Cis-trans Isomerization of Dithiosulphatobisethylenediaminecobalt(III) in Aquatic Solution

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Isomerization of the cationic complex of the type $Coen_2X_2^+$ (X^- = singly charged anionic ligand) in basic solution proceeds through ion-pair formation [1]. The study of isomerization of the present anionic complex was undertaken as with this complex, ion-pair formation is untenable and isomerization may follow a different mechanistic path.

The isomeric forms of the complex were prepared according to literature [2]. Isomerization of the *cis* complex takes place below pH ~ 6.5. Above pH ~ 6.5 *trans* → *cis* conversion takes place, increasing with pH of the medium. Dependence of isomerization on pH indicates a definite role of the hydroxyl ion, which acts as a catalyst only. In basic medium, 'en' transforms to 'amido' form at one end. The combined effect of *trans* labilization of this 'amido' end, spanning of one of the $S_2O_3^{2-}$ ($S_2O_3^{2-}$ may act as a bidentate group also) to adjacent *cis* position and nucleophilicity and ring closing tendency of the partially released end of 'en' gives the required *trans* → *cis* conversion.

Nearly equal entropies of isomerization of both the forms and equilibrium of *cis* $\rightleftharpoons$ *trans* conversion at pH ~ 6.5 indicates a common intermediate for the conversion of both the forms.

References

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Solvent Effect on Electron Transfer Reactions

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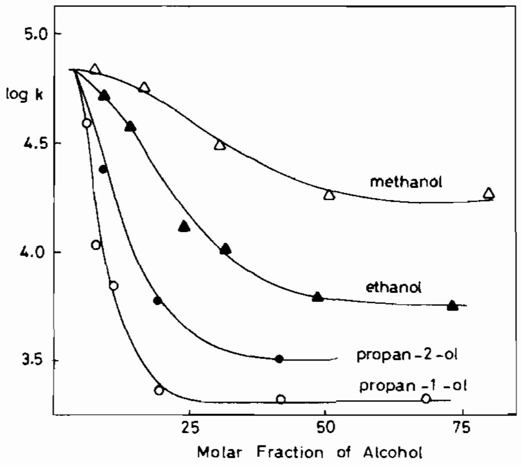

Although electron transfer reactions have been extensively investigated [1], the influence of changes of solvent has received comparatively little attention [2].

The effect of water–alcohol mixtures (methanol, ethanol, propan-1-ol, propan-2-ol) on the electron transfer rates of the following systems is reported in the present communication

$$Co(phen)_3^{3+} + Fe(cp)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Co(phen)_3^{2+} + Fe(cp)_2^{+} \qquad (1)$$

$$Fe^{3+} + Fe(cp)_2 \rightarrow Fe^{2+} + Fe(cp)_2^{+} \qquad (2)$$

$$Fe^{3+} + PTZ \rightarrow Fe^{2+} + PTZ^{\cdot+} \qquad (3)$$

where $Co(phen)_3^{3+}$ represents tris(1,10-phenanthroline)cobalt(III), $Fe(cp)_2$ ferrocene, and PTZ and $PTZ^{\cdot+}$ phenothiazine and the corresponding cation radical, respectively. The reaction rates were followed by means of a stopped-flow spectrophotometric technique.

The dependence of the logarithm of the rate constants as a function of the molar fraction of alcohol is reported in Fig. 1, for the system (1). The variation of the rate constants is not related to macroscopic solvent parameters [3, 4].

References

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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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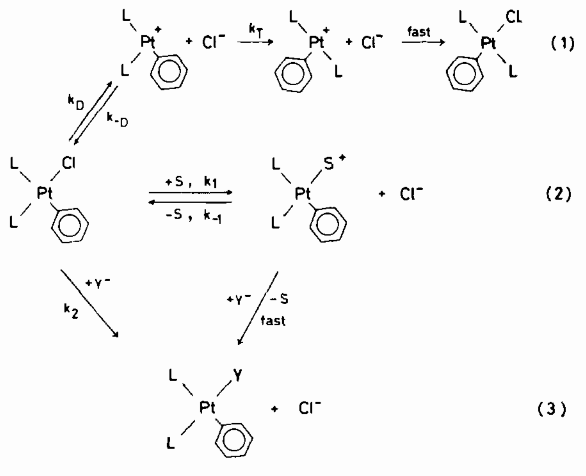

In a series of papers [1] we have suggested a dissociative asynchronous mechanism for the uncatalyzed *cis–trans* isomerization of the complexes *cis*-[$Pt(PEt_3)_2(R)X$] (X = halide ions; R = alkyl or aryl groups). This mechanism contrasts with the well-known capability of the metal to undergo bimolecular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