

## Medium effect on the reactions of coordination complexes : Base hydrolysis of $(\alpha\beta S)(p\text{-hydroxybenzoato})(\text{tetraethylenepentamine})$ - cobalt(III) in methanol-water, acetone-water and acetonitrile-water media

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The kinetics of base hydrolysis of  $(\alpha\beta S)(p\text{-hydroxybenzoato})(\text{tetraethylenepentamine})\text{cobalt(III)}$  has been studied in aqua-organic solvent media using MeOH, Me<sub>2</sub>CO and MeCN as cosolvents at  $20.0 \leq t^{\circ}C \leq 40.0$  ( $I = 0.02 \text{ mol dm}^{-3}$ ) with 80% (v/v) of cosolvents. Only the base catalyzed path ( $k_{\text{obs}} = k_{\text{OH}}[\text{OH}^-]$ ) has been observed. The relative second order rate constant,  $k_{\text{OH}}^{\text{os}}/k_{\text{OH}}^{\text{ow}}$  at  $I = 0$ , increases nonlinearly with increase in mole fraction ( $x_{\text{os}}$ ) of the cosolvents. MeCN and Me<sub>2</sub>CO exert much stronger rate acceleration than MeOH. The relative transfer free energy  $[\Delta_{\text{t}}G(\text{t.s.}) - \Delta_{\text{t}}G(\text{t.s.})]_{(\text{s} \leftarrow \text{w})}^{298 \text{ K}}$  is positive for MeCN and negative for both Me<sub>2</sub>CO and MeCN indicating greater destabilising effect of the solvent on the transition state (t.s.) relative to the initial state (i.s.) for MeCN-H<sub>2</sub>O while the effect is reversed for MeOH-H<sub>2</sub>O and Me<sub>2</sub>CO-H<sub>2</sub>O media. The variation of activation parameters ( $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$ ) with  $x_{\text{os}}$  is non-linear exhibiting extrema supporting the fact that solvent structural effects are important in controlling the energetics of the process through solvation of the initial and transition states.

Of late kinetic studies have been devoted to understand the role of hydrophobic effects, preferential solvation and solvent structural perturbations on chemical reactivity<sup>1-10</sup>. This is primarily linked with the solvent induced changes on chemical potentials of initial and transition states. In an earlier paper we reported the base hydrolysis of  $(\alpha\beta S)$  (salicylato) (tetraethylenepentamine)cobalt(III)<sup>11</sup> in several aqua-organic binary solvent media. The protic cosolvents like MeOH, Pr<sup>i</sup>OH and Bu<sup>t</sup>OH exerted lesser accelerating effect on rate than those of the dipolar aprotic cosolvents like Me<sub>2</sub>CO, MeCN and DMSO. The cosolvent ethylene glycol, however, produced rate retardation. In this case the phenoxide group of the product was involved in the intramolecular acid-base equilibrium  $-\text{O}^- \dots \text{NH}^- = \text{HO} \dots \text{N}^-$  which was responsible to generate the reactive amido conjugate base<sup>12</sup>. As such the phenoxide form of the complex (tetren)CoO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(*o*)O<sup>-</sup> displayed intramolecular phenoxide assisted aquation as well as OH-dependent base hydrolysis. This equilibrium is likely to be absent in the corresponding (*p*-hydroxybenzoato)(tetren) cobalt(III) complex. Consequently it is expected that the overall

solvent perturbation effect of the hydrophobic tetren ligand and the aromatic moiety on the base hydrolysis of the title complex can be interpreted much more coherently. With a view to examining this aspect we made a detailed study of the base hydrolysis of the title complex in aqua-organic binary solvent media which differ in their structural, electrostatic and hydrophobic interaction properties.

### Materials and Methods

The complex  $(\alpha\beta S)$  (*p*-hydroxybenzoato) (tetraethylenepentamine)cobalt(III) diperchlorate [(tetren)CoO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(*p*)OH](ClO<sub>4</sub>)<sub>2</sub> was prepared and characterised as described earlier<sup>14</sup>. AnalaR grade reagents were used in all preparations. The solvents MeOH, Me<sub>2</sub>CO and MeCN were distilled after drying over 4A<sup>o</sup> molecular sieve, the middle cut being used for preparation of solvent mixture. Doubly distilled water was used in all preparations. Solvent mixtures were prepared in volume percentage (v/v); mole fractions,  $x_{\text{os}}$ , were calculated using density data. Spectral measurements were made using a JASCO -7800 U.V.-visible spectrophotometer.

Table 1—Rate data for base hydrolysis of  $(\alpha\beta S)[(\text{tetren})(\text{CoO}_2\text{CC}_6\text{H}_4(p\text{-OH}))]^{2+}$  in aqueous mediumComplex] $_{\text{T}} = (1.2) \times 10^{-4}$  mol dm $^{-3}$ ,  $I = 0.10$  mol dm $^{-3}$  and  $\lambda = 300$  nm.

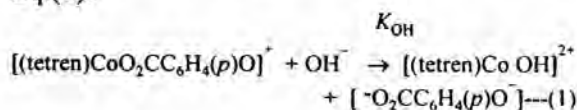
[OH $^{-}$ ]	20.0 $\pm$ 0.01 $^{\circ}$	25.0 $\pm$ 0.01 $^{\circ}$	30.0 $\pm$ 0.01 $^{\circ}$	40.0 $\pm$ 0.01 $^{\circ}$ C
	$k_{\text{obs}}$ (s $^{-1}$ )			
0.01	0.035 $\pm$ 0.001	0.074 $\pm$ 0.002	0.134 $\pm$ 0.004	0.492 $\pm$ 0.022
0.02	0.065 $\pm$ 0.003	0.128 $\pm$ 0.005	0.248 $\pm$ 0.006	1.03 $\pm$ 0.05
0.05	0.163 $\pm$ 0.006	0.318 $\pm$ 0.010	0.645 $\pm$ 0.021	2.62 $\pm$ 0.11
0.10	0.336 $\pm$ 0.015	0.651 $\pm$ 0.022	1.20 $\pm$ 0.05	5.01 $\pm$ 0.26
$k$ (mol $^{-1}$ dm $^3$ s $^{-1}$ )	3.24 $\pm$ 0.08	6.19 $\pm$ 0.22	12.1 $\pm$ 0.4	51.9 $\pm$ 1.1
$\Delta H^{\ddagger}$ (kJ mol $^{-1}$ ) = 104 $\pm$ 3 and $\Delta S^{\ddagger}$ (kJ mol $^{-1}$ ) = 119 $\pm$ 10				

### Kinetics

The kinetics of base hydrolysis in mixed solvents was studied at  $20.0 \leq t^{\circ}\text{C} \leq 40.0$  under pseudo-first order conditions with  $[\text{NaOH}]_{\text{T}} = 0.02$  and  $[\text{complex}]_{\text{T}} = (1.0 - 1.5)10^{-4}$ ,  $I = 0.02$  mol dm $^{-3}$ . Adjustment of ionic strength using electrolyte was avoided to minimise the solute induced solvent structural changes. However, rate measurements in aqueous medium was made at  $0.01 \leq [\text{NaOH}]_{\text{T}} \leq 0.10$ ,  $I = 0.10$  mol dm $^{-3}$  to establish the rate law. The reaction was monitored at  $\lambda = 300$  nm on a HITECH (U.K..) S F 51 stopped flow spectrophotometer interfaced with an APPLE II GS PC as described earlier<sup>11</sup>. The absorbance-time curve for any run was strictly single exponential characteristic of first order kinetics. At least five replicate measurements were made to ascertain  $k_{\text{OBS}}$  and its standard deviation ( $\sigma(k_{\text{obs}}) / k_{\text{obs}} \leq 0.05$ ). All other calculations were made on an IBM PC (486).

### Results and Discussion

The  $pK_{\text{OH}}$  of unbound phenol of  $[(\text{tetren})\text{CoO}_2\text{CC}_6\text{H}_4(p\text{-OH})]^{2+}$  is found to be 10.2 at 25.0 $^{\circ}$ C in 50% (v/v) Bu $^t$ OH -H $_2$ O mixture. Hence the complex will exist in the phenoxide form at  $[\text{OH}^{-}] \geq 0.01$  mol dm $^{-3}$ . The rate constants in fully aqueous medium obeyed the second order relationship,  $k_{\text{OBS}} = k_{\text{OH}}[\text{OH}^{-}]_{\text{T}}$  in the range  $0.01 \leq [\text{OH}^{-}]_{\text{T}}, \text{mol dm}^{-3} \leq 0.10$  at  $20.0 \leq t^{\circ}\text{C} \leq 40.0$  ( $I = 0.10$  mol dm $^{-3}$ ) (see Table 1) in conformity with Eq.(1).

Table 2—Effect of Ionic strength on the rate of base hydrolysis of  $(\alpha\beta S)[(\text{tetren})(\text{CoO}_2\text{CC}_6\text{H}_4(p\text{-OH}))]^{2+}$ T = 25.0 $^{\circ}$ C,  $[\text{Complex}]_{\text{T}} = (1.2) \times 10^{-4}$  mol dm $^{-3}$  and  $\lambda = 300$ 

[OH $^{-}$ ] $_{\text{T}}$ (mol dm $^{-3}$ )	$I$ (mol dm $^{-3}$ )	$k_{\text{obs}}$ (s $^{-1}$ )
0.01	0.01	0.095 $\pm$ 0.004
0.02	0.02	0.169 $\pm$ 0.005
0.05	0.05	0.352 $\pm$ 0.004
0.08	0.08	0.503 $\pm$ 0.006
0.10	0.10	0.594 $\pm$ 0.007
0.10	0.15	0.532 $\pm$ 0.010
0.10	0.20	0.492 $\pm$ 0.006
0.10	0.30	0.438 $\pm$ 0.010
0.10	0.40	0.404 $\pm$ 0.015
0.10	0.50	0.378 $\pm$ 0.018
0.10	0.70	0.344 $\pm$ 0.025

The values of activation enthalpy and entropy [ $\Delta H^{\ddagger} = 104 \pm 3$  kJ mol $^{-1}$  and  $\Delta S^{\ddagger} = 119 \pm 10$  JK $^{-1}$  mol $^{-1}$ ] may be compared to those for the corresponding salicylato complex [ $\Delta H^{\ddagger} = 96 \pm 4$  kJ mol $^{-1}$  and  $\Delta S^{\ddagger} = 92 \pm 15$  JK $^{-1}$  mol $^{-1}$ ]<sup>11</sup>. The large positive values of  $\Delta S^{\ddagger}$  is in keeping with S $_N$ CB mechanism<sup>9,12,13</sup>.

The effect of the ionic strength on  $k_{\text{OBS}}$  (and hence on  $k_{\text{OH}}$ ) was studied in aqueous medium and the relevant data are collected in Table 2. The second order rate constant  $k_{\text{OH}}$  ( $= k_{\text{OH}} \gamma_{\text{C}} + \gamma_{\text{OH}^{-}} / \gamma$ ) is subject to ionic strength variation which on the basis of Debye-Huckel theory is expressed by Eq.(2)

$$\log k_{\text{OH}} = \log k_{\text{OH}}^0 + 2Z_{\text{C}} Z_{\text{OH}} A I^{1/2} / (1 + B a I^{1/2}) \dots (2)$$

where  $k_{\text{OH}}^0 = k_{\text{OH}}$  at  $I = 0$ ,  $Z_{\text{C}}$  and  $Z_{\text{OH}}$  are the

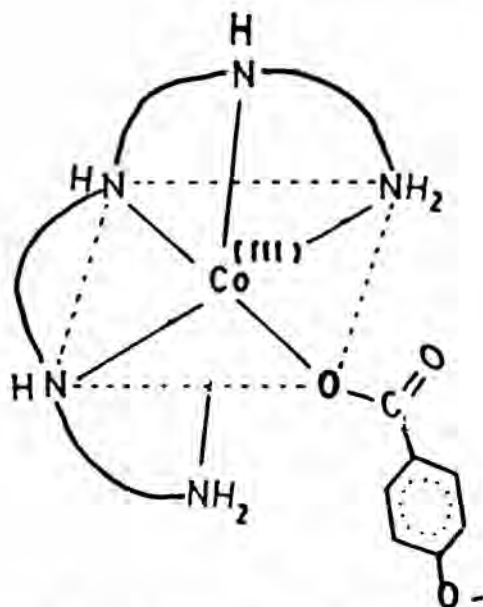
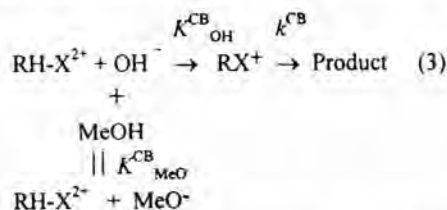


Fig.1 - ( $\alpha$ BS) (*p*-hydroxybenzoato) (tetraethylenepentamine) cobalt(III) ion

charges on the complex and  $\text{OH}^-$  respectively,  $A = 1.824 \times 10^6 / (D_S T)^{3/2}$ ,  $B = 50.29 \times 10^8 / (D_S T)^{1/2}$ ,  $D_S$  = bulk permittivity of the medium. The ionic size parameter 'a' was taken to be independent of the nature of the ion. The least squares best linear plot of  $\log k_{\text{OH}}$  versus  $I^{1/2} / (1 + B a I^{1/2})$  corresponded to  $a = 5A^0$  and yielded  $Z_C = +1.62$ . This value of  $Z_C$  (rather than +1) is not surprising as the +2 and -1 charge centers in the complex (I) are far apart (see Fig. 1).

It may be noted that only for MeOH- $\text{H}_2\text{O}$  medium both  $\text{OH}^-$  and  $\text{MeO}^-$  are expected to generate the reactive conjugate base. The overall reaction for MeOH- $\text{H}_2\text{O}$  medium may be depicted as in Eq.(3).



where  $\text{RH} = \text{Co(III)}(\text{tetren})$ ;  $\text{R} = \text{Co(III)}\{(\text{tetren} - \text{H})\}$  and  $\text{X} = -\text{O}_2\text{CC}_6\text{H}_4(p)\text{OH}$ .

Accordingly  $k_{\text{SH}} = k_{\text{Obs}} / [\text{S}^-]_{\text{T}}$ , ( $\text{S}^-$  denotes the lyate ion) and  $[\text{S}^-]_{\text{T}} = [\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{free}} + [\text{MeO}^-]_{\text{free}}$  and  $k_{\text{SH}}$  takes the form

$$k_{\text{SH}} = k^{\text{CB}} K_{\text{APP}}^{\text{CB}} \dots (4)$$

and

$$K_{\text{APP}}^{\text{CB}} = K_{\text{OH}}^{\text{CB}} \cdot K_{\text{MeO}}^{\text{CB}} / (K_{\text{OH}}^{\text{CB}} + K_{\text{MeO}}^{\text{CB}}) \dots (5)$$

where  $K_{\text{OH}}^{\text{CB}}$  and  $K_{\text{MeO}}^{\text{CB}}$  are the equilibrium constants for the formation of the conjugate base by  $\text{OH}^-$  and  $\text{MeO}^-$  respectively and  $k^{\text{CB}}$  is the first order dissociation rate constant of the conjugate base. The equilibrium constants  $K_{\text{OH}}^{\text{CB}}$  and  $K_{\text{MeO}}^{\text{CB}}$  are ionic strength dependents. The zero ionic strength corrected  $k_{\text{SH}} (= k_{\text{SH}}^0)$  is given by combining Eqs (2),(4) and (5) from which the second order rate constant for  $\text{OH}^-$  alone ( $k_{\text{OH}}^0$ ) could be calculated using activities of  $\text{OH}^-$  and  $\text{MeO}^-$  ions.

$$\begin{aligned} k_{\text{SH}}^0 &= k^{\text{CB}} (K_{\text{APP}}^{\text{CB}})^0 \\ &= k^{\text{CB}} (K_{\text{OH}}^{\text{CB}})^0 / \{1 + (K_{\text{OH}}^{\text{CB}})^0 / (K_{\text{MeO}}^{\text{CB}})^0\} \\ &= k_{\text{OH}}^0 / (1 + a_{\text{MeO}^-} / a_{\text{OH}^-}) \dots (6) \end{aligned}$$

The values of  $k_{\text{SH}}$  for MeOH- $\text{H}_2\text{O}$  and  $k_{\text{OH}}$  for  $\text{Me}_2\text{CO-H}_2\text{O}$  and  $\text{MeCN-H}_2\text{O}$  media ( $I = 0.02 \text{ mol dm}^{-3}$ ) collected in Table 3 were corrected to  $I = 0$  using Eq. (2) where  $Z_C = 1.62$ ,  $a = 5A^0$ , the values of A and B were calculated using dielectric constant data available in literature<sup>15,16</sup>. For MeOH- $\text{H}_2\text{O}$  values of  $k_{\text{OH}}^0$  ( $\text{s}^{-1}$ ) could be calculated from  $k_{\text{SH}}^0$  ( $\text{s}^{-1}$ ) (see Eq..6) by interpolating activity ratio  $a_{\text{MeO}^-} / a_{\text{OH}^-}$  in the solvent composition range available in literature<sup>17</sup> only for 25.0°C.

Marked solvent acceleration, particularly for the dipolar aprotic cosolvents  $\text{Me}_2\text{CO}$  and  $\text{MeCN}$ , was observed from the plot of the ratio of  $k_{\text{OH}}^{\text{os}} / k_{\text{OH}}^{\text{ow}}$  ( $k_{\text{OH}}^0$  at  $I = 0$ ,  $s =$  mixed solvent and  $w =$  water) versus cosolvent mole fraction ( $x_{\text{O.S.}}$ ) at 25.0°C (Fig. 2). The solvent acceleration varies in the order  $\text{MeOH-H}_2\text{O} < \text{MeCN-H}_2\text{O} < \text{Me}_2\text{CO-H}_2\text{O}$  and increased with increase in  $x_{\text{O.S.}}$ . At a fixed dielectric constant ( $D_S = 50$ ) the solvent effect (i.e.  $k_{\text{OH}}^{\text{os}} / k_{\text{OH}}^{\text{ow}}$ ) shows similar trend. Thus the variation is solvent specific. This is evidently due to the electrostatic and non-electrostatic contribution of the media to the solvation of the initial and transition states. Also the nonlinear variation of  $\log k_{\text{OH}}^0$  versus  $D_S$  shows that the simple electrostatic model<sup>18</sup> is inadequate to explain the observed reaction trend.

Table 3—Rate data for base hydrolysis of  $(\alpha\beta S)[(\text{tetren})(\text{CoO}_2\text{CC}_6\text{H}_4(p)\text{OH})]^{2+}$  in mixed media of varying cosolvent content (in vol.%) at different temperature

$I = 0.02 \text{ mol dm}^{-3}$ ,  $[\text{OH}]_T = 0.02 \text{ mol dm}^{-3}$ ,  $[\text{Complex}] = (1.0 - 1.2) \times 10^{-4} \text{ mol dm}^{-3}$ ,  $\lambda = 300 \text{ nm}$ . Values in parentheses denote molefraction of the organic cosolvents ( $x_{\text{O.S.}}$ )

$t^\circ\text{C}$	$a_k (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$									
	5	10	20	30	40	50	60	70	80%(v/v)	
	MeOH									
20.0	3.65±0.40	3.95±0.90	4.10±0.10	4.60±0.10	5.60±0.20	6.60±0.40	8.90±0.35	11.3±0.2	15.9±0.4	
25.0	6.80±0.10	7.40±0.40	9.25±0.10	9.50±0.20	11.3±0.5	14.2±0.60	19.2±0.6	26.2±1.3	33.3±0.9	
30.0	13.9±0.1	15.9±0.3	17.9±0.2	21.6±0.5	22.5±0.6	30.0±0.8	38.9±0.9	51.0±2.0	67.2±2.5	
35.0	27.8±0.2	30.7±0.2	35.2±1.1	39.2±1.1	48.0±0.8	66.0±2.5	79.0±1.0	103±2	137±4	
40.0	65.5±3.5	74.5±1.0	93.0±4.5	101±4	111±5	148±6	193±8	251±10	355±16	
	(0.023)	(0.047)	(0.100)	(0.160)	(0.228)	(0.307)	(0.400)	(0.509)	(0.639)	
	MeCN									
20.0	4.80±0.10	5.55±0.10	8.25±0.15	13.1±0.6	20.5±0.5	32.0±0.9	59.5±1.4	101±2	221±6	
25.0	9.60±0.20	11.9±0.3	17.4±0.4	24.9±3.0	38.5±3.0	68.4±4.1	127±3	220±4	546±19	
30.0	18.0±0.5	20.7±0.3	29.8±1.0	47.8±2.5	83.4±1.9	125±6	228±12	436±7	1000±16	
35.0	36.3±0.6	42.9±0.3	64.4±0.7	89.2±1.0	168±2	272±10	553±20	951±32	1791±18	
40.0	77.0±1.5	92.5±0.5	136±2	203±6	326±16	550±20	1030±40	2060±40	3740±45	
	(0.018)	(0.037)	(0.079)	(0.128)	(0.186)	(0.255)	(0.339)	(0.444)	(0.578)	
	Me <sub>2</sub> CO									
20.0	5.20±0.05	6.40±0.10	10.3±0.2	19.0±0.2	35.4±0.2	66.8±1.4	113±2	176±7	300±5	
25.0	10.8±0.2	14.5±0.5	20.7±0.4	35.4±0.5	64.5±1.0	141±2	218±4	350±15	585±20	
30.0	18.7±0.3	23.6±0.1	38.6±0.3	64.6±1.5	124±4	240±3	428±5	764±10	1185±20	
35.0	42.0±0.8	52.2±1.0	83.0±1.7	125±4	256±11	499±26	940±32	1445±41	2110±30	
40.0	82.8±1.0	104±3	152±3	236±4	520±10	975±15	1780±20	2920±30	3930±75	
	(0.013)	(0.026)	(0.057)	(0.094)	(0.130)	(0.195)	(0.267)	(0.362)	(0.493)	

$a_k/k_{\text{OH}} (\text{dm}^3 \text{ mol}^{-1}) = 0.065 \pm 0.004, 0.128 \pm 0.005, 0.248 \pm 0.006$  and  $0.484 \pm 0.012$  and  $1.03 \pm 0.05$  for aqueous medium at 20.0, 25.0, 30.0, 35.0 and 40.0°C respectively.

Table 4—Calculated values of  $a_1, a_2$  and  $a_3$  (see Eq.8) for base hydrolysis of  $(\alpha\beta S)[(\text{tetren})(\text{CoO}_2\text{CC}_6\text{H}_4(p)\text{OH})]^{2+}$  complex at 25°C

Cosolvent	$a_1$	$a_2$	$a_3$
MeOH	$2.50 \pm 0.17$	$-0.66 \pm 0.85$	$-1.22 \pm 0.96$
MeCN	$6.72 \pm 0.44$	$-10.8 \pm 0.20$	$9.73 \pm 2.41$
Me <sub>2</sub> CO	$10.61 \pm 0.55$	$-19.2 \pm 0.39$	$15.4 \pm 6.0$

A non-linear correlation of  $\log k_{\text{OH}}^0$  with  $x_{\text{O.S.}}$  given by Eq. (7)

$$\log k_{\text{OH}}^{\text{O.S.}} = \log k_{\text{OH}}^{\text{Ow}} + a_1 x_{\text{O.S.}} + a_2 x_{\text{O.S.}}^2 + a_3 x_{\text{O.S.}}^3 \dots (7)$$

was satisfactory for MeCN and Me<sub>2</sub>CO cosolvents (see Table 4 for the values of  $a_1, a_2$  and  $a_3$ ) but not so good for MeOH. But the data for MeOH fitted well for a two parameter Eq.8.

$$\log k_{\text{OH}}^{\text{O.S.}} = \log k_{\text{OH}}^{\text{Ow}} + a_1 x_{\text{O.S.}} + a_2 x_{\text{O.S.}}^2 \dots (8)$$

with values of  $a_1$  and  $a_2$  being  $(2.30 \pm 0.06)$  and  $(0.40 \pm 0.15)$  respectively. The polynomial

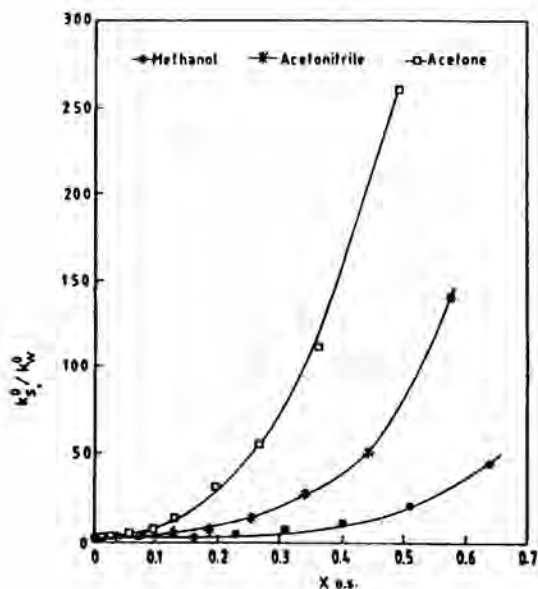


Fig.2 – Plot of  $k_{\text{OH}}^0 / k_{\text{OH}}^{\text{Ow}}$  versus  $x_{\text{O.S.}}$



expansion of this type is an indication of the preferential solvation and solvent structural perturbation effect on the rate<sup>10(a),19,20</sup>. In this context the protic cosolvent MeOH behaves differently from those of the dipolar aprotic cosolvents (MeCN and Me<sub>2</sub>CO).

The plot of  $\log_{21-23} (k_{OH}^0)_{BuCl}^{25}$  and the Grunwald-Winsten parameter  $Y_{25}^{BuCl}$  for all the three cosolvents were linear with slopes -2.07, -1.83 and -1.76 for MeOH, Me<sub>2</sub>CO and MeCN respectively [correlation coefficients  $\geq 0.996$ ]. Thus the rate depends upon the ionising power of the solvent media. However, the dependence of such plots with the nature of the cosolvents indicates specific solvent effect.

The Gibb's excess free energy function<sup>24</sup>  $G^{(E)}$ , often taken as an indicative of the solvent structure<sup>25</sup>, exhibits a less satisfactory linear plot with  $\log k_{OH}^0$  (corr. coeff. 0.891, 0.989 and 0.928 for MeOH, Me<sub>2</sub>CO and MeCN respectively). Despite the fact that the values of  $G^{(E)}$  are rather small as compared to the overall free energy change, the correlation points to the role of solvent structure, however less significant. Our attempt to correlate both  $Y_{25}^{BuCl}$  and  $G^{(E)}$  simultaneously in terms of Eq.(9).

$$\log k_{OH}^0 = \log k_{OH}^{ow} + a_1 x_{O.S.} + a_2 G^{(E)} + a_3 Y_{25}^{BuCl} \dots (9)$$

did not yield satisfactory results. Attempts were also made to correlate  $\log k_{OH}^0$  with the Kamlet Taft's solvatochromic parameters  $\alpha$ ,  $\beta$ ,  $\pi^*$  as given in Eq.(10).

$$\log k_{OH}^0 = C + A_1 \alpha^s + A_2 \beta^s + A_3 \pi^{*s} \dots (10)$$

where  $C = \log k_{OH}^0$  at  $\alpha^s = \beta^s = \pi^{*s} = 0.0$ . The values of these microscopic solvent parameters for the complete mole fraction range of MeCN - H<sub>2</sub>O medium are available. The interpolated values of  $\alpha$ ,  $\beta$ ,  $\pi$  were used to fit the data to Eq.(10) which yielded  $A_1 = -1.87 \pm 0.92$ ,  $A_2 = -2.98 \pm 0.40$  and  $A_3 = -4.99 \pm 0.77$  and  $C = 10.4$ . The solvatochromic parameter  $\pi^*$  representing local polarizability of the solution decreases with increase in  $x_{MeCN}$ . The dissociative transition state of the amido conjugate base  $\{Co(tetren-H)^{2+} \dots O_2CC_6H_4(p)OH\}$  is relatively more polar than the corresponding initial state  $[Co(tetren-H)O_2(C_6H_4(p)OH)]^{2+}$ . Thus the transition state would be destabilised at high MeCN content relative to the initial state, as a

result of which the reaction rate is expected to diminish with increase in  $x_{MeCN}$ . But the observed rate acceleration with increasing MeCN content must be due to the destabilisation of OH<sup>-</sup> in the decreasing polarity of the solvent mixture. The aqueous MeCN mixture is generally believed to be broadly divided into three MeCN mole fraction region<sup>19,27-30</sup>; i) water rich region, ( $0 < x_{MeCN} < 0.15$ ); ii) region exhibiting microheterogeneity ( $0.15 < x_{MeCN} < 0.75$ ) and iii) MeCN rich region ( $0.75 < x_{MeCN} < 1.0$ ). In water rich region the gross structure of H<sub>2</sub>O is believed to remain almost intact (hydrogen bonded)<sup>31</sup> with MeCN molecules occupying the free space<sup>31</sup>. Further addition of MeCN breaks the gross H-bonded structure of H<sub>2</sub>O with molecules of same kind forming hydrogen bonded clusters and are surrounded by the region where molecules of two kinds are near neighbours. This clustering conditions arise due to the difference in interaction energies of the pair H<sub>2</sub>O - H<sub>2</sub>O, H<sub>2</sub>O - MeCN and MeCN - MeCN<sup>32-34</sup> and the preference of a H<sub>2</sub>O molecule for H<sub>2</sub>O rather than a MeCN molecule. The above classification of different ranges of MeCN- H<sub>2</sub>O solution is also corroborated by the fact that vapour pressure of the MeCN-H<sub>2</sub>O solution<sup>35</sup> and the normalised  $E_T^N$  values of MeCN- H<sub>2</sub>O mixture<sup>36,37</sup> vary non-linearly with  $x_{MeCN}$  displaying inflection points at these limiting mole fractions (i.e.  $x_{MeCN} \sim 0.15$  and 0.5). It is reported that the ions I<sup>-</sup> and Cl<sup>-</sup> are preferentially solvated by H<sub>2</sub>O in MeCN-H<sub>2</sub>O medium<sup>38,39</sup>. A calculation based on QLQC (quasi-lattice-quasi-chemical) method<sup>19</sup> shows that H<sup>+</sup> ions is preferentially solvated by H<sub>2</sub>O in MeCN-H<sub>2</sub>O medium in the middle range ( $0.15 < x_{MeCN} < 0.75$ ) to maximum<sup>30</sup> extent than the H<sub>2</sub>O rich or MeCN rich region.

The strong self-association interaction between H<sub>2</sub>O molecules in the H<sub>2</sub>O rich region makes them less available for solvation. Interestingly the plot of  $k_{OH}^0$  versus  $x_{MeCN}$  in the region  $0 < x_{MeCN} < 0.15$  is almost linear with insignificant slope (see Fig. 2]. The solvent acceleration of rate in the middle range is well evident which surely speaks of the preferential solvation of OH<sup>-</sup> and complex ion by H<sub>2</sub>O in this region. As the MeCN content increased, OH<sup>-</sup> and complex ions are likely to be drawn to the aqueous microphase in closer proximity to each other leading to the rate enhancement.

Table 5--: Kamlet-Taft microscopic solvent parameters  $\pi^*$ ,  $\alpha$  and  $\beta$  (Ref. [27])

Solvent	$\pi^*$	$\alpha$	$\beta$
MeOH	0.60	0.93	0.62
MeCN	0.75	0.19	0.31
Me <sub>2</sub> CO	0.71	0.08	0.48

A further observation on the relative rate of the reaction in the cosolvents -H<sub>2</sub>O media may be made from the relative values of the Kamlet-Taft microscopic parameters  $\pi^*$  (local polarity),  $\alpha$  (acidity) and  $\beta$  (basicity) of the solvents, the values of which for the neat solvents are collected in Table 5. Assuming the proportionate variation of these parameters with solvent composition it is note worthy that the deprotonation of the substrate by OH<sup>-</sup> to generate the reactive amido conjugate base would be favoured for a cosolvent of lower acidity ( $\alpha$ ) a higher basicity ( $\beta$ ) and lower polarity ( $\pi^*$ ) values. The values of  $\alpha$  for all the three cosolvents and those of  $\beta$  and  $\pi^*$  (except MeOH) are in agreement with the observed relative reactivity of the complex. Thus again a differential behaviour of MeOH as cosolvent is observed.

MeOH, on the other hand, unlike MeCN is a protic electron pair donor with self-associating ability although it contains a hydrophobic head group. In MeOH- H<sub>2</sub>O system both constituents are capable of hydrogen bonding. A small addition of MeOH to H<sub>2</sub>O causes contraction in volume leading to enhanced H<sub>2</sub>O structure similar to that of a highly pressurised water, a phenomenon commonly referred as hydrophobic interaction. The presence of a hydration shell of water molecule around a MeQH molecule in the form of a disordered cage is indicated by a recent neutron diffraction study. The presence of a solute induces a solute-solvent and solvent-solvent interaction leading to formation of hydrogen bonded dimers/polymers of clathrate like solvation complexes of differently composed microphases. Theoretical investigations on the structural aspect of MeOH- H<sub>2</sub>O mixtures by Kirk Wood-Buff theory indicate the existence of hydrophobic interaction effect. Although the hydrophobic effect does enhance the rate as compared to fully aqueous medium in the present reaction, the extent of the rate enhancement is well below those of MeCN and Me<sub>2</sub>CO. This might be due to the fact that both MeOH and H<sub>2</sub>O are capable of hydrogen

bonding in MeOH-H<sub>2</sub>O medium unlike the other two. Thus there is a competition between H<sub>2</sub>O and the cosolvent MeOH for the solvation of the complex ion and OH<sup>-</sup>. The net preferential solvation effect, being partially compensated, is reduced in magnitude which presumably is the reason for the lower reactivity of the complex in MeOH- H<sub>2</sub>O medium unlike the MeCN-H<sub>2</sub>O and Me<sub>2</sub>CO - H<sub>2</sub>O media. It may be mentioned, in passing, that the situation in the case of Me<sub>2</sub>CO-H<sub>2</sub>O medium might be somewhat more closer to that of MeCN-H<sub>2</sub>O with clustering conditions where greater preferential solvation of OH<sup>-</sup> and complex ion by H<sub>2</sub>O is possible. The presence of two hydrophobic methyl head groups in Me<sub>2</sub>CO is expected to play a definite role in producing higher preferential solvation effect which might account for the higher rate enhancement of the reaction in Me<sub>2</sub>CO-H<sub>2</sub>O medium.

The solvent effect on the stability of the transition state relative to the initial state can be estimated from the calculated values of the relative transfer free energy quantity (Y) as defined in Eq.(11).

$$Y = [\Delta_t G^{\circ}(t.s.) - \Delta_t G^{\circ}(i.s.)]_{(s-w)}^{25^{\circ}C} \\ = RT \ln (k_{OH}^{OW}/k_{OH}^{OS}) + [\Delta_t G^{\circ}(OH^-)]_{(s-w)}^{25^{\circ}C} \quad (11)$$

where i.s. = {Co(tetren-H)<sup>2+</sup>... O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(p)OH} and t.s. = [Co(tetren-H)<sub>25^{\circ}C</sub>(C<sub>6</sub>H<sub>4</sub>(p)OH)<sup>2+</sup> and  $[\Delta_t G^{\circ}(OH^-)]_{(s-w)}$  denotes the transfer free energy of OH<sup>-</sup>, transfer of species being from H<sub>2</sub>O (w) to mixed solvent (s). The values of Y were calculated using the known values of  $[\Delta_t G^{\circ}(OH^-)]_{(s-w)}$  for the solvent media MeOH H<sub>2</sub>O, MeCN- H<sub>2</sub>O and Me<sub>2</sub>CO - H<sub>2</sub>O. The plot of Y versus x<sub>OS</sub> (see Fig. 3) indicates that the transfer free energy (Y) values are essentially positive for MeCN- H<sub>2</sub>O and negative for Me<sub>2</sub>CO - H<sub>2</sub>O and MeOH- H<sub>2</sub>O media, which means the transition state is stabilised in the latter media relative to former.

Incidentally the large positive values of  $[\Delta_t G^{\circ}(OH^-)]_{(s-w)}$  for MeCN- H<sub>2</sub>O medium outweighs the negative transfer free energy of the complex. Clearly Y values are solvent sensitive.

A comparison of Y values of the title complex with those of the corresponding *ortho* analogue i.e. tetrensalicylatocobalt(III)<sup>11</sup> indicates that the Y values of the later also follows the similar trend.

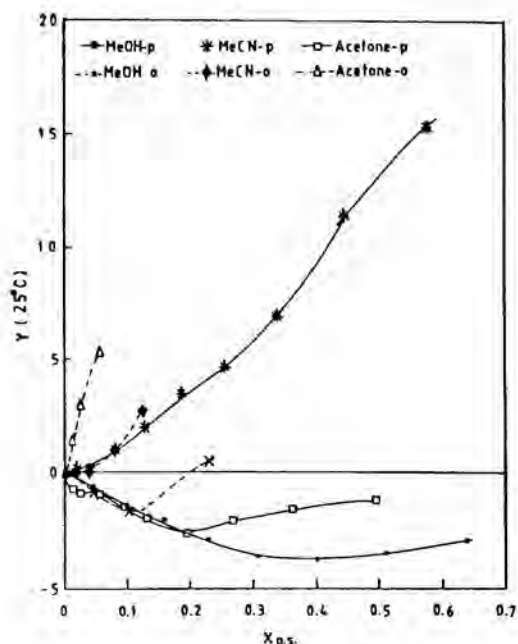


Fig.3 - Plot of  $Y$  ( $25^{\circ}\text{C}$ ) versus  $x_{\text{OS}}$  for *o*- and *p*-hydroxybenzoato complexes.

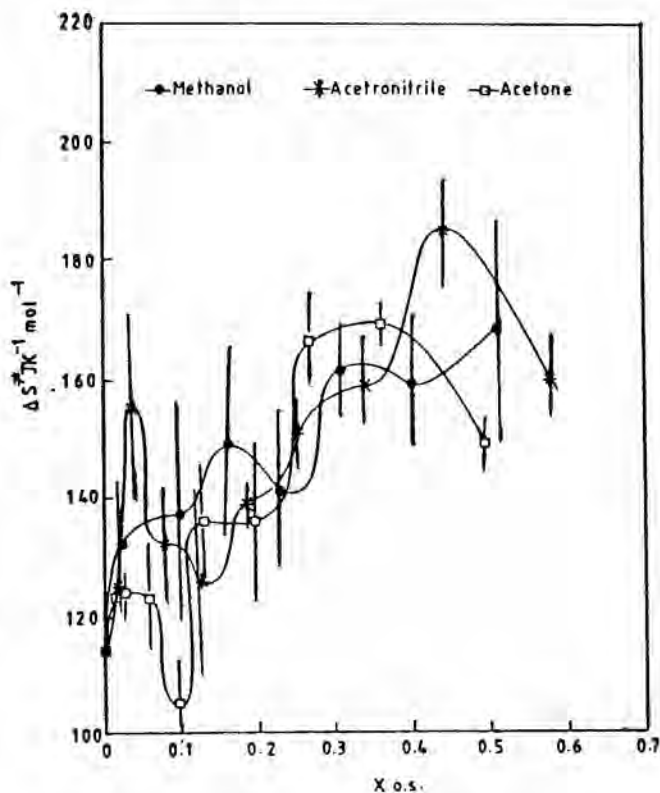


Fig.5 - Plot of  $\Delta S^{\ddagger}$  ( $\text{J K}^{-1} \text{mol}^{-1}$ ) versus  $x_{\text{OS}}$ .

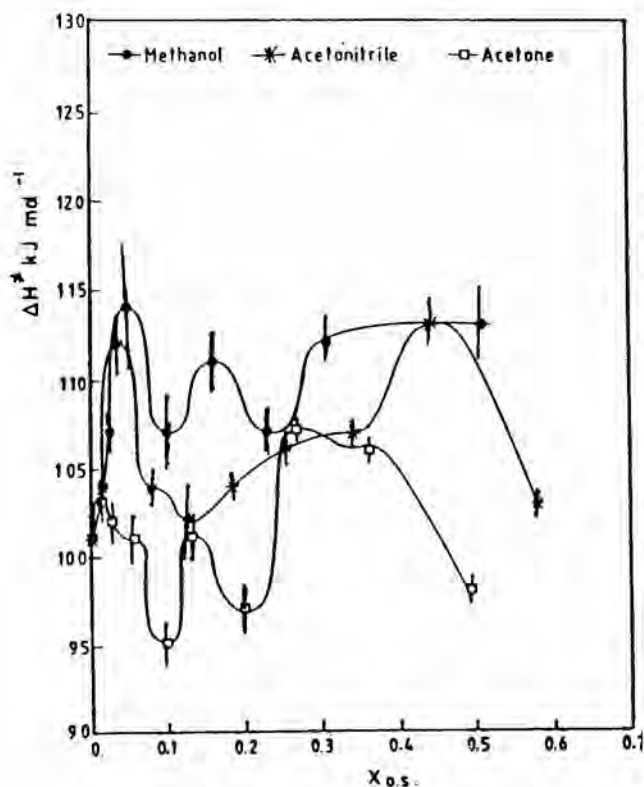


Fig.4 - Plot of  $\Delta H^{\ddagger}$  ( $\text{kJ mol}^{-1}$ ) versus  $x_{\text{OS}}$ .

However, the values of  $Y$  for the later complex are large than those of the former (see Fig. 3) which indicates the greater destabilisation of the transition state of tetrensalicylatocobalt(III) complex relative to its *para* isomer. This explains, at least partly, the nonexistence of the  $k_{\text{OH}}$  path at higher cosolvent composition ( $> 40\%$  (v/v)) for the *ortho* isomer. The activation parameters  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  are calculated taking  $k_{\text{OH}}$  values at the specified temperatures using Eyring equation as described

earlier<sup>11</sup>. The plots of  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  versus  $x_{\text{OS}}$  exhibit extrema (see Figs.4 and 5) which are sensitive to the nature of the cosolvents. This further supports that solvent structural perturbation affects, at least, the solvational component of the energy barrier for the reaction. Further, the plot of  $\Delta H^{\ddagger}$  versus  $\Delta S^{\ddagger}$  covering all data points is also nearly linear indicating the fact that the effect of solvent on  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  are mutually compensatory irrespective of the nature of the solvents.



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