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SHORT COMMUNICATION

MEDIUM EFFECTS ON THE REDUCTION KINETICS OF trans-DICHLORO-bis(1,2-DIAMINOPROPANE)COBALT(III) BY HEXACYANOFERRATE(II) IN AQUEOUS ORGANIC SOLVENTS

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ABSTRACT. The kinetics of iron(II) reduction of trans-dichlorobis(1,2-diaminopropane)-cobalt(III) ion has been studied in different aqueous organic solvent mixtures at 30°C. The association constant of the precursor complex formation and the electron transfer rate constants have been determined in these binary solvent mixtures. The title reaction was carried out at three different temperatures and activation parameters have been computed. The effect of solvent on the kinetics of the reaction has been analysed in the light of various solvent parameters.

INTRODUCTION

Recent studies show the solvent dynamics on electron transfer reactions, which are important in biological and other processes. Generally solvent variations may affect the kinetics and energetics of the electron transfer processes particularly in mixed solvent media, in a complex manner as the physico-chemical properties of the mixed solvent media are often quite different from those of the pure solvents or of their ideal mixtures [1]. Attempts have been made to interpret the solvent effects on the rates of these reactions by considering the solvation of the reactants and the products in the initial and in the transition state of the reduction process [2]. Therefore, in continuation of our previous study on the solvent effect on reaction rates of cobalt(III) complex [3], it was considered worthwhile to investigate the solvent effect on the title reaction.

The electron transfer processes are reactions that proceed through a three-step mechanism. The following scheme represents the general mechanism for an outer-sphere process:

1. $A + D \xrightleftharpoons{K_{IP}} A/D$ fast pre-equilibrium

2. $A/D \xrightarrow{k_{et}} A^{-}/D^{+}$ slow electron transfer

3. $A^{-}/D^{+} \longrightarrow$ Products

For the system, under investigation the following equation applies, provided that [D] >> [A], D being the donor and A the acceptor. The rate constant k_{obs} can be estimated using the following complex equation.

$$k_{obs} = k_{et} K_{IP}[D]/(1+K_{IP}[D]) \qquad (1)$$

The values of K_{IP} and k_{et} can be determined by employing different excesses of the donor concentrations.

EXPERIMENTAL

The trans-$[Copn_2Cl_2]^+$ was obtained by reacting cobaltous chloride hexahydrate with 10% 1,2-diaminopropane aerating for 10 h followed by addition of concentrated hydrochloric acid. The mixture was concentrated till the formation of green crust and filtered to obtain the complex as described in the literature [4]. The purity of $[Copn_2Cl_2]Cl$ was checked by electronic absorption spectroscopy. The organic solvents, sodium perchlorate, $[Fe(CN)_6]^{4-}$ and disodium salt of ethylenediaminetetraacetic acid, $Na_2(H_2edta)$, were AnalaR grade and used without further purification. In all kinetic runs the ionic strength was maintained constant by adding sodium perchlorate(0.3 mol dm^{-3}). The concentration of cobalt(III) complex was always 1 x 10^{-4} mol dm^{-3} and five hexacyanoferrate(II) concentrations were employed, ranging from 1 x 10^{-3} to 2 x 10^{-3} mol dm^{-3}. Addition of $Na_2(H_2edta)$ was necessary to prevent precipitation of $Co_2Fe(CN)_6$. The reaction was followed spectrophotometrically at 420 nm, where the hexacyanoferrate(III) produced in the reaction absorbs. The range of absorbance measured for the iron(III) complex is 0.01-0.12 using 1 cm length quartz cuvette. The other species normally do not absorb at this wavelength. The temperature was kept constant at 30 ± 0.2 °C. The pseudo-first-order rate constants were obtained from the slopes of the linear plots of log (A_i -A_t) versus time, where A_i is the absorbance at infinity and A_t at a particular time t, respectively.

RESULTS AND DISCUSSION

The reduction of cobalt(III) complex by the hexacyanoferrate(II) was studied in aqueous mixtures of methanol, ethanol, glycol and 1,4-dioxane over 298-308 K range. The electron transfer rate constant (k_{et}) values and the association constant (K_{IP}) values for the precursor ion-pair were calculated from the intercepts and slopes of the plots of $1/k_{obs}$ versus $1/[Fe(CN)_6^{4-}]$ using least squares procedure at different dielectric constant of the medium (Tables 1 and 2). Variation of the rate constant with the total number of moles of the mixed solvent is given using the mathematical expression [5];

$$\ln k = \ln 2.08 \times 10^6 T - \Delta\mu^* (n_1 + n_2) / RT \qquad (2)$$

where n_1 and n_2 are the number of moles of the organic solvent and water, respectively. A plot of log k versus (n_1 + n_2) should be linear, the slope of which gives the change in the chemical potential ($\Delta\mu^*$) of a specified process. The estimated values of $\Delta\mu^*$ at 303 K are found to be -271, -152, -77 and -140 J/mol in methanol-water, ethanol-water, glycol-water and 1,4-dioxane-water mixtures respectively. The change in molar Gibb's function is given by change in chemical potential [6] and hence

$$\Delta G_m^* = \Delta\mu^* = - RT \ln K \qquad (3)$$

where K is the equilibrium constant of the reactant/activated complex equilibrium. The calculated values of K for the reduction reaction in the solvent mixtures studied are found to be greater than unity giving a strong evidence for the association of the reactants.

Table 1. Pseudo-first-order rate constants ($10^3\ k_{obs}$,s) for the reduction of trans-$[Copn_2Cl_2]^+$ by $[Fe(CN)_6]^{4-}$ in various water-organic solvent mixtures at 303 K.

Dielectric constant (D)	$10^3[Fe(CN)_6^{4-}]$ mol dm^{-3}				
	1.0	1.25	1.50	1.75	2.0
water- methanol					
74.36	7.16	8.04	8.69	9.17	9.52
72.17	8.36	9.53	10.42	11.11	12.06
69.97	9.82	11.34	12.65	13.78	14.77
67.78	11.82	13.69	15.87	17.86	---
water-ethanol					
73.95	6.70	7.78	8.63	9.29	9.98
71.35	7.59	8.92	10.12	11.17	12.12
68.75	8.71	10.37	11.89	13.28	14.54
66.15	9.56	11.53	13.37	15.08	16.61
water-glycol					
74.66	7.64	8.05	9.36	10.81	11.39
72.76	8.27	8.82	10.27	11.85	12.49
70.87	9.01	9.70	11.31	13.04	13.76
68.97	9.84	10.73	12.54	14.45	15.24
water-1,4-dioxane					
72.83	4.97	5.18	6.78	7.04	7.60
69.12	5.51	6.26	7.58	8.25	9.01
65.40	6.32	7.88	8.59	9.82	10.78
61.68	7.14	9.92	9.87	11.99	13.39

$[Copn_2Cl_2^+] = 1 \times 10^{-4}$ mol dm^{-3}; $[Na_2(H_2edta)] = 5 \times 10^{-5}$ mol dm^{-3}; $[NaClO_4] = 3 \times 10^{-1}$ mol dm^{-3}.

The solvent effect of the title reaction has been studied in four different water-organic solvent mixtures(5,10,15 and 20% v/v of organic solvent) at three different temperatures. It was observed that k_{obs} and k_{et} values increase with decrease in dielectric constant of the medium. It is in good agreement with the fact that, due to increase in organic component of the medium the possibility of association between the charged reactants is favoured, which can be explained by Laidler-Eyring [7] equation.

$$d \ln k/d(1/D) = e^2 Z^2 (1/r - 1/r^*)/2kT \qquad (4)$$

where k in the above equation is replaced by k_{obs}, D is the dielectric constant of the medium, Z the net charge, r the effective radius and r^* is the radius of the activated species. Plot of log k_{obs} verses 1/D is linear (correlation coefficient $r > 0.99$ and Exner's statistical parameter ψ [8], which indicates the best fit of the data plotted, is in the range of 0.06-0.19) with positive slope in all the solvent mixtures studied, which gives some indication that the reaction proceeds through an associative reduction path where $r^* > r$. It is further observed that the slope decreases with increase in temperature.

Table 2. Values of k_{obs}, K_{IP} and k_{et} for the reaction of trans-$[Copn_2Cl_2]^+$ with $[Fe(CN)_6]^{4-}$ in several water-cosolvent mixtures at 303 K.

D	10^3 k_{obs} s^{-1}	K_{IP} mol^{-1} dm^3	10^2 k_{et} s^{-1}
water-methanol			
74.36	7.16	997.9	1.44
72.17	8.36	672.1	2.08
69.97	9.82	492.4	2.98
67.78	11.82	257.6	5.72
water-ethanol			
73.95	6.79	564.3	1.88
71.35	7.59	337.7	3.01
68.75	8.71	246.9	4.39
66.15	9.56	172.3	6.5
water-glycol			
74.66	7.64	466.6	2.32
72.76	8.27	430.8	2.66
70.87	9.01	401.5	3.06
68.97	9.84	366.0	3.58
water-1,4-dioxane			
72.83	4.97	363.9	1.81
69.12	5.51	263.8	2.61
65.40	6.32	227.0	3.45
61.68	7.14	111.1	7.36

$[Fe(CN)_6^{4-}] = 1 \times 10^{-3}$ mol dm^{-3}; $[Copn_2Cl_2^+] = 1 \times 10^{-4}$ mol dm^{-3}; $[Na_2edta] = 5 \times 10^{-5}$ mol dm^{-3}
$[NaClO_4] = 3 \times 10^{-1}$ mol dm^{-3}.

In water-organic solvent medium, the relation between rate constants and Grunwald-Winstein solvent parameter (Y-values) [9] gives a much better insight into the mechanism of the reaction. Plots of log k_{obs} versus Y-values are linear ($r = 0.999$; $\psi = 0.06$) with slopes (m) equal to -0.57, -0.43 and -0.33 in methanol-water, ethanol-water and 1,4-dioxane-water media respectively. The negative values of m indicate that the present complex undergoes redution by an associative process which can be compared to the solvolysis of alkyl halides via S_N2 mechanism [10]. It is well known that in an S_N2

reaction between two oppositely charged ions the transition state is more easily attained in media of lower dielectric constants. Therefore, it may be concluded that the reactants under present study attain the transition state more easily, hence, the increase in rate with decrease in dielectric constant of the media is observed. Further, near similarity in m-values was ascribed to similarity of the mechanism in the binary solvents studied.

The reduction reaction between Co(III) and Fe(II) has been studied at three different temperatures in all these water-organic solvent media. The activation parameters were evaluated by plotting 1/T versus log k_{obs} using Eyring's equation (Table 3). The low $\Delta H^{\#}$ values and large negative $\Delta S^{\#}$ values suggested associative mechanism. The free energy of activation ($\Delta G^{\#}$) appears to be almost independent of solvent composition. But on splitting it into $\Delta H^{\#}$ and $\Delta S^{\#}$ the solvent dependence is evident and this clearly indicates that both enthalpy and entropy effects are mutually compensatory. It is further confirmed that the plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ is linear ($r > 0.99$) in all the four solvent mixtures studied. This could be an indication of constancy of the mechanism over the solvent composition range studied. However Exner [11] criticised the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$, as these quantities are dependent on each other. Therefore log k_{obs} values at 303 K was plotted against log k_{obs} values at 298 K and a linear correlation ($r > 0.99$) was observed in all the aqueous-cosolvent mixtures. Such a good correlation indicate that the reaction in all the solvent compositions investigated follow a common mechanism [12].

Table 3. Activation parameters for the electron transfer reaction in several water- cosolvent mixtures.

Activation parameter	Cosolvent % (v/v)			
	5	10	15	20
water-methanol				
$\Delta H^{\#}$	12.6	17.4	17.9	22.6
$-\Delta S^{\#}$	194.5	178.3	175.7	159.9
water-ethanol				
$\Delta H^{\#}$	23.6	26.4	25.8	35.1
$-\Delta S^{\#}$	158.5	148.6	150.3	119.2
water-glycol				
$\Delta H^{\#}$	36.3	25.9	15.2	3.7
$-\Delta S^{\#}$	116.2	150.2	185.1	222.9
water-1,4-dioxane				
$\Delta H^{\#}$	28.3	30.0	24.3	22.6
$-\Delta S^{\#}$	144.0	138.1	156.1	161.5

$\Delta H^{\#}$ in kJ/mol; $\Delta S^{\#}$ in JK^{-1} mol^{-1}; $[Fe(CN)_6^{4-}] = 1 \times 10^{-3}$ mol dm^{-3}; $[Copn_2Cl_2^{+}] = 1 \times 10^{-4}$ mol dm^{-3}; $[Na_2edta] = 5 \times 10^{5}$ mol dm^{-3}; $[NaClO_4] = 3 \times 10^{1}$ mol dm^{-3}.

The variation of log k_{obs} with log $[H_2O]$ is linear ($r > 0.99$) at constant temperature for different solvent compositions. The slopes obtained are found to be less than unity indicating that the internal structure of the media studied suffered serious changes on addition of the organic solvent component. The same behaviour was observed by Tomila [13] indicating that hydrogen bond between organic solvent molecule and water is stronger than that between two water molecules. Thus hydrogen bonding between neighbouring water molecules will be replaced gradually by hydrogen bonding with organic solvent molecules and the tetrahedral structure of water is then largely broken [14].

The effect of solvent polarity was analysed qualitatively by using Kamlet's [15] solvent parameter π^*, which is an index of solvent dipolarity/polarizability. The plots of log k_{obs} versus π^* are linear ($r > 0.98$) in all the solvent mixtures studied indicating that the polarity of the medium very much affects the reaction rate.

In conclusion, the reduction of trans-$[Copn_2Cl_2]^+$ by $[Fe(CN)_6]^{4-}$ proceeds via associative mechanism in all the binary solvent mixtures studied. In all the solvent composition range investigated the mechanism closely resembles. An increase in rate of the reaction with decrease in dielectric constant of the medium is observed. The rate data depict substantial solvent effect on the reaction, showing the strong dependence of the amount of organic solvent added in the mixture.

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