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Kinetics of Exchange of N,N-Dimethylformamide between the Coordination Sphere of Co^{2+} and Ni^{2+} and the Bulk Solvent Utilizing ^{17}O Nuclear Magnetic Resonance[1]

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Observations of the transverse relaxation times in ^{17}O nuclear magnetic resonance spectra of N,N-dimethylformamide solutions of Ni^{2+} and Co^{2+} carried out over a substantial temperature range permit determination of rates and activation parameters for the rapid exchange reaction between bulk solvent molecules and solvent molecules coordinated to the paramagnetic ions. The parameters for the exchanges at 25° are: Ni^{2+}, $k = 7.7 \times 10^3$ sec^{-1}, $\Delta H^* = 9.4 \pm 0.5$ kcal/mole, $\Delta S^* = -9 \pm 2$ eu; Co^{2+}, $k = 2.3 \times 10^5$ sec^{-1}, $\Delta H^* = 7.1 \pm 0.5$ kcal/mole, $\Delta S^* = -10 \pm 2$ eu. These data are compared to previous reports of similar exchange reactions in water, methanol, and ammonia. The mechanistic significance of the results is considered.

Introduction

A number of recent studies have reported rates of solvent exchange between bulk solution and the ligand sphere of paramagnetic ions utilizing the correlations between the rate of the chemical exchange process and the transverse relaxation time (T_2) in nuclear magnetic resonance (nmr) spectra of nuclei in the solvent (and ligand) molecule. Notable examples include water-exchange rates for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} derived by Swift and Connick[3] from ^{17}O nmr data, ammonia-exchange rates for Ni^{2+} and Co^{2+} obtained by Hunt, Dodgen, *et al.*,[4] from ^{14}N nmr data, and methanol-exchange rates for Ni^{2+} and Co^{2+} derived from proton nmr data by Luz and Meiboom.[5] This report describes the preparation of ^{17}O-enriched N,N-dimethylformamide (DMF) and the exchange rates for Ni^{2+} and Co^{2+} ions in this solvent.

Theory

The basic relations used in interpreting the data have been derived by Swift and Connick.[3] For convenience, the results are summarized below. The notation is not consistent in the literature. Ours is based on a combination of usage from ref 3 and 5 which seems to be generally convenient.

The equations are derived for a system in which there are two possible environments for ^{17}O nuclei, the coordination sphere of the paramagnetic ion and the bulk solvent. We designate these by subscripts M and A, respectively. It is assumed that the number of nuclei in the A environment is much larger than the number in the M environment (a condition fulfilled in all reasonably dilute solutions of paramagnetic ions). The ratio of nuclei in the M environment to nuclei in the A environment may be written P_M, where $P_M = 6m/1000/MW$ (m is the molal concentration of metal ions and MW the molecular weight of DMF). The coordination number is assumed to be six on the basis of structural studies of DMF complexes[6] and analytical data on our solid samples. According to the assumption $P_M \ll 1$. Nuclei may exchange between the two environments at a rate characterized by the average residence time of nuclei in the M environment, τ_M. The line widths observed in nmr spectra will be controlled by the transverse relaxation times in the A and M environments, T_{2A} and T_{2M}. The full width at half-height of the absorption line, $\Delta\nu$, yields one observed relaxation time T_2 from the equation $1/T_2 = \pi\Delta\nu$. Modified to conform to the present notation, the results of Swift and Connick[3] show that $1/T_2$ is given by eq 1, where $\Delta\omega_M$ designates the frequency shift of the resonance peak in the M environment relative to the frequency in the A environment.

$$1/T_2 = 1/T_{2A} + P_M \frac{1/T_{2M}(1/T_{2M} + 1/\tau_M) + (\Delta\omega_M)^2}{\tau_M(1/T_{2M} + 1/\tau_M)^2 + \tau_M(\Delta\omega_M)^2} \quad (1)$$

As Luz and Meiboom[5] observed, $1/T_{2A}$ is made up of a contribution due to interactions between paramagnetic ions and solvent molecules beyond the first coordination sphere and a contribution due to relaxation mechanisms which operate in the absence of paramagnetic ions. The former contribution may be estimated from studies at temperatures low enough that chemical exchange is very slow and does not significantly affect line widths. It becomes a small term at temperatures near room temperature in the systems under study. The latter contribution may be estimated from study of the line width in the pure solvent. In ^{17}O work the solvent line width is sizable as a result of quadrupolar relaxation effects.

The quantity $(1/T_2) - (1/T_{2A})$ is the term from which the value of τ_M is to be extracted. There are

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[2] (a) Texas Company predoctoral Fellow, 1965–1966. (b) Amherst College.

[3] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[4] (a) J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963); (b) H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 1061 (1965); (c) H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 206 (1965).

[5] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

[6] R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

two useful limiting forms of eq 1 which make the extraction of τ_M reasonably straightforward. If $\Delta\omega_M^2 \gg 1/T_{2M}^2, 1/\tau_M^2$, then eq 1 reduces to

$$(1/T_2) - (1/T_{2A}) = P_M/\tau_M \qquad (2)$$

The relaxation is controlled by the rate of chemical exchange. This circumstance may be recognized by the temperature dependence, which should be of the form of eq 3 for a chemical reaction rate constant.

$$1/\tau_M = kT/h \exp(-\Delta H^*/RT + \Delta S^*/R) \qquad (3)$$

ΔH^* and ΔS^* are the enthalpy and entropy of activation for a first-order solvent-exchange reaction. The temperature range in which (2) holds will be called the Arrhenius region. At some higher temperature region when the chemical exchange process has become significantly faster, a second limiting case arises. If $1/\tau_M^2 \gg \Delta\omega_M^2 \gg (1/T_{2M}\tau_M)$, then eq 1 reduces to

$$(1/T_2) - (1/T_{2A}) = P_M\tau_M(\Delta\omega_M)^2 \qquad (4)$$

In this region, again the *principal* factor in the temperature dependence will be the activation parameters for the chemical exchange, but it is now the reciprocal of the first-order rate constant that appears in the relaxation equation. The temperature dependence in this limit will be close to the inverse of that in the lower temperature region. [Magnetic dipolar interaction between the paramagnetic electron and the ^{17}O nucleus provides another possible relaxation mechanism. The ^{17}O results of Swift and Connick[3] suggest that it is unimportant here. In any event, both the "$\Delta\omega_M$" and dipolar mechanisms (or a combination of the two) will follow eq 2 in the Arrhenius region.]

The advantage in using nmr data on the nucleus coordinated directly to the metal atom (*e.g.*, ^{17}O in preference to ^1H in this study) is connected with obtaining a large $\Delta\omega_M$ and access to the region described by eq 2.

Experimental Section

Materials.—N,N-Dimethylformamide was purified by refluxing over barium oxide and distillation under reduced pressure. ^{17}O water enriched to 4.36 atom % was obtained from YEDA Research and Development, Rehovoth, Israel. N,N-Dimethylformamide (5.68 g, 0.078 mole) was placed in a stainless steel bomb. Under vacuum, thionyl chloride (10.8 g, 0.091 mole) was distilled into the bomb and allowed to react for 10 hr. The sulfur dioxide produced was separated from the reaction product, dimethylformamide chloride.[7] The chloride, $[(CH_3)_2NCHCl]^+Cl^-$, was then hydrolyzed with the ^{17}O-enriched water. The hydrogen chloride gas produced was separated from ^{17}O-enriched DMF by distillation. The product was further purified by several distillations through a barium oxide column. A proton magnetic resonance spectrum of the enriched DMF showed no water present.

The metal complexes of DMF are known and were prepared easily. A solution of the hydrated metal perchlorate in DMF was mixed with a sufficient amount of benzene to form an azeotrope with water. Dehydration was effected by azeotropic distillation of benzene. The volatile material was then removed by pumping at reduced pressure until a solid product was obtained. The complexes were recrystallized from an amide–ether mixture.

Anal. Calcd for $[Ni(DMF)_6](ClO_4)_2$: C, 31.05; H, 6.08; N, 12.07; Ni, 8.433. Found: C, 30.83; H, 5.92; N, 11.84; Ni, 8.460.

Anal. Calcd for $[Co(DMF)_6](ClO_4)_2$: C, 31.04; H, 6.08; N, 12.07. Found: C, 30.71; H, 5.90; N, 11.59.

Nmr Measurements.—The ^{17}O nmr spectra were obtained using a Varian dual-purpose spectrometer equipped with an 8.1-Mc radiofrequency unit and probe. The ^{17}O resonance spectra in the pure solvent and paramagnetic solutions of several concentrations (Ni^{2+}: 0.0156, 0.0387, 0.103, and 0.119 *M*; Co^{2+}: 0.00318 and 0.00746 *M*) were obtained as derivatives of the absorption curves. The experimental value of $1/T_2$ was taken to be $\pi\sqrt{3}$ times the peak-to-peak separation. Calibration of the spectra was effected by means of side bands generated 1000 c from the main resonance. The radiofrequency power was kept below the saturation level, and artificial line broadening due to the modulation frequency was minimized. The temperature of the system was controlled to ±1° using a Varian variable-temperature unit. A minimum of three spectra were taken at each temperature with the average line width reproducible to within 3 to 10% depending on the width of the observed line. ^{17}O-enriched DMF solutions of paramagnetic ions were prepared by distilling the DMF onto the dry solvato complex using vacuum-line techniques.

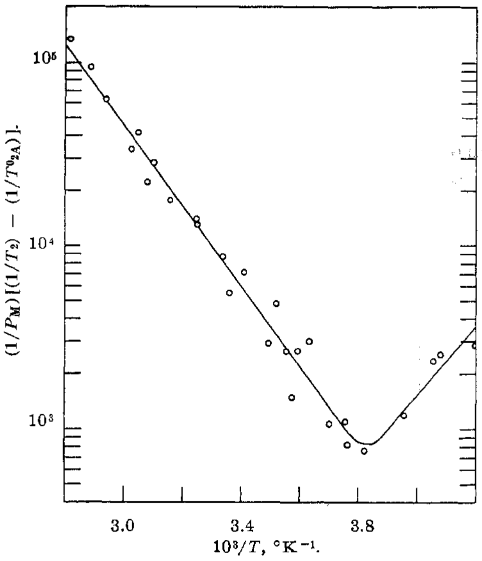

Figure 1.—Temperature dependence of log $(1/P_M)[(1/T_2) - (1/T^0_{2A})]$ for Ni^{2+} solutions in ^{17}O-enriched DMF.

Results and Treatment of Data

In order to locate the temperature ranges in which chemical exchange controls the relaxation times we wish to construct a logarithmic plot of $(1/T_2) - (1/T_{2A})$ *vs.* the reciprocal of the absolute temperature. According to eq 3, the relevant regions will be linear. One of the contributions to T_{2A} is readily evaluated from the measurements of line widths in the pure solvent. This is designated T^0_{2A}. The other is less directly accessible. In Figures 1 and 2 the logarithmic plot of $(1/P_M)[(1/T_2) - (1/T^0_{2A})]$ *vs.* $1/T$ is presented. It is evident that Arrhenius regions corresponding to the requirements of eq 2 and 3 exist in both figures. In the data on Co^{2+} in Figure 2, it is clear that a high-temperature region conforming to eq 4 appears.

In the low-temperature region of Figure 1 (<260°K), line broadening becomes small and increases as the temperature decreases. This behavior corresponds to the theoretical expectation for relaxation due to interactions between the paramagnetic ions and solvent molecules beyond the first coordination sphere.[8]

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[7] H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

Table I

Rate Parameters for Solvent-Exchange Reactions

Solvent	k, sec^{-1} (25°)		k_{Ni}/k_{Co}	ΔH^*, kcal/mole		ΔS^*, eu	
	Ni^{2+}	Co^{2+}		Ni^{2+}	Co^{2+}	Ni^{2+}	Co^{2+}
NH_3	1.0×10^5	7.2×10^6	72	11.0	11.2	2.0	10
Aqueous NH_3 (7–14 M)	5.6×10^4			9.5		−5	
H_2O	2.7×10^4	1.1×10^6	42	11.6	8.0	0.6	−4.1
DMF	7.7×10^3	2.3×10^5	30	9.4	7.0	−9.1	−10.2
CH_3OH	1.0×10^3	1.8×10^4	18	15.8	13.8	8.0	7.2

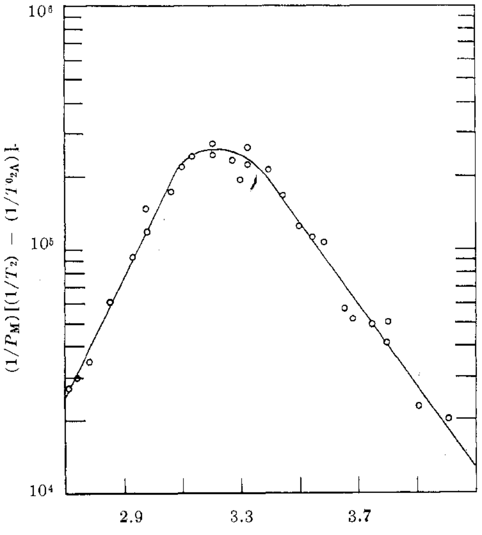

Figure 2.—Temperature dependence of log $(1/P_M)[(1/T_2) - (1/T^0_{2A})]$ for Co^{2+} solutions in ^{17}O-enriched DMF.

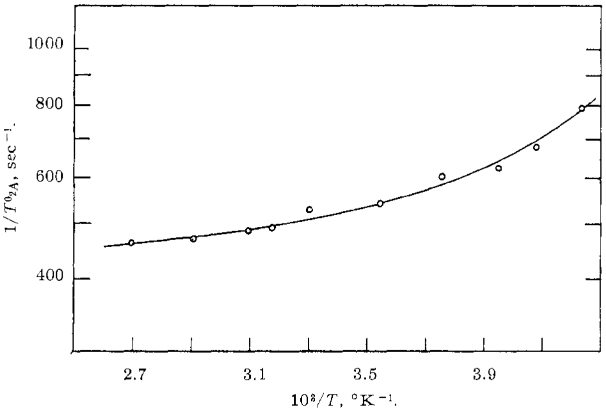

Figure 3.—Temperature dependence of log of ^{17}O relaxation time of ^{17}O-enriched DMF.

The broadening effect displayed in the low-temperature regions of Figure 1 is the remaining contribution to T_{2A}. If the line drawn through the low-temperature points is extrapolated to higher temperatures, it is possible to estimate the remaining correction to the observed line width in order to obtain $(1/T_2) - (1/T_{2A})$ as a function of temperature. In the case of Ni^{2+} in DMF, the correction is essentially negligible. Unfortunately, the Co^{2+} data do not allow direct evaluation of the final small correction to T_{2A}. By analogy with Ni^{2+}, it is probably negligible. The analogy is supported by the results of Luz and Meiboom on the proton of methanol.[5]

Kinetic parameters are collected in Table I. Data on other solvent systems are included for comparison.

Discussion

An obvious interpretation of the results in Table I would suggest that the exchange-rate order $NH_3 > H_2O > DMF > CH_3OH$ reflects the varying nucleophilicities of the solvents. The reaction would seem associative with the entering ligand playing an energetically important part in the transition state. This would be an oversimplified view. A dissociative mechanism is possibly just as consistent. If it were assumed that dissociative activation occurred in all cases, the observed rate order might be expected to depend upon at least the following factors: (1) metal–ligand bond energies, (2) solvation differences between ground and transition states, (3) steric requirements of the different ligands, and (4) the ability of the ligands to provide electronic stabilization for a state of reduced coordination number. It is not now possible to evaluate either the relative importance of these factors or the correct ordering of the four solvents with respect to each. Detailed mechanistic interpretations should become possible when data for complex formation reactions become available from, *e.g.*, temperature-jump studies.[9] The results on aqueous solutions elaborated in Eigen's laboratories[10] strongly suggest a dissociative activation process.

When reactions of the two metal ions in the same solvent are compared, all factors except the first become more nearly constant. Table I shows that in all cases the cobalt complex reacts faster than the nickel complex. In this context, it is interesting to note that the relative reactivities at Co and Ni centers have often been discussed, perhaps naïvely, in terms of crystal field theory. The three ligands H_2O, DMF, and CH_3OH have identical values of the Ni^{2+} crystal field parameter (Dq = 850 cm^{-1}),[11] yet the Co:Ni rate ratio varies as much among these three ligands as it does on going from H_2O to NH_3 where Dq changes from 850 to 1080 cm^{-1}.[12]

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(8) See ref 5, especially footnotes 13 and 14.

(9) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966. (Chapter 3 discusses the ways in which comparison of solvent exchange and complex formation rates may lead to quite detailed mechanistic information. See especially p 85 ff.)

(10) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(11) R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1964).

(12) Note Added in Proof.—Recently Matwiyoff [*Inorg. Chem.*, **5**, 788 (1966)] determined the kinetic parameters of the exchange of DMF with Co^{2+} and Ni^{2+} from a study of the nmr line width of the formyl proton of DMF. These results do not agree with the ^{17}O data reported here. The disagreement is well outside the limits of experimental error. Although the reason for this discrepancy is not clear, the ^{17}O results are more likely to give true exchange rates, since that is the nucleus directly bonded to the metal. A further study of this problem is now in progress.