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

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Isomerization of the cationic complex of the type Coen$_2$X$_2^+$ (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$_2$O$_3^{2-}$ (S$_2$O$_3^{2-}$ 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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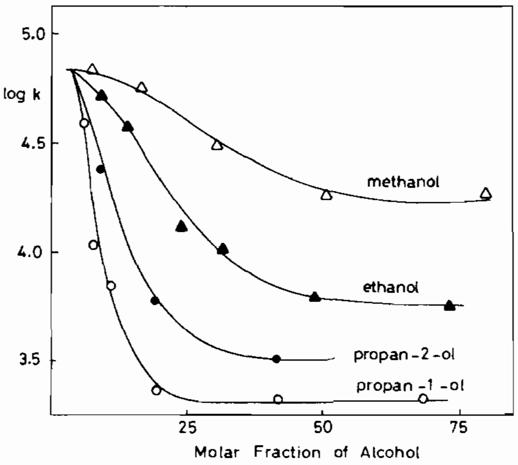
Although electron transfer reactions have been extensively investigated [1], the influence of changes of solvent has received comparatively little attention [2].



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

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

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

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

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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