*m*-**Carborane-1,7-bis(sulfonic acid).**—A 250-ml, three-neck flask equipped with mechanical stirrer, reflux condenser, and nitrogen inlet was charged with 13.3 g (0.039 mol) of 1,7-bis(chlorosulfonyl)-*m*-carborane, 125 ml of dry benzene, and 10.7 g (0.080 mol) of aluminum chloride. The reaction mixture was heated to reflux for 3 hr and then cooled to 0° and hydrolyzed with dilute hydrochloric acid. The resulting precipitate was recrystallized from dilute hydrochloric acid to yield 13 g of the bis(sulfonic acid). *Anal.* Calcd for $B_{10}C_2H_{12}S_2O_6$: C, 7.86; H, 4.23; B, 35.5; S, 21.0; equiv wt 152; mol wt 304. Found: C, 8.28; H, 4.25; B, 36.36; S, 20.97; equiv wt 142; mol wt (osmometry) 306.

**Bis(1-phenyl-*o*-carboran-2-yl) Disulfide.**—Dropwise addition of 55 g of 1-phenyl-2-mercapto-*o*-carborane in 100 ml of diethyl ether to a solution of 62.5 g of 1-phenyl-2-chlorosulfenyl-*o*-carborane in 150 ml of diethyl ether maintained at 0.5° resulted in HCl evolution accompanied by the formation of an insoluble product. Recrystallization from hexane yielded 67 g (60.4%) of the topic compound, mp 219–220°. *Anal.* Calcd for $C_{16}H_{32}B_{20}S_2$: C, 38.2; H, 6.35; B, 43.0; S, 12.6; mol wt 504. Found: C, 38.17; H, 6.60; B, 42.19; S, 12.81, mol wt (osmometry) 491.

**Bis(1-phenyl-*m*-carboran-7-yl) Disulfide.**—Using the procedure described above for the ortho disulfide the reaction of 11.4 g of 1-phenyl-7-chlorosulfenyl-*m*-carborane with 10.0 g of 1-phenyl-7-mercapto-*m*-carborane yielded, after recrystallization from hexane, 13 g (65%) of the desired meta derivative, mp 99–100°. *Anal.* Calcd for $C_{16}H_{32}B_{20}S_2$: C, 38.2; H, 6.35; B, 43.0; S, 12.6; mol wt 504. Found: C, 38.18; H, 6.08; B, 41.73; S, 12.53, mol wt (osmometry) 492.

*o*-**Carborane-1,2-bis(phenyl thioether) (I).**—Preparation was in accordance with that described by Smith, *et al.*[8] The corresponding *m*- and *p*-carboranebis(phenyl thioethers), II and III, respectively, were prepared *via* slight modifications of the above procedure.

*m*-**Carborane-1,7-bis(1-phenyl-*m*-carboran-7-yl thioether) (IV).**—Dropwise addition of 2.91 × $10^{-2}$ mol of dilithio-*m*-carborane in 25 ml of anhydrous ether to a solution of 15 g (2.98 × $10^{-2}$ mol) of bis(1-phenyl-*m*-carboran-7-yl) disulfide yielded a clear solution with no detectable evolution of heat. Prolonged boiling of the reaction mixture (16 hr), followed by 24 hr of stirring at ambient temperature and acid hydrolysis, yielded 4.5 g (24.8%) of an insoluble white solid which was recrystallized from toluene.

*m*-**Carborane-1-(1-phenyl-*o*-carboran-2-yl thioether) (V).**—The reaction of 0.14 mol of dilithio-*m*-carborane with 0.14 mol of bis(1-phenyl-*o*-carboran-2-yl) disulfide according to the procedure described for IV yielded 12.5 g of V which was recrystallized from hexane.

**Oxidation Reactions.**—The various carborane thioethers were oxidized by two general methods illustrated below by specific examples.

(I) **Oxidation by Hydrogen Peroxide in Formic Acid.** *m*-**Carborane-1,7-bis(sulfonylbenzene) (VII).**—A 1000-ml flask was charged with 5 g of II and 450 ml of 97% formic acid and the resulting dispersion was stirred rapidly at 70° with dropwise addition of 30% hydrogen peroxide. After addition of the stoichiometric quantity (6.3 g) of peroxide, a clear solution was obtained. After 30 min an additional 6.3 g of oxidant was slowly added. The resulting precipitate was filtered, washed, and recrystallized from hot toluene to yield 5.2 g of VII.

(II) **Oxidation by *p*-Nitroperbenzoic Acid.** *o*-**Carborane-1,2-bis(sulfinylbenzene) (VI).**—A 500-ml, three-neck flask equipped with a mechanical stirrer was charged with a solution of 13.76 g (7.53 × $10^{-2}$ mol) of *p*-nitroperbenzoic acid in 200 ml of chloroform. Then 3.6 g ($10^{-2}$ mol) of I dissolved in 50 ml of chloroform was added dropwise at ambient temperature. After the mixture had been stirred overnight, a negative test with aqueous iodide indicated that no excess peracid was present. The reaction mixture was extracted with a saturated aqueous solution of sodium bicarbonate, and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed at reduced pressure to yield 2.5 g of crude product which was recrystallized from hexane.

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## A Nuclear Magnetic Resonance Study of the Ligand-Exchange Kinetics of Nickel(II) with *N*,*N*-Dimethylformamide in Mixed Solvents

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Ligand-exchange kinetics of octahedral paramagnetic transition metal complexes are usually studied in a pure solution of the ligand by nmr.[2] Recently we have reported that the ligand-exchange parameters for Co- and $Ni(DMSO)_6^{2+}$ (DMSO = dimethyl sulfoxide) in mixed solvents were independent of the composition of the solvent.[3] These results strongly support a D mechanism, which has recently been further supported by anation kinetic results.[4] To ascertain if this conclusion is applicable to other complexes of this type we wish to report data for $Ni(DMF)_6^{2+}$ (DMF = *N*,*N*-dimethylformamide) in DMF–nitromethane mixed solvents.

DMF was purified and $Ni(DMF)_6(ClO_4)_2$ prepared[5] as previously described. The mole per cent of water in the purified DMF was found to be 0.12% by integrating the residual water peak *vs.* one of the $^{13}C$ satellites of the methyl group of DMF. The nitromethane-$d_3$ utilized was identical with that previously described.[3] All data were obtained on a Varian A-60 spectrometer.

The temperature dependence of the observed transverse relaxation rate, $1/T_{2p}$, corrected for the ligand relaxation rate in the absence of the metal complex, can be analyzed using the results of Swift and Connick.[6] The limiting equation applicable in this study is $1/T_{2p} = P_M/\tau_M$, where $P_M$ is the probability that a DMF molecule is in the primary coordination sphere of the metal ion, and $1/\tau_M = k$, the ligand exchange rate. Transition state theory is used to obtain $\Delta H^*$ and $\Delta S^*$, the activation enthalpy and entropy, respectively.

A plot of $(P_M T_{2p})^{-1}$ *vs.* reciprocal temperature for $Ni(DMF)_6^{2+}$ in DMF and DMF–nitromethane mixed solvents is given in Figure 1. The compositions of the solutions utilized are also given in Figure 1. The high-temperature data, $3.90 \times 10^{-3} > T^{-1} > 3.35 \times 10^{-3}$, correspond to a large positive activation energy. In this temperature region $(P_M T_{2p})^{-1}$ is controlled by the solvent-exchange rate. At low temperatures, $T^{-1} > 4.20 \times 10^{-3}$, ligand exchange is slow and the observed relaxation time is due to second-sphere relaxation effects which will be subsequently discussed. The data in Figure 2, which have been corrected for second-sphere relaxation effects *via* extrapolation of the low-temperature data, were utilized to obtain the kinetic parameters. The data in pure DMF are almost identical with those of the mixed solvent. A least-squares treatment of the data in Figure 2 gives the following results: $\Delta H^*$ =

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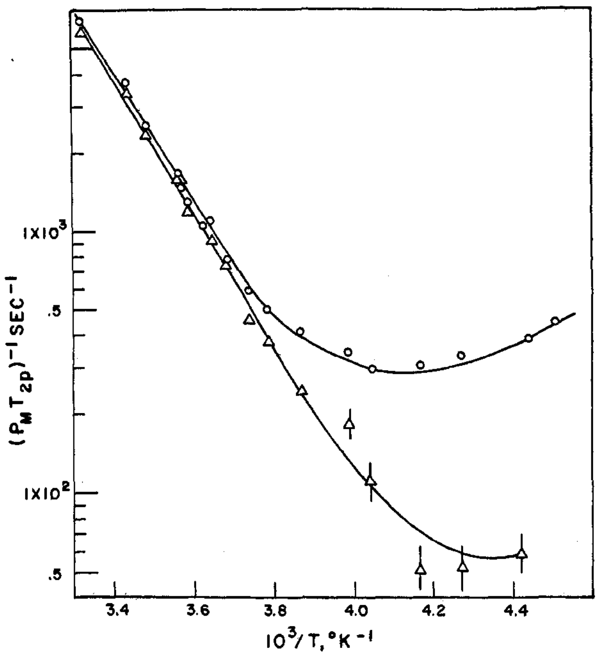

Figure 1.—Temperature dependence of $(P_M T_{2p})^{-1}$ for the formyl proton of DMF in solutions of $Ni(DMF)_6^{2+}$. Composition of solutions: [Ni] = $12.58 \times 10^{-2}$ *M* in DMF (O); [Ni] = $2.26 \times 10^{-2}$ *M* and [DMF] = 1.84 *M* in $CD_3NO_2$ (Δ).

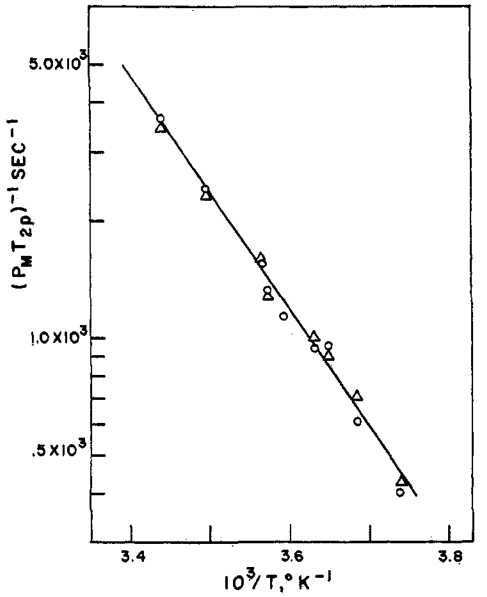

Figure 2.—Data used to obtain kinetic parameters. All data were corrected for second-sphere relaxation time effects.

14.0 kcal/mol, $\Delta S^* = 6$ eu, $k(25°) = 6.9 \times 10^3$ sec$^{-1}$ in pure DMF; $\Delta H^* = 13.0$ kcal/mol, $\Delta S^* = 3$ eu, $k(25°) = 6.5 \times 10^3$ sec$^{-1}$ in the mixed solvent. The difference between the activation parameters in pure DMF and the mixed solvent is approximately equal to the experimental error. Considering the general agreement found among other studies,[3,7-11] our results are in satisfactory agreement with those previously reported in pure DMF,[11] $\Delta H^* = 15.0$ kcal/mol, $\Delta S^* = 8$ eu, and $k(25°) = 3.8 \times 10^3$ sec$^{-1}$. Rate constants for a single temperature were found to be virtually independent of the composition of the solution (see Table I).

TABLE I

LIGAND-EXCHANGE RATES OF $Ni(DMF)_6^{2+}$ AT 27° IN DMF AND DMF–$CD_3NO_2$ MIXED SOLVENTS

| Solvent | $10^2$[Ni], *M* | [DMF], *M* | $10^3k$, sec$^{-1}$ |
|---|---|---|---|
| DMF | 12.58 | 12.9 | 6.75 |
| DMF | 5.72 | 12.9 | 6.65 |
| DMF in $CD_3NO_2$ | 5.20 | 4.74 | 6.20 |
| DMF in $CD_3NO_2$ | 2.49 | 3.25 | 6.10 |
| DMF in $CD_3NO_2$ | 1.84 | 2.26 | 6.10 |
| DMF in $CD_3NO_2$ | 1.26 | 1.79 | 6.00 |
| DMF in $CD_3NO_2$ | 0.74 | 0.98 | 6.30 |

At low temperatures, $T^{-1} > 4.20 \times 10^{-3}$, the formyl proton relaxation time has a small negative activation energy and is given by $1/T_{2p} = P_S/T_{2S}$, where $P_S$ is the probability that a DMF molecule is in the second coordination sphere and $T_{2S}$ is the relaxation time of the formyl proton in the second coordination sphere. Under the above conditions the observed relaxation times may be utilized to estimate the degree of preferential solvation in the second coordination sphere.[4,12-16] This conclusion follows from a consideration of $P_S$ assuming $1/T_{2S}$ is constant. The low-temperature data in Figure 1 imply that nitromethane preferentially solvates $Ni(DMF)_6^{2+}$. In the mixed solvent, the error is relatively large because the excess line widths are small at the metal concentration employed and a more quantitative interpretation is not warranted.

As was the case for $Ni(DMSO)_6^{2+}$ [3] the ligand-exchange parameters in mixed solvents with nitromethane are independent of the composition of the mixed solvent. Ligand-exchange reactions of this type are generally accepted to be dissociative in nature.[2,8,16-18] Two mechanistic paths are possible. The so-called D mechanism requires a true five-coordinate intermediate. This intermediate must be stable with respect to the lifetime of the second coordination sphere. Therefore, if primary-sphere activation occurs when a nitromethane molecule is solvating the active site, the intermediate must have a sufficient lifetime to wait for a DMF molecule to be in an advantageous position in the second coordination sphere. A second possibility retains the entering ligand as a stoichometric component of the transition state. The latter mechanism has been called dissociative interchange ($I_d$ mechanism). The independence of the exchange parameters on the solvent composition coupled with the fact that the solvation shell is not pure DMF (actually nitromethane preferred) clearly supports the D mechanism as was the case for $Ni(DMSO)_6^{2+}$.[3]

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