KINETIC STUDIES OF SOLVENT SOLUTE INTERACTIONS IN THE SOLVOLYSIS IN ORGANIC-AQUEOUS MIXTURES

ASHUTOSH ABHAY

Research Scholar

Department of Chemistry

Veer Kunwar Singh University Ara, Bihar

ABSTRACT

The kinetics of solvolysis of trans-$[Co(L)_4Cl_2]ClO_4$ were followed spectro photo metrically in water – dioxane and water – dimethylsulf oxide media (0 – 60% v=v) over the temperature range (40-55°C). Non-linear plots were found for the logarithm of the rate constant of the first-order reaction versus the reciprocal of the relative permittivity, e_r, of the mixed solvent. This behaviour can be attributed to the differential solvation of the initial and transition states of the complex. The enthalpies and entropies of activation showed compensating extrema with the mole fraction of solvent, leading to a small variation in the free energy of activation. By applying a free-energy cycle, it was found that the difference between the values of the free energy of transfer of the cations in the transition and initial states were negative, indicating that the cation in the transition state is more solvated than that in the initial state.

KEYWORDS: Kinetics, solvolysis, cobalt(III) complex, pyridine derivatives, dioxane, dimethy lsulfoxide, thermodynamic parameters

INTRODUCTION

The interaction of cobalt pyridine complexes with DNA has received much attention over the past decade. These complexes can bind to DNA in noncovalent modes such as electrostatic, intercalative and groove binding. The interaction of these complexes with calf thymus DNA has been investigated.

These complexes have been found to promote the photocleavage of plasmid DNA under irradiation. Cytotoxicity results for the complexes also show anticancer activity [1-6]. Reactions in aqueous organic mixed solvents are more complicated than those in pure solvents because of

preferential solvation phenomenon and the extensive mutual interactions among the solvent molecules that complicate the solvation process [7]. Therefore, the rates of chemical reactions are affected both by the nature of the solvent used and by the nature and concentration of ionic species present in the reaction mixture. The operation of a limiting S1 N mechanism for ligand substitution has been suggested for a variety of transition metal complexes [8]. Following our earlier investigations of the solvolysis of trans-dichlorotetra(3-Rpyridine) cobalt(III) ions in binary organic aqueous mixtures [9-14], we have extended the work to cover cations which present a greater hydrocarbon surface presented by the complex. The choice of this complex allows the achieving of a relatively higher contact area, for 4-t-butyl pyridine between the bulk of the solvent and the hydrocarbon of the ligand due to the electrostatic effect. Consequently, the kinetics of solvolysis of trans-dichlorotetra(4-t-butylpyridine) cobalt (III) ion was studied in binary aqueous mixtures of dioxaneþwater and DMSO þwater. Furthermore, the aim of this study was to point out the kinetic and thermodynamic properties of the solvolysis of trans-$[Co(L)4Cl2]ClO4$ where over a wide range of solvent compositions (dioxane and DMSO) and temperatures, where their data can be linked firstly to obtain information about the effect of the solvent on the initial and the transition states, and secondly, to test any possible correlation of the rate constant with the relative permittivity of the medium.

EXPERIMENTAL

Chemicals and reagents Hydrochloric and perchloric acids were obtained from Merck, cobalt chloride was of BDH Analar grade, pure dioxane and dimethylsulfoxide (DMSO) were supplied from Fluka Chemika, pure 4-tert-butylpyridine (L) was of analytical grade quality and purchased from Aldrich. The studied complex was prepared as described before [15]. Kinetic runs were followed using a Jasco V-650 spectrophotometer controlled by a personal computer and equipped with a thermostated cell holder heated by water circulation from a Grant R1 thermostat.

Kinetic measurements

The rates of solvolysis of trans-$[Co(L)4Cl2]ClO4$ were measured over a wide range of temperature (40⎕55^{0}C) and composition (0-60% v=v) in dioxane-water and DMSO-water mixtures. Measurements were made in duplicate or triplicate for each set of conditions. The observed first-order rate constants for different temperatures and compositions were computed and are collected in Table 1. The least-squares procedure was applied to the linear plots obtained for log(rate constant) against the reciprocal of the absolute temperature. The thermodynamic parameters of the activated complex ⎕H, ⎕S and ⎕G with their standard errors at 25°C were calculated and are tabulated in Table 2.

Table 1 First-order constants for the solvolysis of trans in water and co solvent mixtures at various mole fractions and temperatures

x_2	v=v %			Temperature ($^\circ$C)			
		35	45	55	65	75	
			Dioxane –water mixtures				
0.000	0	0.11	2.94	5.50	11.700	30.20	
0.023	10	0.69	2.66	3.33	10.650	19.50	
0.050	20	0.16	2.31	5.44	9.663	17.90	
0.083	30	0.77	2.11	5.72	9.486	14.80	
0.125	40	0.27	2.63	2.61	6.152	8.797	
0.174	50	0.08	3.47	6.16	7.019	13.20	
0.241	60	0.25	2.00	3.22	7.305	15.00	
			DMSO – water mixtures				
0.027	10	0.13	1.77	2.80	4.36	5.688	
0.059	20	1.10	2.41	3.20	3.99	3.963	
0.098	30	0.16	1.75	3.00	4.50	5.678	
0.147	40	1.25	3.52	4.53	6.25	9.536	
0.202	50	0.16	1.91	3.98	7.79	15.90	
0.276	60	1.33	3.72	6.05	9.09	12.50	

Table 2 Thermodynamic parameters of activation for solvolysis of trans in water and co solvent mixtures at 25^0C

x_2	v=v %	ΔH^{++}	ΔS^{++}	ΔG^{++}
		(kJ mol^{-1})	(J mol^{-1}K^{-1})	(kJ mol^{-1})
		Dioxane – water mixtures		
0.000	0	$121+2$	$120+4$	$92+2$
0.023	10	$102+1$	$88+1$	$79+1$
0.050	20	$126+1$	$97+3$	$95+1$
0.083	30	$117+1$	$71+1$	$79+1$
0.125	40	$81+1$	$56+1$	$67+1$
0.174	50	$71+1$	$51+1$	$96+1$
0.241	60	$115+1$	$70+3$	$99+2$

RESULTS AND DISCUSSION

<u>Variation of rate constant with solvent composition and temperature</u>

The absorbance At, was monitored with time at 336 nm using dioxane and 346 nm using DMSO for the solvolysis of trans-$[Co(L)4Cl2]ClO_4$. Good linear plots were obtained for log(rate constant) against the reciprocal of the absolute temperatures for the same composition of the cosolvents. It was found that the rate constant in water – dioxane mixtures is higher than that in water –DMSO mixtures; this trend can be attributed to the properties of the medium, such as the structure of the solvent, ionizing power, basicity and dielectric constant which greatly influence the solvolysis rate of the complex [16,17].

Variation of rate constant with solvent parameters

It is known that the kinetics of solvolysis in a mixture of cosolvent with water for transition metal complexes involving the rate-determining loss of a halide ion does not generally follow a linear dependence of log(rate constant) with the reciprocal of the relative permittivity, er, of the mixed solvent. Moreover, the dependence of log(rate constant) versus of previously studied metal complexes in different media can be grouped into three classes: (a) co-linear plots irrespective of the cosolvent; (b) linear plots, but with different slopes depending on the type of cosolvent; (c) curved plots. Thus to take into account the structure of the solvent and the effect of changes in structure with solvent composition on the activation step based on the following reaction,

$$c_c^z \rightarrow M_M^Z ----X_M^Z \rightarrow M_M^Z + X_M^Z \qquad (1)$$

the equation of Laidler and Landskroener, based on the Born and Kirkwood
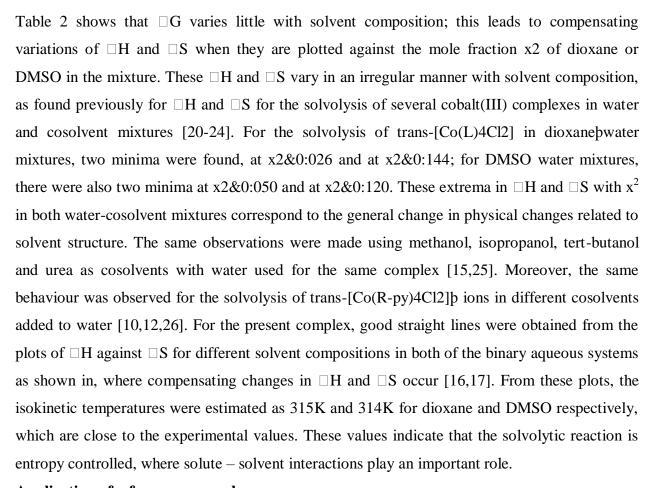
expressions [18], was modified by Wells [19] where the initial state is Czc and the transition state has the M"X bond sufficiently extended to correspond to separated ions; Z_C, Z_M and Z_X are the charges, N is Avogadro's number, ew is the relative permittivity of pure water, e is the electronic charge, G_M, G_X and G_C are related to the dipole moments, $\Box G_t^o$ is the free energy of transfer from water to the mixture and r is the appropriate molecular radius. $\Box G_t^o (i)_n$ here includes all the contributions from structural changes in the solvent resulting from the transfer of ion i.e So linear plots of log k against are obtained only if Equ (2) holds.

$$\Delta G_t^0(C)_n = \Delta G_t^0(C)_m + \Delta G_t^0(X)_n \qquad (2)$$

Thus deviations from the approximate equality of Eqn (2) will result first in noncoincidence of log k against plots with varying cosolvents, leading eventually to curved plots. For this reason and because of neglecting specific solute – solvent interactions, the electrostatic approach to

medium effects often failed in correlating observed solvent effects with physical solvent parameters [19]. For the solvolysis of the complex under investigation, it was found that the plots of log(rate constant) versus the reciprocal of the interpolated values of the relative permittivity of dioxane and DMSO at 25_C were non-linear .Thus the deviation from linearity in the form of curvature occurs from the differential effect of solvent structures between the initial and transition states [17].

Variation of activated state parameters with solvent composition

Table 2 shows that □G varies little with solvent composition; this leads to compensating variations of □H and □S when they are plotted against the mole fraction x2 of dioxane or DMSO in the mixture. These □H and □S vary in an irregular manner with solvent composition, as found previously for □H and □S for the solvolysis of several cobalt(III) complexes in water and cosolvent mixtures [20-24]. For the solvolysis of trans-[Co(L)4Cl2] in dioxaneþwater mixtures, two minima were found, at x2&0:026 and at x2&0:144; for DMSO water mixtures, there were also two minima at x2&0:050 and at x2&0:120. These extrema in □H and □S with x^2 in both water-cosolvent mixtures correspond to the general change in physical changes related to solvent structure. The same observations were made using methanol, isopropanol, tert-butanol and urea as cosolvents with water used for the same complex [15,25]. Moreover, the same behaviour was observed for the solvolysis of trans-[Co(R-py)4Cl2]þ ions in different cosolvents added to water [10,12,26]. For the present complex, good straight lines were obtained from the plots of □H against □S for different solvent compositions in both of the binary aqueous systems as shown in, where compensating changes in □H and □S occur [16,17]. From these plots, the isokinetic temperatures were estimated as 315K and 314K for dioxane and DMSO respectively, which are close to the experimental values. These values indicate that the solvolytic reaction is entropy controlled, where solute – solvent interactions play an important role.

Application of a free energy cycle

For an Id mechanism the Co3"Cl_ bond in the transition state is sufficiently extended to be a good approximation for complete separation. It is essential to apply Gibbs free energies of transfer of individual ions with the Gibbs energies of activation in water and in aqueous mixtures using the Gibbs free energy cycle [19] in order to cover all effects in the medium on the rate constant. In such a cycle, all effects on the rate constant resulting from the arrangement of solvent molecules around the ions are accounted for in the various □G^o_t in Eqn (1). Such total

Gibbs energies of transfer of individual ions involve all contributions, including $\square G^o_t$ from electrostatic influences and $\square G^o_t$ resulting from the transfer of the electrostatically neutral bulk of the ions [19], as indicated in Eqn (3).

$$\Delta G^O_t(i) = \Delta G^O_t(i)_e + \Delta G^O_t(i)_n \tag{3}$$

It has been shown that from the above cycle, Eqn (4) can be obtained:

$$\Delta G_S{}^{\#} = \Delta G^{\#}_W + \Delta G^O_t(Cl^-) + \Delta G^O_t[Co\,(L)_4Cl^{2+}] - \Delta G^O_t[Co\,(L)_4Cl^{2+}] \tag{4}$$

This equation can be converted into Eqn (5):

$$RT\ln(k_w/k_s) - \Delta G^O_t(Cl^-) = \Delta G^O_t(Cl^-) + \Delta G^O_t[Co\,(L)_4Cl^{2+}] - \Delta G^O_t[Co\,(L)_4Cl^{2+}] \tag{5}$$

Values for kw and ks have been calculated at 25_C and$\square$ $\square\square$Go are available by using the solvent sorting method [21]. The left-hand side of Eqn (3) plotted versus the mole fractions of dioxane and DMSO. The indicating negative values for all compositions investigated. These negative values can be compared with similar negative values obtained for the solvolyses of these complexes in mixtures of alcohols with water [16,17,24]. In all these cases, irrespective of whether the cosolvent, when added to water, increases or decreases the relative permittivity, or enhances or destroys structure in the solvent, it is found that the Co3þ cation in the transition state is more stable in the mixture than the Co3þ cation in the initial state. Moreover, these negative values indicate that trans-[Co(L)4Cl2]þ is more stable in dioxane and DMSO binary aqueous mixtures than trans-[Co(L)4Cl]2þ and this stability increases as the mole fraction, x^2, of the cosolvent increases.

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