J. Chem. Research (S),
2001, 353
J. Chem. Research (M),
2001, 0919–0946

Outer-sphere redox reactions of cobalt(III)-amine complexes. A solvent, chelation and temperature-dependence kinetic study

Gopalakrishnan Karthikeyan*, Krishnamoorthy Anbalagan and Kuppanagounder P. Elango

Department of Chemistry, Gandhigram Rural Institute (Deemed University), Gandhigram 624 302, India

The effect of solvent on the outer-sphere redox reactions between cobalt(III)-amine complexes and hexacyanoferrate(II) studied in aqueous methanol/1,4-dioxane is discussed quantitatively in terms of various solvent–solvent–solute interactions.

Keywords: cobalt(III)-amine complexes, kinetics of electron transfer

Most of the work on the influence of the solvent on the kinetics of electron transfer processes has centered around the dielectric continuum model (DCM) applied by Marcus and Hush,[1–2] which assumes that the solvent approximates a dielectric continuum and the solute–solvent interactions are negligible. Thus, any single bulk solvent property like the relative permittivity will poorly describe the microenvironment around the reacting species, hence the rate of electron transfer.[3] To account for the discrepancies in the DCM, various treatments for these solvent–solvent–solute interactions based on linear free energy relationships have been developed,[4] a few of which were employed by us, in studies of solvent effects on the iron(II) reduction and photoreduction of cobalt(III) complexes in mixed solvent media.[5–11]

In the present work the electron transfer reaction between *trans*-$[Co(NH_3)_4Cl_2]^+$, *trans*-$[Co(en)_2Cl_2]^+$, $[Co(dien)Cl_3]$, $[Co(trien)Cl_2]^+$ and $[Co(tetren)Cl]^{2+}$ and $Fe(CN)_6^{4-}$ was studied in aqueous mixtures of methanol and 1,4-dioxane under pseudo-first-order conditions at 288–303 K and ionic strength 0.3 M. The study was carried out to establish possible correlations between the amount and nature of cosolvent added and the ion-pair formation constant (K_{IP}), the electron transfer rate constant (k_{et}) and the activation parameters.

The negative correlation existing between log k_{et} and the Grunwald-Winstein[12] solvent ionising power, *Y*, indicates that the transition state is less polar than the reactants. Since no single macroscopic physical parameter could possibly account for the multitude of non-specific and specific solvent–solvent–solute interactions, multiparameter correlation studies are attempted by employing Swain's[16] biparameter and Kamlet–Taft's[19] triparameter equations. The excess Gibbs free energy of the mixture is also used, in addition to Swain's anion solvating tendency, A, and cation solvating tendency, B, as an adequate solvent parameter to consider the influence of the distruption and reorganisation of the solvent–solvent interactions on reactivity.[17] The results indicate that the transition state is more hydrophobic than the reactants. Such a transition state will more easily be attained with increase in mole fraction of organic cosolvent in the mixture and hence the observed increase in rate of electron transfer in this direction.

An excellent correlation existing between log k_{et} and Kamlet–Taft's solvent HBD, HBA, and polarisability/dipolarity terms indicates the existence of both non-specific and specific solvent–solvent–solute interactions. From the values of the regression coefficients, the contribution of each parameter, to reactivity, on a percentage basis were calculated[20] and listed in Table 4. These results indicate that the ion-pair solvation is more dominant in water–methanol mixtures than in water-1,4-dioxane mixtures, leading to a higher rate of electron transfer in the former mixture. The structural variation studies show that the reactions depend on steric factor and charge distribution in addition to chelation effects of the ligands investigated.

Table 4 Iron(II) reduction of cobalt(III)-amine complexes in aquo-organic solvent mixtures. Multiple correlation analysis of log k_{et} against Kamlet–Taft's solvatochromic parameters and their weighted percentage contributions

Complex	Percentage contributions*		
	$P\alpha$	$P\beta$	$P\pi^*$
Water–methanol mixtures			
$[Co(NH_3)_4Cl_2]^+$	41	17	41
$[Coen_2Cl_2]^+$	40	21	39
$[Co(dien)Cl_3]$	39	23	38
$[Co(trien)Cl_2]^+$	40	21	39
$[Co(tetren)Cl]_2^+$	40	21	39
Water–1,4-dioxane mixtures			
$[Co(NH_3)_4Cl_2]^+$	19	51	30
$[Coen_2Cl_2]^+$	24	44	32
$[Co(dien)Cl_3]$	30	35	35
$[Co(trien)Cl_2]^+$	22	47	31
$[Co(tetren)Cl]^{2+}$	23	45	32

*Computed using eqns (7) and (8) and an average of three values at three different temperatures.

References: 29

Tables: 6

Figures: 6

Received 15 March 2001; accepted 20 June 2001
Paper 01/819

References cited in this synopsis

4 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.
16 C.G. Swain, M.S. Swain, A.L. Powell and S. Alunni, *J. Am. Chem. Soc.*, 1983, **105**, 502.
19 M.J. Kamlet, J.M. Abboud, M.H. Abraham and R.W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.

---

* To receive any correspondence. E-mail: gricc@vsnl.com