Effect of solvent on reactions of coordination complexes: Part 11†—Kinetics of solvolysis of cis-(chloro) (cyclohexylamine) bis(ethylenediamine) cobalt (III) in acetone + water media

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The kinetics of solvolysis of cis-(chloro)(cyclohexyl-amine)bis(ethylenediamine) cobalt (III) ion have been investigated in acetone + water (0-50 wt% acetone) in the temperature range of 35-50°C. The plots of $\log k^s_{obs}$ versus the reciprocal of the bulk dielectric constant (D_s^{-1}) of the mixed solvent and $\log k^s_{obs}$ versus solvent 'Y$_{t-Bucl}$' parameter were nonlinear. The plots of $\log k^s_{obs}$ versus X_{org} (X_{org} = mol fraction of acetone) at $35 \leqslant t°$, $C \leqslant 50$ are strikingly linear with the common gradient = -3.14 ± 0.10. These facts are in keeping with the importance of the solvent structural effects and the lack of appreciable preferential solvation of the substrate under the conditions of rate measurements. It is striking to note that unlike for the alcohol-water solvent systems and a variety of cobalt (III) substrates, ΔH^* (and ΔS^*) solvent composition profile in the present case, displaying a weak maximum at $X_{Me_2CO} \simeq 0.01$ is little sensitive to the medium beyond $X_{Me_2CO} \simeq 0.05$.

In a preceding paper[2] the rate and activation parameters for the solvolysis of cis-[Co(en)$_2$(ChXNH$_2$)Cl]$^{2+}$ (ChXNH$_2$ = cyclohexylamine) in methanol + water, propan-2-ol + water, ethylene glycol + water (0-80 wt % of alcohols) and t-butanol + water (0-50 wt% of t-butanol) were reported. Title investigation is an extension of our earlier work[2].

Experimental

Cis-(chloro)(cyclohexylamine) bis(ethylenediamine) cobalt (III) diperchlorate was prepared and its purity checked as described earlier[2]. Acetone (AR, Glaxo, India, 99.5% pure) was dried over molecular sieve (4A), distilled and the middle fraction was collected. Solvent mixtures were prepared by wt% basis. Spectral measurements were made with a Hitachi model 200-20 UV-visible spectrophotometer.
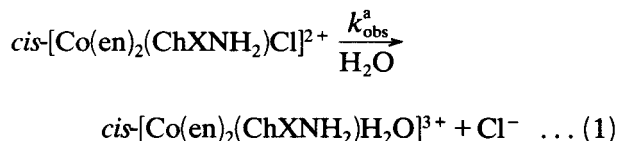
Kinetic measurements

The kinetics of solvolysis of the complex was followed by potentiometric titration of the liberated chloride. The experimental procedure for rate measurement and calculation of the pseudo-first order constants from replicate runs were the same as described earlier[3].

Results and discussion

Successive spectral scans for the reaction mixture at 45°C in 50 wt% of acetone + water medium exhibited isosbestic point at 396 nm, which remained unchanged even after a long time interval, ruling out · the possibility of any other secondary reaction. The primary solvolytic reaction may be represented by Eq. (1).

$$cis\text{-}[Co(en)_2(ChXNH_2)Cl]^{2+} \xrightarrow[H_2O]{k^a_{obs}}$$

$$cis\text{-}[Co(en)_2(ChXNH_2)H_2O]^{3+} + Cl^- \ \dots (1)$$

The rate of acid hydrolysis of the title complex is insensitive to changes in [H$^+$] in the range of 0.0010-0.050 mol dm^{-3}. Hence [HClO$_4$]$_T$ was fixed at 0.0010 mol dm^{-3} for all the runs. The rate data are presented in Table 1, while the activation parametrs, calculated by a weighted least squares procedure[3], are collected in Table 2.

Variation of rate constant (k^s_{obs}) with solvent composition

The k^s_{obs} decreased with increase in acetone content of the solvent mixture. The variation of $\log k^s_{obs}$ with D_s^{-1} where D_j^{-1} = reciprocal of the bulk dielectric constant[4]) is non-linear at all temperatures which may be attributed to (i) failure of both the point charge model of the complex ion and the dielectric continuum model of the reaction media, and (ii) non-linear variation of the non-electrostatic component of the relative transfer free energy term $[\Delta G_t(t.s.) - \Delta G_t(i.s.)]_{(s \leftarrow w)}$ with the solvent composition due to the solvent structural effects (see later).

The plot of $\log k^s_{obs}$ (25°C) versus Y_{t-BuCl}, the Grunwald Winstein solvent ionising parameter[5], is S-shaped) (see Fig. 1) indicating that the reference
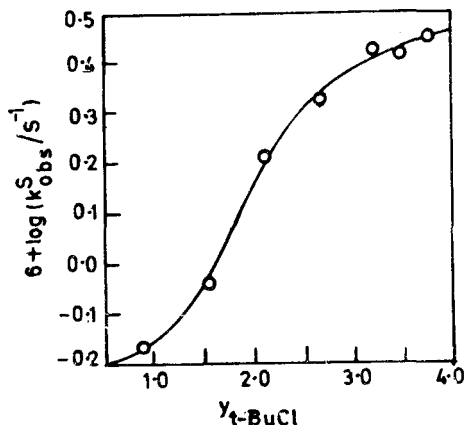
†For Part 10 see ref. 1

Table 1—Pseudo first order rate constants of solvolysis of $cis[Co(en)_2(cyclohexylamine)Cl]^{2+}$ in acetone + water media

$([Complex] = 2 \times 10^{-3}, [HClO_4]_T = 0.001 \text{ mol dm}^{-3})$

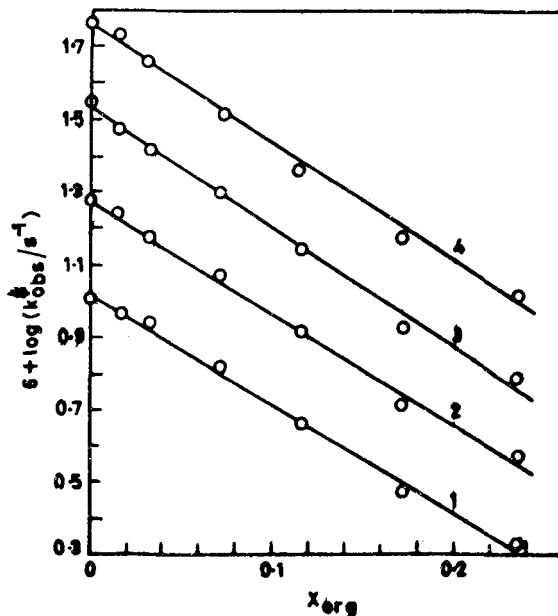| Acetone wt %	X_{Me_2CO}	$10^5 \, k_{obs}^s$ (s^{-1})			
		$35 \pm 0.1°$	$40.1 \pm 0.1°$	$45 \pm 0.1°$	$50 \pm 0.1°C$
0	0	0.98 ± 0.01	1.87 ± 0.06	3.54 ± 0.08	5.81 ± 0.18
5	0.0160	0.93 ± 0.01	1.71 ± 0.11	2.96 ± 0.12	5.46 ± 0.12
10	0.0330	0.86 ± 0.01	1.49 ± 0.08	2.57 ± 0.06	4.44 ± 0.17
20	0.0720	0.65 ± 0.02	1.16 ± 0.06	1.98 ± 0.12	3.21 ± 0.17
30	0.1170	0.45 ± 0.02	0.82 ± 0.03	1.38 ± 0.06	2.26 ± 0.16
40	0.1710	0.29 ± 0.02	0.51 ± 0.03	0.84 ± 0.05	1.47 ± 0.09
50	0.2360	0.21 ± 0.01	0.37 ± 0.01	0.61 ± 0.02	1.06 ± 0.07

Table 2—Activation enthalpy, entropy and free energy data at various acetone-water solvent compositions of acetone + water media

Wt % of acetone	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1}) (323.2K)
0	93.9 ± 2.6	− 36 ± 8	105.5 ± 0.08
5	94.7 ± 0.9	− 34 ± 3	105.8 ± 0.06
10	87.3 ± 0.7	− 59 ± 2	106.3 ± 0.1
20	86.1 ± 1.2	− 65 ± 4	107.2 ± 0.1
30	87.4 ± 1.9	− 64 ± 6	108.1 ± 0.2
40	86.6 ± 1.6	− 70 ± 5	109.3 ± 0.2
50	85.1 ± 1.6	− 78 ± 5	110.2 ± 0.2

Fig. 2—6 + $\log(k_{obs}^s/s^{-1})$ versus X_{org} plots at different temperatures (1) 35°C, (2) 40.1°, (3) 45° and (4) 50°C]

Fig. 1—6 + $\log(k_{obs}^s/s^{-1})$ versus Y_{t-BuCl} plot at 25°C

substrate (i.e. t-BuCl) and the title complex undergo solute-solvent interaction differently although from the mechanistic grounds the solvolytic process of both these substrates may be very much alike (i.e. dissociative interchange).

The familiar dissociative interchange mechanism, $(I_d)^6$, in which the Co-Cl bond is believed to be stretched to the maximum limit of cleavage in the transition state, may be depicted as in Scheme 1 of ref. 7 for which the rate constants are related

to the free energy of transfer of the transition state $[\Delta G_t(\text{t.s.})_{(s \leftarrow w)}$ and the initial state $[\Delta G_t(\text{i.s.})]_{(s \leftarrow w)}$ as given by Eq. (2)

$$\log k_{obs}^s = \log k_{obs}^w - \left(\frac{1}{2.303 \, RT}\right)[\Delta G_t(\text{t.s.})$$

$$- \Delta G_t(\text{i.s.})]_{(s \leftarrow w)} \qquad \ldots (2)$$

where

$k_{obs}^s = k_{obs}^w$ at $X_{Me_2CO} = 0$ and

$[\Delta G_t(\text{t.s.}) - \Delta G_t(\text{i.s.})]_{(s \leftarrow w)}$

denote the transfer free energy of the transition state (t.s.) relative to that of the initial state (i.s.) for the transfer of species from water (w) to the mixed solvent (s). A linear correlation between
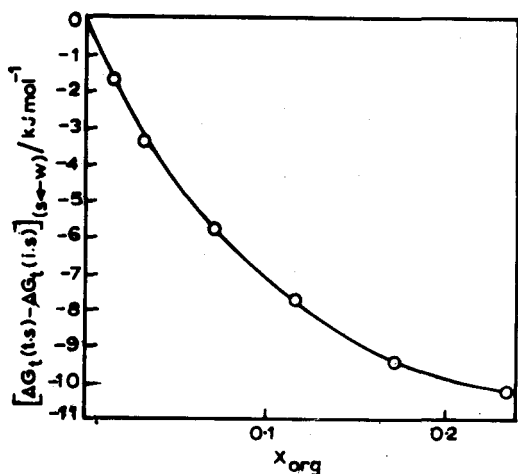
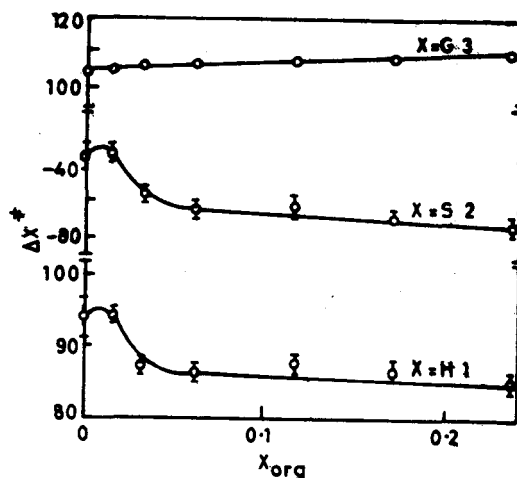Fig. 3—$[\Delta G_t(C^{3+}) - \Delta G_t(i.s.)]_{(s \leftarrow w)}/kJ\,mol^{-1}$ versus X_{org} plot at 25°C

Fig. 4—Dependence of activation parameters on X_{org}. [(1)$x\Delta H^{\neq}/kJ\,mol^{-1}$ versus X_{org}; (2) $\Delta S^{\neq}/JK^{-1}\,mol^{-1}$ versus X_{org}; and (3) $\Delta G^{\neq}_t/kJ\,mol^{-1}$ versus X_{org} at 323.2K]

$\log k^s_{obs}$ and X_{org} is expected if the relative transfer free energy function varies linearly with X_{org}. As per expectation the plots of $\log k^s_{obs}$ versus X_{Me2CO} (see Fig. 2) are linear with gradients = -3.14 ± 0.10 at 35° to 50°C. Hence the effect of preferential solvation seems to be insignificant[2]. Furthermore, such linear plots reflect that solvation of the initial state and transition state is grossly controlled· by the acidity and basicity of the mixed solvent which also vary linearly with the mol fraction of the cosolvent[3,8]. In the dissociative interchange transition state the leaving group is virtually dissociated from the cobalt (III) centre. Hence the additivity principle may be assumed to be valid for $\Delta G_t(t.s.)$ and in the t.s. the respective charges of the leaving groups are fully developed. We can then write

$$[\Delta G_t(t.s.)]_{(s \leftarrow w)} = [\Delta G_t(C^{3+})]_{(s \leftarrow w)} + [\Delta G_t(Cl^-)]_{(s \leftarrow w)} \quad \ldots (3)$$

where $[\Delta G_t(C^{3+})]_{(s \leftarrow w)}$ denotes the transfer free energy of the dissociative transition state. $\{C^{3+} = (cis\text{-}[Co(en)_2(ChXNH_2)]^{3+})^*\}$. The values of the relative transfer free energy term $[\Delta G_t(C^{3+}) - \Delta G_t(i.s.)]_{(s \leftarrow w)}$ at various X_{Me2CO} at 25°C were calculated using Eq. (4) obtained by combining Eqs (2) and (3) and the calculated values of

$$[\Delta G_t(C^{3+}) - \Delta G_t(i.s.)]_{(s \leftarrow w)} = 2.303RT \log(k^w_{obs}/k^s_{obs})$$
$$- [\Delta G_t(Cl)]_{(s \leftarrow w)} \quad \ldots (4)$$

$[\Delta G_t(Cl^-)]_{(s \leftarrow w)}$ reported by Wells[9]. The values of $[\Delta G_t(C^{3+}) - \Delta G_t(i.s.)]_{(s \leftarrow w)}$ were negative at all compositions and decreased non-linearly with increase in X_{Me2CO} tending to reach asymptotic limit (Fig. 3). This reflects a strong propensity of the

tripositive cobalt (III) species (C^{3+}) to solvation, and relative to fully aqueous medium such a species is stabilized in the mixed solvent to a greater extent than the corresponding dipositive initial state. However, the negative values of $[\Delta G_t(C^{3+}) - \Delta G_t(i.s.)]_{(s \leftarrow w)}$ do not lead to the rate enhancement since the positive values of $[\Delta G_t(Cl^-)]_{(s \leftarrow w)}$ (= 1.92 to 13.8 kJ mol^{-1} for 0.016 $\leqslant X_{Me2CO} \leqslant$ 0.236 at 25°C) tip the balance in favour of rate retardation with increase in X_{Me2CO}.

Variation of activation parameters with solvent compositions

Plots of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ versus X_{Me2CO} displayed a weak maximum around $X_{Me2CO} \simeq 0.01$ (Fig. 4), in contrast to the well-defined extrema observed for this substrate in methanol + water, propan-2-ol + water, ethyleneglycol + water, t-butanol + water media[2]. Also it is worth noting that $\Delta H^{\neq}$ (or $\Delta S^{\neq}$) versus X_{Me2CO} plot for acetone + water medium for the cyclohexylamine bis(ethylenediamine) complex is very much different from that of the cis-$[(en)_2Co(2\text{-aminothiazole})Br]^{2+}$ in acetone + water media for which multiple maxima and minima are observed[7]. This is suggestive of the fact that the non-labile ligand envelope of the substrate has a significant role in modulating at least the solvational components of these activation parameters $(\Delta X^{\neq}_{overall} = \Delta X^{\neq}_R + \Delta X^{\neq}_S$ where X=H, S and the subscripts R and S denote the reaction and solvational components[10] respectively). The observed variation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with X_{Me2CO} may be compared with that of $trans$-$[Co(en)_2Cl_2]^+$ in ethanonitrile + water media reported by Wells $et\,al.$[11]. The $\Delta H^{\neq}$ (and $\Delta S^{\neq}$)-composition profile indicat-

ed that the solvent structural promotion is significant around $X_{Me_2CO} \approx 0.01$. However, $\Delta G^{\neq}$ increased linearly with X_{org} over the entire composition range. Evidently the rate enhancing effect due decrease in $\Delta H^{\neq}$ is compensated by large negative values of $\Delta S^{\neq}$. To a large extent the effects of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ on the rate are mutually compensatory (see Fig. 4). The large negative values of $\Delta S^{\neq}$, being consistent with the stereoretentive solvolysis, corroborate the fact that the transition state is much more solvated than the initial state. This might be a consequence of the hydrophobic association between the molecules of the organic cosolvent and the hydrophobic ligand moiety of the cobalt (III) substrate. The validity of the compensation law ($\Delta H^{\neq} = \alpha + \beta \Delta S^{\neq}$; $\alpha = 105.5 \text{ kJ mol}^{-1}$, $\beta = 288.5 \text{ K}$) irrespective of the nature of the organic solvent and the solvent composition is in keeping with the fact that perturbations in the reaction zone and the solvent network remain proportional to each other with increase in X_{org}.

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