

Electron transfer between aquapentaamminecobalt(III) and sulphur(IV) in aquo-organic solvent media: Delineation of solvent effects

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The kinetics of intramolecular electron transfer between Co^{III} and S^{IV} in O-sulphitopentaamminecobalt(III), $(\text{NH}_3)_5\text{CoOSO}_2^+$, have been investigated in aquo-organic solvent media comprising dipolar protic cosolvents (methanol, *n*-propanol, isopropanol, *tert*-butanol, and ethyleneglycol) and dipolar aprotic cosolvents (acetonitrile, ethylene carbonate) at 25-40°C. Rate acceleration is generally observed with increasing mole fraction (X_{org}) of the cosolvent except for ethyleneglycol+water. Correlation of rate ($\ln k_{\text{red}}^s$) with X_{org} , G^E (Gibbs excess free energy), E_T^N and dielectric constants of the solvent mixtures using multiparameter regression indicates that preferential solvation and solvent structural effects are important in controlling the reactivity. The correlation of rate with solvent hydrogen bonding acidity (α), basicity (β) and polarizability (π^*) for acetonitrile+water $\{\ln k_{\text{red}}^s = (2.5 \pm 0.4) - (2.0 \pm 0.6)\alpha + (0.2 \pm 0.4)\beta - 4.0 \pm 0.4\pi^*\}$ indicates that the electron transfer rate conformed well with the Taft model of solvation. The activation enthalpy and entropy versus X_{org} plots display extrema at low X_{org} , ΔH^\ddagger versus ΔS^\ddagger plot is linear indicating that the solvent structure effects on these parameters are mutually compensatory.

Solvent has a great role to play in controlling the dynamics of chemical reactions. Preferential solvation and solvent structure are important aspects of solvent effects. The former may be considered as a marker of molecular recognition in the light of solute-solvent and solvent-solvent interactions at the molecular level. These interactions for a given solute are, however, governed by acidity, basicity and polarity/polarizability of the solvent. A number of solvent polarity scales based on equilibrium constants, rate constants, spectral shift of dyes using absorption spectroscopy etc. have been established to quantify the effect of solvents on the chemical reactivity¹. Intermolecular interactions influence the structure of the solvent. Progressive addition of organic cosolvents to water profoundly affects its three dimensional hydrogen bonded network structure². The ways in which solvent effects in mixed solvent media operate to control the dynamics and energetics of reactions are not yet fully understood.

The redox reactions involve charge transfer between the oxidant and the reductant. Considerable solvent shell reorganisation in this process is envisaged. Such reactions are likely to be sensitive to preferential solvation and solvent structural changes. We have chosen a redox reaction be-

tween strongly hydrophilic substrates, $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ and S^{IV} (as SO_2), which can be preferentially solvated by water in mixed aquo-organic solvent media. Our aim is to examine closely the solvent parameters which are responsible for controlling the rate of electron transfer reaction. The aquo-organic solvent media comprising dipolar protic and aprotic cosolvents such as methanol (MeOH), *n*-propanol(Pr^nOH), isopropanol (Pr^iOH), *tert*-butanol(Bu^tOH), ethylene-glycol(EG), ethylene carbonate(EC) and acetonitrile(AN) are used in this study. The hydrophobicity of the solvent mixtures is thus varied to favour preferential solvation of the substrate by water.

The reduction of aquapentaamminecobalt(III) by S^{IV} is an intramolecular process as the O-sulphito complex, $(\text{NH}_3)_5\text{CoOSO}_2^+$, is the reactive species³. We thus report here a study of the medium effect of a typical unimolecular electron transfer reaction which has not been reported earlier.

Materials and Methods

The $[(\text{NH}_3)_5\text{CoOH}_2](\text{ClO}_4)_3$ was prepared by the published method⁴. Its purity was checked by analysis of cobalt; UV-visible spectra agreed with those reported in the literature⁴. All reagents and organic solvents (purity 99.5%) were analytical

grade. Solvents were stored over 4Å molecular sieve (except ethylene carbonate which was a solid) and distilled before use. The middle fraction of the distillate was used. Further check of the purity of solvents was made by density measurements. Distilled water was redistilled over alkaline KMnO₄. Solvent mixtures were prepared by volume per cent; conversion to mole fraction of the cosolvent (X_{org}) was made using density data.

Sodium meta bisulphite, Na₂S₂O₅, was the source of S^{IV}. This salt is stable in the solid state but hydrates rapidly in aqueous medium to yield a mixture of SO₂, HSO₃⁻ and SO₃²⁻ depending on pH of the medium⁵.

UV-visible spectra were recorded on a JASCO 7800 spectrophotometer. The pH measurements were made using a ELICO (Hyderabad) digital pH meter LI 120; a combined glass-Ag/AgCl, Cl⁻ (2 mol dm⁻³ NaCl) electrode model CL 51 was used as pH sensor (± 0.01 pH unit). Standard buffers of pH 4.01 and 9.2 were used to calibrate the pH meter.

Kinetics

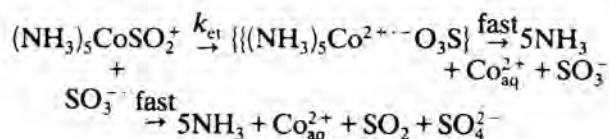
The kinetic measurements were performed on a HI-TECH(U.K.) SF 51 stopped flow spectrophotometer automated by an APPLE II GS P.C. The flow module and drive syringes were thermostated by circulating water from a C85 D thermostat through a cooler FC 200 (Hi-TECH, U.K.). The pseudo-first order conditions leading to complete conversion of the aqua complex to O-sulphito complex on mixing (ms time scale) were maintained ($\{[(\text{NH}_3)_5\text{CoOH}_2^{3+}]_{\text{T}} = 2.0 \times 10^{-4}$, $[\text{S(IV)}]_{\text{T}} = (2.0-4.0) \times 10^{-2}$ mol dm⁻³, $6.2 < \text{pH} < 7.2$) and decrease of absorbance due to the reduction of Co(III) was monitored at 330 nm at which the sulphito complex (NH₃)₅CoOSO₂⁺ (ϵ , 330 nm = 21,000 dm mol⁻¹ cm⁻¹) was the most significantly absorbing species. The aqua complex and the sulphite buffer were prepared in the mixed solvent media of same solvent composition. Ionic strength adjustment was avoided as addition of supporting electrolyte was likely to affect the solvent properties. At least five measurements were made for each run to get the rate constant (k_{red}) and its standard deviation. A nonlinear least squares computer programme, ADS₂ software from M/s HI-TECH Scientific Ltd (U.K.) was used to calculate the rate constants. The time base and signals could be expanded up to 500s and sixteen-fold at the most respectively to cover slow reaction and analyse the signals precisely. Replicate measurements using fresh solutions indicated that the rate constant for any run was reproducible within its

standard deviation. All other calculations were made on IBM compatible 486 PC.

Results and Discussion

Preliminary observations

The reaction of (NH₃)₅CoOH₂³⁺ with S^{IV} involved initial rapid formation of the species, (NH₃)₅CoOSO₂⁺ followed by slow intramolecular reduction of the cobalt(III) centre by the O-bonded sulphite³. The O-sulphito complex has been further characterised by O¹⁷ NMR spectroscopy⁶. The SO₃⁻ radical generated in the one electron transfer process is further rapidly scavenged by the O-sulphito complex³. Under the condition of complete conversion of the aqua complex to the O-sulphito form, the redox reaction is given as shown in Scheme 1:



Scheme 1

for which

$$k_{\text{red}} = 2k_{\text{et}} \quad \dots (1)$$

The factor 2 in Eq. (1) denoted stoichiometry of the reaction which was further verified by analysis of SO₄²⁻ as BaSO₄ (ref. 3). The redox reaction was studied at high [S^{IV}]_T ($100 \leq [\text{S}^{\text{IV}}]_{\text{T}}/[\text{Co}^{\text{III}}]_{\text{T}} \leq 200$) and analysis of Co(II) by Kitson's method⁷ showed that the reduction was quantitative [$\text{Co}^{\text{II}}]_{\text{T}}$ yield > 96%). However, the spectral scans of the reaction mixture after ca. 10t_{1/2} at high cosolvent contents indicated a small absorption peak around 325 nm. Also the absorbance-time curves in the stopped flow runs at high cosolvent contents deviated from first order kinetics (i.e. the initial decrease in absorbance was followed by a slow increase with time). The secondary reaction at high cosolvent contents was due to the isomerisation of the O-sulphito complex to its S-bonded analogue followed by NH₃ loss from the cobalt(III) centre due to the strong *trans* effect of the S-bonded sulphite. This aspect was not pursued further. Hence we were constrained to conduct experiments at low cosolvent contents $\{0 \leq X_{\text{MeOH}} \leq 0.398$; $0 \leq X_{\text{Pr}^n\text{OH}} \leq 0.194$, $0 \leq X_{\text{Pr}^i\text{OH}} \leq 0.189$; $0 \leq X_{\text{Bu}^t\text{OH}} \leq 0.306$; $0 \leq X_{\text{EG}} \leq 0.325$; $0 \leq X_{\text{EC}} \leq 0.323$; $0 \leq X_{\text{AN}} \leq 0.442$ where X = mole fraction of the cosolvent}.

Table 1—Rate data for the intramolecular electron transfer reaction of $(\text{NH}_3)_5\text{CoOSO}_2$

X_{org}^a	25.0°	30.0°	35.0°	40.0°C	X_{org}^a	25.0°	30.0°	35.0°	40.0°C
	$10^2 k_{\text{red}} (\text{s}^{-1})$					$10^2 k_{\text{red}} (\text{s}^{-1})$			
	MeOH + H ₂ O					EG + H ₂ O			
0.0	1.3 ^b	2.5 ^b	5.5 ^b	12.2 ^b	0.017	1.3	2.7	5.5	11.1
0.023	1.5	2.8	6.2	14.4	0.035	1.4	2.7	5.4	11.4
0.047	1.6	3.4	7.5	16.4	0.075	1.3	2.7	5.5	11.1
0.099	1.9	4.0	9.3	21.4	0.121	1.3	2.7	5.5	11.0
0.159	2.1	4.9	11.9	26.3	0.177	1.3	2.7	5.5	11.2
0.227	2.3	5.4	12.9	28.0	0.243	1.2	2.4	5.0	10.1
0.306	2.4	5.8	13.0	30.5	0.325	1.1	2.2	4.5	9.4
0.398	2.5	6.0	14.7	31.0		EC + H ₂ O			
	Pr ⁿ OH + H ₂ O				0.010	1.5	2.9	6.9	14.8
0.013	1.4	2.8	5.5	12.2	0.022	1.7	3.4	7.8	17.4
0.26	1.6	3.2	6.4	13.9	0.049	2.4	4.8	10.9	22.6
0.057	1.7	3.7	7.4	17.5	0.088	3.0	5.9	13.5	30.2
0.094	1.8	3.9	8.0	18.3	0.120	3.5	7.4	17.2	38.7
0.138	2.1	4.3	9.2	20.4	0.169	4.1	9.8	22.7	48.2
0.194	2.5	5.0	10.6	22.7	0.234	5.1	12.0	26.8	61.0
	Pr ⁱ OH + H ₂ O				0.323	6.0	15.1	32.9	76.8
0.013	1.4	3.2	6.4	15.0		AN + H ₂ O			
0.025	1.6	3.5	7.1	16.3	0.018	1.4	3.0	6.4	14.4
0.055	1.9	3.9	8.8	19.1	0.037	1.7	3.8	7.9	17.9
0.091	2.2	4.6	10.3	25.1	0.078	2.4	5.3	11.8	26.7
0.136	2.5	5.2	11.5	27.4	0.127	3.1	7.3	16.7	37.3
0.189	2.9	5.8	12.6	28.3	0.185	4.0	9.9	21.1	50.2
	Bu ⁱ OH + H ₂ O				0.254	5.0	13.0	28.1	60.3
0.010	1.5	3.2	6.5	13.7	0.328	5.6	13.9	30.2	70.5
0.020	1.6	3.3	7.4	15.8	0.442	7.3	14.5	32.9	75.6
0.045	1.8	3.9	9.0	18.5					
0.075	2.0	4.3	9.8	21.0					
0.112	2.3	4.7	10.5	22.3					
0.159	2.1	5.3	10.8	22.5					
0.221	2.0	5.5	10.9	23.0					
0.306	2.1	5.7	11.2	23.4					

^a X_{org} = mole fraction of the organic cosolvent, volume % of the cosolvent corresponding to X_{org} are 0, 5, 10, 20, 30, 40, 50, 60 and 70 respectively.

^baverage of 20 measurements and the error limit is within $\pm 5\%$

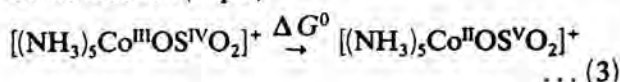
The rate data are collected in Table 1. van Eldik and Harris³ reported $k_{\text{red}} = (1.4 \pm 0.3) \times 10^{-2} \text{s}^{-1}$ at 25°C ($I = 1.0 \text{ mol dm}^{-3}$) in fully aqueous medium which compares well with our data ($k_{\text{red}} = (1.3 \pm 0.2) \times 10^{-2} \text{s}^{-1}$ at 25°C, $I = 0.04 \text{ mol dm}^{-3}$). Evidently ionic strength has little influence on k_{red} . The rate data (see Table 1) clearly indicate the rate accelerating effect of the mixed solvent media. The effect is relatively more prominent for the dipolar aprotic cosolvents (AN, EC). Among the protic cosolvents BuⁱOH + H₂O system exerts the smallest rate acceleration which, however, levels off at $X_{\text{Bu}^i\text{OH}} = 0.112$. For EG + H₂O apparently no solvent effect is evident, up to $X_{\text{EG}} = 0.177$ and thereafter a small retardation is evident.

Interpretation of solvent effects on the electron transfer rate

The electron transfer within the preassembled intermediate, $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{OS}^{\text{IV}}\text{VO}_2^+$, is rate determining. Hence the activation free energy, ΔG^* , in accord with the Marcus theory⁸, is given by Eq. (2):

$$\Delta G^* = \frac{\lambda}{4} \left[\left(\frac{1 + \Delta G^0}{\lambda} \right)^2 \right] \quad \dots (2)$$

where λ and ΔG^0 denote respectively, the reorganisation energy and standard free energy change of the reaction (Eq. 3):



The most recent data for the potential of the redox couple $\text{SO}_3^-/\text{SO}_3^{2-}$ in aqueous medium reported by Stanbury *et al.*⁹ is 0.72V (25°C, $I=0.1$ mol dm⁻³). The potential of the couple $\{(\text{NH}_3)_5\text{Co}^{3+}/(\text{NH}_3)_5\text{Co}^{2+}\}_{\text{aq}}$ (NHE scale) based on $E^0(\text{Co}^{\text{III}}/\text{Co}^{\text{II}})_{\text{aq}} = 1.808$ V (ref. 10) and the stability constants of $(\text{NH}_3)_5\text{Co}^{3+}_{\text{aq}}$ and $(\text{NH}_3)_5\text{Co}^{2+}_{\text{aq}}$ ($\log K_{(\text{NH}_3)_5\text{Co}^{\text{III}}} = 35.21$ and $\log K_{(\text{NH}_3)_5\text{Co}^{\text{II}}} = 5.13$, 25°C)¹¹ is ca. 0.294V. These data yield $\Delta G^0 = -41.1$ kJ mol⁻¹ (25°C) ($\Delta G^0 = -\Delta E^0F$). The transition state equation, $k_{\text{ET}} = \xi(k_{\text{B}}T/h)\exp(-\Delta G^\ddagger/RT)$ ($\xi=1$, $k_{\text{ET}}=k_{\text{red}}/2$), yields $\Delta G^\ddagger = 85.6$ kJ mol⁻¹ (25°C aqueous medium). Combining these data the values of λ calculated from Eq. (2) were 420 or 4 kJ mol⁻¹. The latter value of λ is clearly unacceptable considering the fact that (i) the activation free energy of the self exchange reaction of $\text{SO}_3^-/\text{SO}_3^{2-}$ couple is estimated to be as high as 65 kJ mol⁻¹ (ref. 9) and (ii) substantial contribution of the couple $(\text{NH}_3)_5\text{Co}^{\text{I}}/(\text{NH}_3)_5\text{Co}^{\text{II}}$ from the innersphere effect alone will arise due to metal ligand bond shifts ($\delta r = 16$ pm¹² for $(\text{NH}_3)_6\text{Co}^{\text{III}}/(\text{NH}_3)_6\text{Co}^{\text{II}}$). It may be further noted that about 97% of the innersphere component of ΔG^\ddagger ($\Delta G^\ddagger_{\text{is}} = 36.8$ kJ mol⁻¹) for the self exchange reaction of $\text{SO}_3^-/\text{SO}_3^{2-}$ couple is believed to be contributed by the barrier to bond bending mode to achieve electron transfer⁹. Evidently the overall reorganisation energy barrier to achieve electron transfer in the O-sulphitopentaamminecobalt(III) is substantially large. Eq. (2) can be approximated to Eq. (4) (as $\Delta G^0)^2/4\lambda = 1$ kJ mol⁻¹ for $\lambda = 420$ kJ mol⁻¹).

$$\Delta G^\ddagger = \lambda/4 + \Delta G^0/2 \quad \dots (4)$$

The reorganisation energy λ , is the sum of λ_{in} and λ_{out} of which the former depends on the internal parameters of the system and as such can be assumed to be independent of solvent. Thus the overall solvent effect on ΔG^\ddagger can be understood in terms of the medium effects on the outersphere components⁸ of λ (λ_{out}) and ΔG^0 . The solvent dipoles surrounding the reactants orient responding to the demands of the charge distribution accompanying the electron transfer. Assuming that the medium is structureless continuum of uniform permittivity and the ion is a nonpolarizable conducting sphere (DCM theory), λ_{out} is expressed^{8,13} as:

$$\lambda_{\text{out}} = Ne^2\{1/2r_1 + 1/2r_2 - 1/r\}[1/D_{\text{op}}^s - 1/D^s] \dots (5)$$

where r_1 , r_2 are the radii of the cobalt(III) moiety and SO_3^{2-} respectively and r is the closest distance of their approach at the actual act of electron transfer, N =Avogadro number, e =electronic

charge, D_{op}^s and D^s are the optical and static dielectric constants of the medium, s respectively. Combining $k_{\text{red}}^s/k_{\text{red}}^w = \exp(\Delta G^{\ddagger s} - \Delta G^{\ddagger w}/RT)$ with Eqs (4) and (5) we obtain Eq. (6):

$$\ln k_{\text{red}}^s = \ln k_{\text{red}}^w + (Ne^2/4RT)F(r)F(D) - (1/2RT)[\Delta_t G^0]_{s-w} \quad \dots (6)$$

where

$$F(r) = \{1/2r_1 + 1/2r_2 - 1/r\},$$

$$F(D) = (1/D_{\text{op}}^w - 1/D^w) - (1/D_{\text{op}}^s - 1/D^s)$$

and

$$[\Delta_t G^0]_{s-w} = \Delta G^{\text{os}} - \Delta G^{\text{ow}}$$

The optical dielectric constants of AN+water media were calculated ($D^s = (n^s)^2$) from the experimental values of the refractive indices¹⁴. For all other mixed solvent media, the refractive indices were calculated by $n^s = n^w + (n_w - n_{\text{org}})X_{\text{org}}$ (ref. 15) to get the values of D_{op}^s . The values of the refractive indices of the pure solvents (n_w , n_{org}) and the static dielectric constants (D^s) of the mixed solvent media ($0 \leq X_{\text{org}} \leq 1$) are available¹⁶. The $\ln k_{\text{red}}^s$ versus $F(D)$ plots (see Fig. 1) display specific solvent effects and failure of the DCM model. It is also worth noting that both the dipolar aprotic cosolvents, acetonitrile and ethylene carbonate, substantially enhance the rate while the dielectric constant of AN+water decreases with increase in X_{AN} ($78.6 \leq D_s \leq 49.2$ for $0 \leq X_{\text{AN}} \leq 0.442$) and that of EC+water increases with increase in X_{EC} ($78.6 \leq X_{\text{EC}} \leq 82.6$ at $0 \leq X_{\text{EC}} \leq 0.323$).

Recently Lay *et al.*¹⁷ have attempted correlations of the formal electrode potentials of metal amine complexes in several pure solvents with hydrogen bonding acidity (α), hydrogen bonding basicity (β), polarizability (π^*) and the internal order of the solvents by a multiparameter regression. The importance of specific solvent effects in electron transfer reaction between tetraamminepyrazinecarboxylatocobalt(III) and aquapentacyanoferrate(II) has been delineated by Moya, Sanchez and Burgess^{17b}. Abbot and Rusling¹³ also observed that the rates of outersphere electron transfer reactions of several systems in different pure solvent media correlated with α , β , and π^* on the basis of Taft model¹⁸⁻²⁴ by a multiparameter regression better than with the solvent permittivity on the basis of DCM model. The Taft model points to the recognition of specific solute-solvent interaction in the activation process. If the outer sphere components of λ and ΔG^0 are assumed to be linearly related

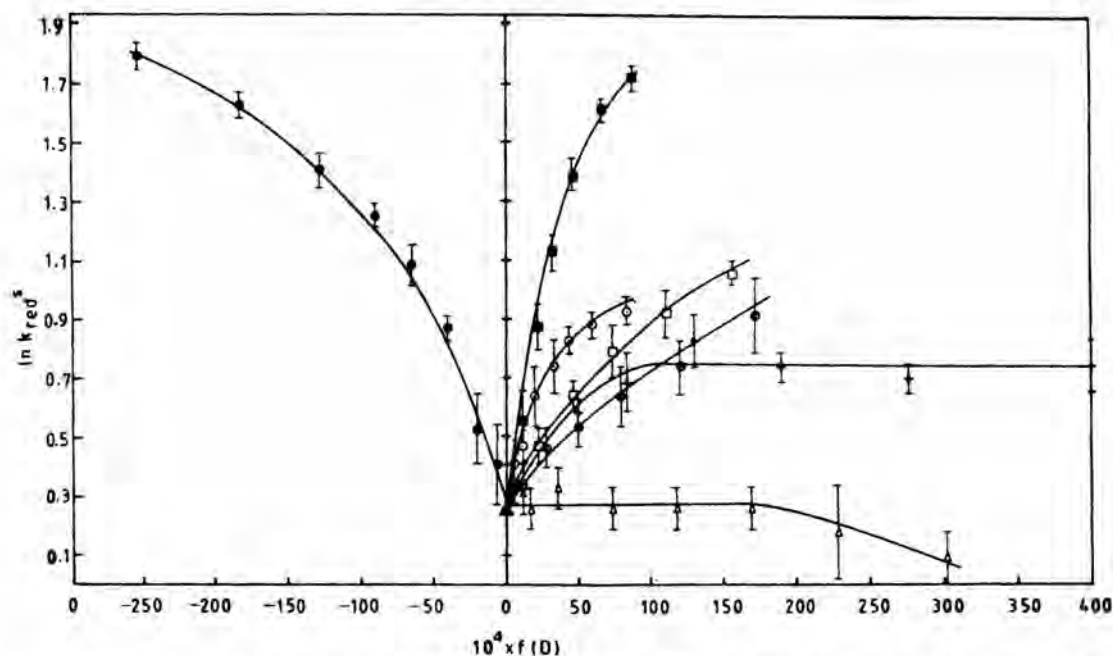


Fig. 1— $\ln k_{\text{red}}^s (\text{s}^{-1})$ versus $10^4 R(D)$ plots (see Eq. 6) at 25°C : \circ —MeOH, \square —PrⁱOH, \odot —PrⁿOH, + BuⁱOH, \ominus —Ec, Δ —EG
 \blacksquare —AN

to α , β , π^* then Eq. (4) yields Eq. (7).

$$\ln k_{\text{red}}^s = A_0 + A_1\alpha + A_2\beta + A_3\pi^* \quad \dots (7)$$

where $A_0 = \ln k_{\text{red}}^s$ for a hypothetical solvent for which $\alpha = \beta = \pi^* = 0$. Eq. (7) was tested for $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ system at 25°C for which, α , β , π^* values are available²⁵. Values of α , β , π^* at appropriate compositions were obtained by interpolation of the plots of α , β , or π^* versus X_{AN} . Rate data at 25°C , fitted to Eq. (7) by a weighted least squares programme²⁶, yielded $A_0 = 2.5 \pm 0.4$, $A_1 = -2.0 \pm 0.6$, $A_2 = 0.2 \pm 0.4$ and $A_3 = 4.0 \pm 0.4$ (corr. coef. = 0.967). The coefficient of β is statistically insignificant. The correlation indicates that the electron transfer rate is favoured with decreasing hydrogen bonding acidity and decreasing polarizability of the medium. The parameters α , β for $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ fit a fourth degree power series in X_{AN} while the series is truncated to X_{AN}^2 for π^* (ref. 25). For other solvent systems the nonlinear dependence of $\ln k_{\text{red}}^s$ with X_{org} , therefore, indirectly reflects the general applicability of the Taft model.

The cosolvents perturb the three dimensional hydrogen-bonded network structure of water when the composition of the mixed solvent media is altered between the bounds $0 \leq X_{\text{org}} \leq 1$. Despite extensive theoretical and experimental studies on the structural aspects of the aquo-organic solvent media^{14,25,27-34} it is hardly possible to find a suitable parameter to correlate the kinetic and ther-

modynamic data of reactions with the solvent structure. However, the excess Gibbs free energy of mixing (G^E) of the mixed solvent media (relative to water) is considered as a measure of the solvent structural effect. Attempts to correlate the rates of substitution reactions of inorganic complexes with G^E have met with some success³⁵. Considering the fact that ΔG^0 and the non-electrostatic component of λ_{out} are influenced by solvent structure (G^E), polarity (E_T^N) and preferential solvation Eq. (5) can be transformed to Eq. (8):

$$\ln k_{\text{red}}^s = \ln k_{\text{red}}^w + a_1 X_{\text{org}} + a_2 F(D) + a_3 (E_T^{\text{Ns}} - E_T^{\text{Nw}}) + a_4 G^E \quad \dots (8)$$

The G^E (25°C) data for $\text{CH}_3\text{OH} + \text{H}_2\text{O}$, PrⁿOH + H_2O , PrⁱOH + H_2O , BuⁱOH + H_2O , EG + H_2O and $\text{CH}_3\text{CN} + \text{H}_2\text{O}$ at $0.1 \leq X_{\text{org}} \leq 1.0$ are available [ref. 14, p 190]. The values of G^E (kJ mol^{-1}) at the desired mole fractions were obtained by interpolation/extrapolation of G^E versus X_{org} curves. The values of the polarity parameter (E_T^{Ns}) were computed using the relationship suggested by Bosch and Roses (see Eq. 10 of ref. 36). The rate data at 25°C were fitted to Eq. (8). We obtained $a_1 = 1.76 \pm 0.15$, $a_2 = -20.2 \pm 2.2$ and $a_3 = -0.41 \pm 0.11$ and $a_4 = 0.79 \pm 0.04$ ($F^{26} = 121$ over 43 data points). The plot of k_{red} (calcd) versus k_{red} (exp.) (see Fig. 2) reflects the goodness of fit.

The solvent systems (except EG + H_2O) used for correlation analysis are characterized by G^E

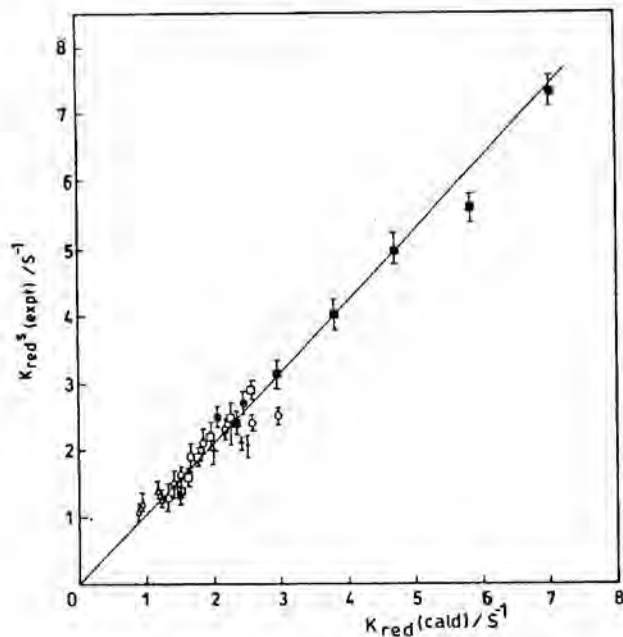


Fig. 2— $k_{\text{red}}^0(\text{calcd})(\text{s}^{-1})$ vs $k_{\text{red}}^0(\text{expt})(\text{s}^{-1})$ plots at 25°C.

positive¹⁶ (except EG + H₂O for which G^{E} is negative) over the entire range of composition. Hence the mixed solvent media (except EG + H₂O) are destabilized relative to the pure solvents. Since the coefficient of G_{E} is positive, it is inferred that the destabilization of solvent, which is also a reflection of the solvent structural effect, results in the rate acceleration. It may be noted that the charges of the oxidant and reductant centres are reduced numerically by one unit each owing to the electron transfer resulting in a transition state which is less polar and hence less hydrophilic than the initial state. With increasing proportions of the cosolvents which are less hydrophilic, the initial state is destabilised more than the transition state resulting in the rate acceleration. The small rate retardation observed for EG + H₂O system at high X_{EG} also fits into this interpretation. However, in this case the initial state is rather stabilised to a greater extent than the transition state at high X_{EG} . Thus the solvent structural effect on the rate is linked with the stabilisation of the transition state relative to the initial state.

From $a_2\{ = Ne^2/4RT)F(r)\}$ it is possible to calculate the distance of closest approach between S^{IV} and Co^{III} centres (r) during the electron transfer. Considering $r_1 = 3.3 \text{ \AA}$ ^{17b} and $r_2 = 1.5 \text{ \AA}$ ($r_{\text{S-O}}$ SO_3^- ref. 37) this distance is ca. 1.6 Å which is close to the value of r_2 . Similar observation has been made by Moya *et al.*^{17b} in the intramolecular electron transfer of the preassembled complex of (pyrazene-

Table 2—Activation enthalpy and activation entropy data for the intramolecular reduction of $(\text{NH}_3)_5\text{CoOSO}_2^+$ in mixed solvent media^{a,b}

X_{org}	ΔH^{\ddagger} (kJ mol ⁻¹)	ΔS^{\ddagger} (JK ⁻¹ mol ⁻¹)	X_{org}	ΔH^{\ddagger} (kJ mol ⁻¹)	ΔS^{\ddagger} (JK ⁻¹ mol ⁻¹)
MeOH + H ₂ O			Pr ⁿ OH + H ₂ O		
0.023	128 ± 4	165 ± 1	0.013	111 ± 2	91 ± 7
0.047	118 ± 2	134 ± 5	0.028	111 ± 2	93 ± 8
0.099	130 ± 2	174 ± 6	0.056	120 ± 3	122 ± 11
0.159	125 ± 2	162 ± 6	0.093	119 ± 4	120 ± 13
0.227	126 ± 2	165 ± 7	0.138	118 ± 4	117 ± 13
0.306	129 ± 2	175 ± 5	0.193	116 ± 2	114 ± 5
0.398	127 ± 3	168 ± 10			
Pr ⁿ OH + H ₂ O			Bu ⁿ OH + H ₂ O		
0.013	120 ± 15	140 ± 15	0.010	112 ± 2	113 ± 6
0.025	120 ± 4	141 ± 12	0.020	124 ± 1	154 ± 3
0.055	117 ± 4	134 ± 13	0.045	122 ± 1	148 ± 4
0.091	132 ± 5	183 ± 14	0.075	125 ± 2	160 ± 6
0.135	128 ± 3	172 ± 10	0.112	122 ± 1	150 ± 4
0.189	117 ± 3	139 ± 8	0.159	119 ± 4	123 ± 11
			0.221	121 ± 5	126 ± 16
			0.306	114 ± 4	126 ± 13
EG + H ₂ O			AN + H ₂ O		
0.017	107 ± 1	79 ± 5	0.018	119 ± 1	137 ± 4
0.035	104 ± 1	69 ± 3	0.037	123 ± 4	154 ± 12
0.075	107 ± 1	78 ± 3	0.078	127 ± 1	168 ± 4
0.121	107 ± 2	79 ± 2	0.127	127 ± 1	172 ± 7
0.177	108 ± 1	81 ± 5	0.185	127 ± 1	174 ± 4
0.243	106 ± 3	72 ± 8	0.254	122 ± 1	160 ± 12
0.325	108 ± 1	81 ± 2	0.338	127 ± 2	177 ± 7
			0.442	128 ± 4	180 ± 9
EC + H ₂ O					
0.010	124 ± 3	154 ± 9			
0.022	126 ± 2	163 ± 4			
0.049	115 ± 2	129 ± 7			
0.086	127 ± 1	169 ± 3			
0.120	124 ± 2	163 ± 7			
0.169	122 ± 2	160 ± 6			
0.234	129 ± 1	183 ± 3			
0.323	129 ± 2	183 ± 6			

^a ΔH^{\ddagger} (kJ mol⁻¹) = 121 ± 4 and ΔS^{\ddagger} (JK⁻¹mol⁻¹) = 122 ± 12 for aqueous medium.

^b $I = 0.04 \text{ mol dm}^{-3}$

carboxylato)(tetraammine)cobalt(III) and aquapentacyanoferrate(II), $[(\text{NH}_3)_4\text{CoO}_2\text{CpzFeCN}_5]^-$.

$E_{\text{T}}^{\text{N}^{\text{W}}} > E_{\text{T}}^{\text{N}^{\text{S}}}$ and $E_{\text{T}}^{\text{N}^{\text{S}}}$ decreases with increasing X_{org} for all mixed solvent media (except EC + H₂O for which $E_{\text{T}}^{\text{N}^{\text{S}}}$ data are not available). The coefficient of $E_{\text{T}}^{\text{N}^{\text{S}}} - E_{\text{T}}^{\text{W}}(a_3)$ is negative. Hence the rate acceleration increases with decreasing solvent polarity. The positive correlation of $\ln k_{\text{red}}$ with X_{org}

($a_1 = 1.76$) might indicate specific interaction of the cosolvent molecules with the initial state and transition state which lead to relatively greater destabilisation of the former.

Effect of solvent composition on activation parameters, ΔH^\ddagger and ΔS^\ddagger :

The activation enthalpy and entropy for fully aqueous medium are $121 \pm 4 \text{ kJ mol}^{-1}$ and $122 \pm 12 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively ($I = 0.04 \text{ mol dm}^{-3}$). These data may be compared with those reported by van Eldik and Harris³ ($\Delta H^\ddagger = 122 \pm 5 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 97 \pm 18 \text{ JK}^{-1}$, $I = 1.0 \text{ mol dm}^{-3}$). The reaction is also associated with substantially large positive volume of activation³⁸ ($\Delta V^\ddagger = 34 \pm 3 \text{ cm}^3 \text{ mol}^{-1}$, 25°C) which has a direct bearing on the structural changes in the transition state. The activation parameters (ΔH^\ddagger , ΔS^\ddagger) are sensitive to the nature of the cosolvent and also to the solvent composition for a given cosolvent (see Table 2). The plots of ΔH^\ddagger and ΔS^\ddagger versus X_{org} display extrema at relatively low molefractions of the cosolvents. The ΔH^\ddagger (ΔS^\ddagger) versus X_{org} plots for substitution reactions of several cobalt(III) substrates in the mixed solvent media also display extrema³⁹⁻⁴³. This general observation is taken to indicate that the solvation components of the activation parameters (ΔH^\ddagger , ΔS^\ddagger) are sensitive to solvent structural perturbations. It is worth noting that ΔH^\ddagger versus ΔS^\ddagger plot is linear [ΔH^\ddagger (kJ mol^{-1}) = $87.5 (\pm 2.7) + 0.228 (\pm 0.016) \Delta S^\ddagger$ ($\text{JK}^{-1} \text{ mol}^{-1}$) corr. coeff. = 0.92] indicating that the overall effects of solvation on these activation parameters are mutually compensatory.

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