TABLE I. Rate Constants for Some Reactions of *cis*[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] in Various Solvents.

Solvent	$10^2\ k_1, s^{-1}$ [a]	k_1, s^{-1} [b]	$k_2, M^{-1}\ s^{-1}$ [c]
1) Methanol	186 ± 8	2.92 ± 0.06	13050 ± 140
2) Ethanol	10.2 ± 0.24	1.93 ± 0.11	18900 ± 320
3) 1-Propanol	3.65 ± 0.18	1.54 ± 0.05	31350 ± 330
4) 1-Butanol	1.62 ± 0.08	1.60 ± 0.03	47140 ± 720
5) 2-Methoxyethanol	1.21 ± 0.10	0.456 ± 0.01	10200 ± 270
6) 2-Propanol	0.91 ± 0.006	0.658 ± 0.002	45100 ± 630
7) 2-Methyl-2-propanol	0.0204 ± 0.0014	0.115 ± 0.007	67700 ± 720
8) Acetonitrile	0.042 ± 0.005	0.203 ± 0.018	4600 ± 160

[a] Rates of uncatalyzed isomerization at 40 °C. [b] Rates of solvolysis at 30 °C, obtained from the reagent independent path (2) in Scheme, using I^- as a nucleophile. [c] Rates of choride displacement by thiourea at 30 °C, calculated from the slopes of linear plots of $k_{obsd.}$ (s^{-1}) *vs.* [thiourea].

Solvent Effect on the Rates of Uncatalyzed Isomerization and Ligand Substitution at a Square Planar Platinum(II) Complex

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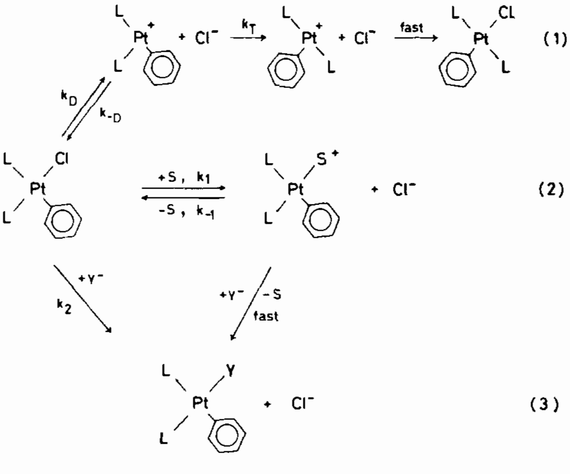
In a series of papers [1] we have suggested a dissociative asynchronous mechanism for the uncatalyzed *cis–trans* isomerization of the complexes *cis*-[$Pt(PEt_3)_2(R)X$] (X = halide ions; R = alkyl or aryl groups). This mechanism contrasts with the well-known capability of the metal to undergo bimolecular attack and with the general mechanistic picture established for the nucleophilic displacement of ligands in square planar complexes.

In this study we use solvent effects as a further criterion to distinguish between associative and dissociative reaction paths. The rates of isomerization, solvolysis and nucleophilic substitution of the complex *cis*-[$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] have been measured in a series of alcohols and in acetonitrile. These processes represent three different ways for removing the chloride ion from the coordination sphere of the metal; the magnitude of the solvent effect is found to depend on the degree of charge separation occurring in the transition state.

For all the solvents employed, the rates of solvolysis (path 2) are of many order of magnitude greater than the rates of isomerization. This large difference of reactivity, already observed and discussed in methanol [1c], argues strongly against a bimolecuar solvolysis being the initial step of the isomerization and rules out the possibility of a common intermediate for either solvolysis or isomerization. The rates of solvolysis as well as that of nucleophilic displacement by thiourea are little influenced by solvent changes, in keeping with the nature essentially associative of the activation processes, which do not require large changes of polarity or charge formation.



By way of contrast, the spontaneous *cis–trans* isomerization of [$Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl$] is extremely sensitive to changes in the nature of the solvents employed, as shown by a decrease in rate of four orders of magnitude on going from methanol to 2-methyl-2-propanol. Fairly good straight lines correlate these rates and some empirical parameters which measure the relative electrophilic character of the solvents, such as the α values of the Taft HBD scale or the Dimroth–Reichard's E_T values. The role of the solvent is to promote the breaking of the Pt–Cl bond in the rate determining step leading to a cationic intermediate. Electrophilic solvation of the leaving chloride ion through hydrogen bonding is the major factor in determining the large differences in rates observed, the contribution of non specific solvent–solute interactions being negligible or constant.

References

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Complexation of Hexaaquoiron(III) with Highly Charged Ligands: Kinetics of Conversion of outer- into inner-Sphere Complexes

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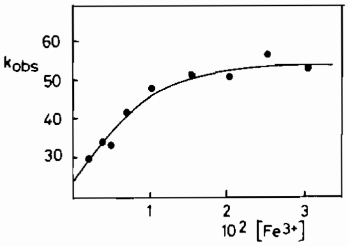
The introduction of fast mixing and relaxation techniques has made possible to establish that complex formation occurs through discrete steps which are characterized by the presence of outer-sphere (or solvent separated) and inner-sphere (or contact) complexes in equilibrium with the free ions. According to Eigen and Tamm [1] this can be depicted by the scheme (1)

$$\mathrm{M(H_2O)_6 + L \xrightleftharpoons{K_{os}} \underset{\text{outer-sphere}}{M(H_2O)_6, L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{inner-sphere}}{M(H_2O)_5L} + L} \qquad (1)$$

where K_{os} is the equilibrium constant for the formation of the outer-sphere complex, k_1 and k_{-1} are rate constants for the step of conversion of the outer- into the corresponding inner-sphere complex and *vice-versa.* For the above mechanism the observe first-order rate constant is [2]



$$k_{obs} = \frac{K_{os}k_1[M]}{1 + K_{os}[M]} + k_{-1} \qquad (2)$$

provided that $[M] >> [L]$.

In the majority of the investigated systems is $K_{os}[M] << 1$ and eqn. (2) is reduced to [2, 3]

$$k_{obs} = K_{os}k_1[M] + k_{-1} \qquad (3)$$

The only way to obtain k_1 is to estimate K_{os} with the help of appropriate equations which suffer of the disadvantage of introducing arbitrary assumptions about the distance apart of the ions in the outer-sphere complex [4].

The systems investigated in the present study $Fe^{3+}/Fe(CN)_6^{3-}$ and $Fe^{3+}/Co(CN)_6^{3-}$ are characterized by high values of K_{os} and represent two rare cases in which the rate law hold in the full form (eqn. 2). This is shown in Fig. 1 where, for the system $Fe^{3+}/Co(CN)_6^{3-}$ at ionic strength 0.3 *M*, the rate levels off at M > 0.02 *M*. Values of k_1, k_{-1} and K_{os} are reported in Table I (Temperature 25 °C.) The experimental K_{os} agree with the values calculated with the Fuoss [5] equation (a = 6 Å). The values of k_1 must correspond to the rate of water exchange at the metal ion (k_{H_2O}) if the interchange mechanism is dissociative [1]. In our cases k_1 are about one order of magnitude lower than k_{H_2O} suggesting that complexations of iron(III) are associative in nature and the solvent molecules are retained in the transition state.

References

1 M. Eigen and K. Tamm, *Z. Electrochem., 66,* 93 (1962).
2 J. Burgess, 'Metal Ions in Solution', John Wiley, New York (1978), p. 349.

TABLE I.

Ligand	k_1 (sec^{-1})	k_{-1} (sec^{-1})	K_{os} (M^{-1})	$K_{os\ calcd}$ (M^{-1})
$Fe(CN)_6^{3-}$	30	23	100	90
$Co(CN)_6^{3-}$	50	24	70	90