31}P nmr studies of the tetrakis complexes.[3] The preparation of material formulated as $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_3$ has recently been reported.[9,10]

We wish to report a detailed account of the preparation and properties of a three-coordinate phosphite complex of Ni(0), tris(tri-*o*-tolyl phosphite)nickel. Spectrophotometric data are presented which permit determination of the ligand-association equilibrium constant to form the tetrakis-phosphite complex, whose preparation is also described. Measurements of K in benzene at 10, 30, 50, and 70° were made to determine ΔH° and ΔS°. Finally, rapid reactions of the coordinatively unsaturated tris complex with CO and C_2H_4 will be described.

Experimental Section

Because of the sensitivity of these complexes to oxygen, all synthetic operations were carried out in a nitrogen atmosphere with degassed solvents. Special precautions were taken in the spectrophotometric experiments. Reagent grade benzene solvent was thoroughly deoxygenated by three cycles of freezing,

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[1] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

[2] References to the preparation of a number of these are given in ref 3.

[3] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

[4] (a) P. W. Jolly and K. Jonas, *Angew. Chem., Int. Ed. Engl.*, **7**, 731 (1968); (b) K. Jonas and G. Wilke, *ibid.*, **8**, 519 (1969).

[5] Molecular weight evidence for $Ni[P(C_6H_5)_3]_3$ was given by P. Heimbach, *Angew. Chem.*, **76**, 586 (1964).

[6] M. A. McCall and H. W. Coover, British Patent 1,146,074 (1969).

[7] R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, **3**, 1062 (1964).

[8] N. von Kutepow, H. Seibt, and F. Meier, U. S. Patent 3,346,608 (1967).

[9] J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 96 (1970).

[10] The formation of this tris complex under the conditions reported is surprising in view of our studies of zero-valent nickel compounds. More of our results will be reported in detail later.