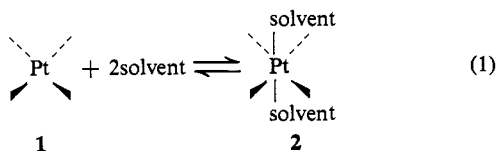


Solvation in Platinum(II) Complexes Evaluated by a Kinetic Method¹

Sir:

The problem of solvent interaction with tetragonal-planar complexes, e.g., platinum(II) complexes (1), has been given important significance in the chemistry of these systems.² There has been frequent assumption of symmetrical solvation by two solvent molecules (2) (eq 1). We can now report kinetic evidence that bears on this hypothesis.



We have extended our observations of catalyzed isomerizations of planar platinum(II) complexes³ into mixed solvents. Our standard solvent is cyclohexane, for which results have been reported.^{3,4} When more polar solvents (S) (diethyl ether, chloroform, nitromethane, acetonitrile, and methanol) are added, the rate of isomerization drops significantly. For example, 0.1 M CH₃CN in cyclohexane results in an observed second-order rate constant $k_2' = 1.6 \times 10^2 M^{-1} \text{sec}^{-1}$ for isomerization of *cis*-[(*n*-C₄H₉)₃P]₂PtCl₂ (C) catalyzed by (*n*-C₄H₉)₃P. In the absence of acetonitrile, $k_2 = 4.5 \times 10^2 M^{-1} \text{sec}^{-1}$. The rate decrease on addition of polar solvents is not linear in concentration, but appears to be a reciprocal dependence.

If we assume that the solvated complex cannot isomerize because it must first dissociate so that the catalytic ligand can associate,³ then we derive the following.



$$K = \frac{[CS_n]}{[S]^n[C]} \quad (3)$$

$$[C] = [C]_{\text{total}} / (1 + K[S]^n)$$

$$\text{rate} = k_2[C] = k_2'(\text{obsd})[C]_{\text{total}}$$

$$k_2' = k_2 / (1 + K[S]^n) \quad (4)$$

$$1/k_2' = 1/k_2 + [S]^n K/k_2 \quad (5)$$

The reciprocal equation (5) can be plotted in logarithmic form to obtain *n*. Excellent correlation with the hypothesis of integral solvation is found (Table I), and, in all solvents except methanol, only one solvent molecule is released in eq 2.

Table I. Solvation Numbers and Equilibrium Constants for Solvent Association with *cis*-Pt[(*n*-C₄H₉)₃P]₂Cl₂^a

Polar solvent ^b	<i>n</i> ^c	<i>K</i> ^c
CH ₃ NO ₂	1.00 ± 0.01	21.1 ± 1.0
CH ₃ CN	1.05 ± 0.05	16.8 ± 0.4
(CH ₃ CH ₂) ₂ O	1.07 ± 0.03	3.5 ± 0.2
CHCl ₃	0.99 ± 0.04	0.284 ± 0.005
CH ₃ OH	2.04 ± 0.05	110 ± 2

^a See eq 2 and 3. ^b Added to cyclohexane in low concentration. ^c Standard deviations from least-squares treatments of eq 5.

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(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.

(3) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).

(4) P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969).

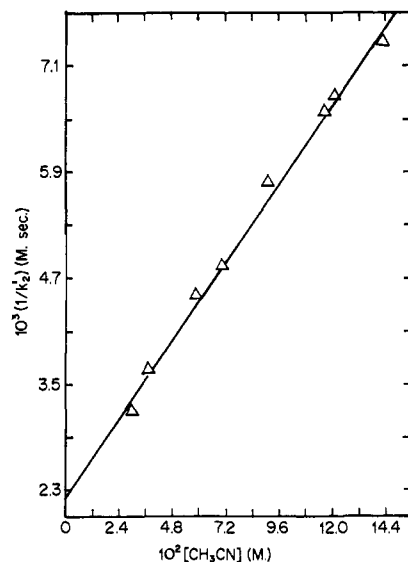


Figure 1. Dependence of $1/k_2'$ on $[CH_3CN]$ using eq 5, $n = 1$.

The adequacy of the correlation can be judged by the linear plot in Figure 1. The slope in Figure 1 then enables calculation of the equilibrium constants for solvation which are also given in Table I and are in line with expectations based on principles of bonding to Pt(II).² The intercept, k_2 , is the same in these mixtures as in pure cyclohexane, and since there is no deviation even at high concentrations of added polar solvent, S , k_2 appears to remain unchanged. That is, the Pt species which isomerizes appears to be identical with that in cyclohexane, so the only solvent which solvates this Pt(II) complex appears to be released in eq 2. Therefore, the *n* values in Table I appear to be total solvation numbers.

The reason for the solvation number of 2 for methanol is unclear, but it may be associated with the fact that CH₃OH is the only hydrogen-bonding solvent which was investigated.

These results appear to be of considerable importance in understanding the chemistry of tetragonal-planar complexes. The explanations based on symmetrical solvation (2) need to be reconsidered. Tetragonal-planar complexes appear to preferentially bind one additional ligand in a weak association which may be generally a distorted pentacoordinate structure.³ From this association, the chemistry ensues. It is significant that a solvent-associated complex appears to interact with the catalyst very slowly or not at all. If a tetragonal pyramid were formed with the platinum atom in the basal plane, the catalyst would be expected to be able to displace S from the opposite face. Therefore, the geometry of associated complexes appears to involve distortion from such a tetragonal-pyramidal state. For example, the platinum atom may be above the plane of the four original ligands in the pentacoordinate, associated state with distortion toward a trigonal bipyramid.⁵

(5) See ref 3 and references therein.

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