Kinetics and mechanism of anation of (α, β)S-(hydroxo) (tetraethylenepentamine)cobalt (III) by sulphite in basic medium, the role of anionic micelles

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Abstract. The anation of (α, β)S-(tetren)CoOH^{2+} by SO$_3^{2-}$ in alkaline medium ($pH > 12$) produced the S-bonded sulphito complex exclusively. The reaction is reversible and $k_{obs} = (k_1 + k_2[OH^-])[SO_3^{2-}]_T + k_{-1}[OH^-]$ is obeyed at $[SO_3^{2-}] = 0.005 - 0.06$, $[OH^-]_T = 0.02 - 0.30 \, mol \, dm^{-3}$ $(30\text{-}45°C, I = 1.0 \, mol \, dm^{-3})$. At 35°C, $k_1 = (3.6 \pm 0.6) \times 10^{-3} \, dm^3 mol^{-1}s^{-1}$, $\Delta H^{\neq} = 55 \pm 10 \, kJ \, mol^{-1}$, $\Delta S^{\neq} = -112 \pm 34 \, JK^{-1} mol^{-1}$, $k_2 = (4.3 \pm 0.6) \times 10^{-2} \, dm^6 mol^{-2}s^{-1}$, $\Delta H^{\neq} = 44 \pm 11 \, kJ \, mol^{-1}$, $\Delta S^{\neq} = -130 \pm 36 \, JK^{-1} mol^{-1}$. The unusually high rate of sulphite substitution particularly in the OH$^-$ independent path is attributed to the involvement of a reactive internal conjugate base due to the coordinated OH$^-$ assisted NH-deprotonation of the tetren moiety (Co(tetren)OH$^{2+} \rightleftharpoons$ Co(tetren-H)OH$_2^{2+}$). Substantially low values of the activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) particularly the activation entropy is consistent with associative interchange mechanism (I_a) which is further supported by the rate retardation by anionic micelles of SDS. For the pseudo-phase ion-exchange equilibrium (tetren) in the reaction CoOH$_W^{2+}$ + 2Na$_M^+ \rightleftharpoons$ (tetren) CoOH$_M^{2+}$ + 2Na$_W^+$, the calculated value of K'_{ex} is 219 $\pm$ 60 at 35°C.

Keywords. Anation; sulphito complex; (hydroxo) (tetren) cobalt(III).

1. Introduction

It has been shown earlier that the oxygen bonded sulphito complex is the sole initial product of the reaction of (tetren)CoOH^{2+} with SO$_3^{2-}$|HSO$_3^-$|SO$_2$ buffer at $pH \leqslant 7$ (Dash *et al* 1981) which, however, rearranges to the S-bonded isomer over an extended time period. The O-bonded sulphito complex is formed by direct SO$_2$ addition to Co^{III}-OH without Co-O bond heterolysis. Several recent studies involving Co(III) (Van Eldik and Kraft 1985; Dash and Padhy 1989; Dash and Acharya 1993), Cr(III) (Moritzen *et al* 1985), Pt(IV) (Koshy and Harris 1983), Fe(III) (Van Eldik and Kraft 1989; Ritter and Van Eldik 1992) have substantiated this finding. However, direct sulphite substitution at Co(III) centre leading to S-bonded sulphito complex has been reported for *cis*-(AA)$_2$Co(OH$_2$)$_2^{3+}$ (AA = dipyridyl, 1,10-phenanthroline at $pH = 2\text{-}7$) (Joshi *et al* 1986) and for *trans*-Co(en)$_2$(SO$_3$)OH at $pH > 8$ (Stranks and Yandell 1970); the latter is due to strong *trans* activation of the S-bonded sulphite (Ratson *et al* 1978). The sulphite substitution reaction at cobalt(III) centre of the cobalt(III) amine complexes particularly in alkaline medium under which condition the dissociatively

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activated amido conjugate base can be generated to offer scope to examine the selectivity of the amido base in trapping the oxygen end or sulphur end of SO_3^{2-} to generate O-, S- or both O- and S-bonded sulphito complexes. This investigation reports the kinetics and mechanism of substitution of SO_3^{2-} at the cobalt(III) centre in alkaline medium for the robust complex, $(\alpha, \beta)S\text{-(tetren)}CoOH^{2+}$. This reaction is also investigated in anionic micellar medium to shed more light on the mechanistic aspect.

2. Experimental

The $[(\text{tetren})CoCl](ClO_4)_2$ was prepared by the method of House and Garner (1966, 1967) and purity was checked by the analysis of Co and Cl. The $(\alpha, \beta)S\text{-}[Co(\text{tetren})OH_2](ClO_4)_3$ was prepared *in situ* by the base hydrolysis of the chloro complex (Snow *et al* 1969; Snow 1972) followed by acidification. The aquo complex ($pH \simeq 6$) was stored in a refrigerator and used for kinetic study. The kinetic behaviour of an aged aquo complex sample was not different from that of a freshly prepared one.

Sodium dodecyl sulphate (SDS) was E Merck (GR, $\geqslant 99\%$ pure). All other chemicals used for kinetic study were of AR grade. $Na_2S_2O_5$ was used as the source of sulphite. The ionic strength was adjusted wherever necessary using $NaClO_4$. The UV-visible spectral measurements were made on a Jasco 7800 UV-visible spectrophotometer using 10 mm matched quartz cells.

2.1 *Kinetics*

The kinetics of reversible anation was studied by the sampling technique under pseudo first-order conditions at $30\cdot0 \leqslant t \leqslant 45\cdot0°C$ and $I = 1\cdot0\,\text{mol}\,\text{dm}^{-3}$. The ionic strength adjustment was not made for study in micellar medium. The samples of the reaction mixture thermally equilibrated in a water thermostat were withdrawn at known time intervals into test tubes kept in ice-bath and the absorbance was recorded at 330 nm at which the S-bonded sulphito complex absorbs strongly. The infinite absorbance (A_∞) for any run was chosen from the asymptotic region of the plot of absorbance versus time which corresponded to the absorbance at $\approx 9\,t/2$. Small variation of A_∞, at still

Table 1. Rate data for the anation of $(\alpha, \beta)S\text{-}[Co(\text{tetren})OH]^{2+}$ by SO_3^{2-} [a].

$[SO_3^{2-}]_T$ (mol dm^{-3})	$k_{abs}^6 \times 10^4 (\text{s}^{-1})$ at $[OH]_T (\text{mol dm}^{-1})$					
	0·020	0·040	0·10	0·15	0·20	0·30
0·005	0·70 ± 0·01	0·85 ± 0·02	1·50 ± 0·02	1·90 ± 0·03	2·20 ± 0·03	3·00 ± 0·03
0·010	1·00 ± 0·02	1·30 ± 0·03	2·00 ± 0·04	2·60 ± 0·03	3·00 ± 0·04	4·00 ± 0·03
0·020	1·80 ± 0·03	2·20 ± 0·05	3·30 ± 0·04	4·20 ± 0·04	5·01 ± 0·05	7·01 ± 0·05
0·040	3·40 ± 0·04	3·90 ± 0·04	6·00 ± 0·05	7·00 ± 0·08	8·20 ± 0·04	11·0 ± 0·1
0·060	5·10 ± 0·10	5·80 ± 0·06	8·60 ± 0·06	10·0 ± 0·20	11·5 ± 0·1	16·3 ± 0·4
$10^3 k_1$ [ce]		7·2 ± 0·3				
$10^2 k_2$ [cf]		5·1 ± 0·3				
$10^4 k_{-1}$ [cg]		7·8 ± 1·4				
		$(7\cdot2 \pm 0\cdot3)$[d]				

[a] $40\cdot0 \pm 0\cdot1°C$, $\lambda = 330\,\text{nm}$, $[\text{complex}]_T = 3\cdot6 \times 10^{-4}$, $I = 1\cdot0\,\text{mol}\,\text{dm}^{-3}$; [b] from duplicate runs; errors are average deviations from the mean value; [c] see (1); [d] average value by independent rate measurement at $[OH^-]_T = 0\cdot02$, $0\cdot04$, $0\cdot10$, $0\cdot15$, $0\cdot20$ and $0\cdot30\,\text{mol}\,\text{dm}^{-3}$ ($40°C$, $I = 1\cdot0\,\text{mol}\,\text{dm}^{-3}$) using (tetren) $CoSO_3^+$; [e] $\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$; [f] $\text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1}$; [g] $\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$
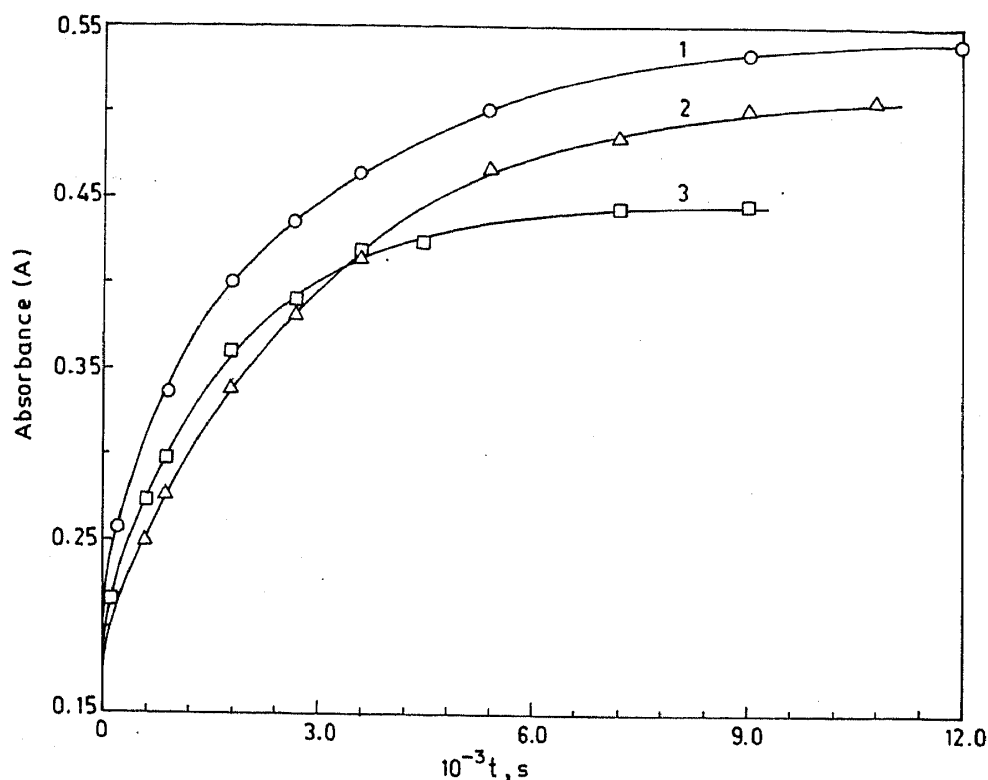
much larger time intervals was noticed which may be due to the base-catalysed isomerisation of the product S-bonded sulphito complex under *trans*-activation of S-bonded sulphite (Schneider *et al* 1986) leading to a different isomeric form presumably $(\alpha\alpha)$-(tetren)CoSO$_3^+$. However, the $\ln(A_\infty - A_t)$ versus time plots (using A_∞ at $\approx 9\,t/2$) were good straight lines the slope of which yielded k_{obs} with $\sigma(k_{obs}) \sim 5\%$ (corr. coeff. $= 0.99$). Runs were made at least in duplicate and the average deviation of k_{obs} was $\pm 5\%$. All calculations were made using a least squares program adapted to Apple II GS PC. The rate data at 40°C are collected in table 1.

3. Results and discussion

3.1 *Reaction in absence of SDS*

The infinite absorbance (A_∞) was strongly dependent on $[OH^-]_T$ and $[SO_3^{2-}]_T$ and increased with increasing $[SO_3^{2-}]_T$ at a fixed $[OH^-]_T$, thus indicating that the reaction approached equilibrium. The plots of k_{obs} versus $[SO_3^{2-}]_T$ at a given $[OH^-]_T$ were linear. Noteworthy is the fact that the gradients of such plots at different $[OH^-]_T$, when plotted against $[OH^-]_T$ yielded nonzero intercept and gradient consistent with the following for k_{obs} in accordance with the reaction scheme 1.

$$k_{obs} = (k_1 + k_2[OH^-])[SO_3^{2-}] + k_{-1}[OH^-] \tag{1}$$

The calculated value of k_{-1} at 40°C satisfactorily agreed with the second order base hydrolysis rate constant of (tetren)CoSO$_3^+$ (see footnote (d) of table 1). At other temperatures k_1 and k_2 values were calculated from the plots of $(k_{obs} - k_{-1}[OH^-]_T)/[SO_3^{2-}]$ versus $[OH^-]_T$ (see figure 1), k_{-1} values being used from our earlier work (Dash *et al* 1981). Values of k_1, k_2 at various temperatures and the associated activation parameters are collected in table 2.

Addition of SO$_3^{2-}$ to an aqueous solution of (α, β)S-(tetren)CoOH^{2+} caused a shift of the absorption maximum from 490 to 444 nm with an isosbestic point at 490 nm. Simultaneously, the absorption peak of the hydroxo complex at 350 nm also disappeared with time (see figure 2). The extinction coefficient of the product at 444 nm after 5 h was found to be 240 dm^3 mol^{-1} cm^{-1} which closely agreed with that of (α, β)S-(tetren)CoSO$_3^+$ (Dash and Harris 1981). It may be noted that the corresponding O-bonded sulphito complex has λ_{max} at 510 and 330 nm with $\varepsilon = 150$ and 1928 dm^3 mol^{-1} cm^{-1} respectively (Dash and Harris 1981). The above facts closely supported the hypothesis that sulphite substitution yielded the S-bonded sulphito complex, (tetren)CoSO$_3^+$, as the only product. The anation reaction of aquoaminecobalt(III) complexes have been recently reviewed (Banerjee *et al* 1988). The ion-pair dissociative interchange mechanism is valid for these reactions and the rate, essentially of second

Scheme 1.

Figure 1. $K_{obs} - k_{-1}[OH^-]_T/[SO_3^{2-}]_T dm^3 mol^{-1} s^{-1}$, versus $[OH^-]_T$ (mol dm^{-3}) plots at 30·0 (1), 35·0 (2) and 45·0°C (3); $10^4 k_{-1}(dm^3 mol^{-1} s^{-1}) = 1·6$ (30·0°C), 3·4 (35·0°C) and 14·3 (45·0°C) (Dash *et al* 1981).

Table 2. Calculated values of k_1, k_2 and activation parameters.

Temp. (°C) ($\pm 0·1$)	$10^3 k_1$ (dm^3 mol^{-1} s^{-1})	$10^2 k_2$ (dm^6 mol^{-2} s^{-1})
30·00	2·7 ± 0·2	2·1 ± 0·1
35·0	3·6 ± 0·6	4·3 ± 0·6
40·0	7·2 ± 0·3	5·1 ± 0·2
45·0	8·6 ± 0·2	5·7 ± 0·2
$\Delta H^{\neq}$ (kJ mol^{-1})	55 ± 10	44 ± 11
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	− 112 ± 34	− 130 ± 36

order and sensitive to the charge of the ion-pairing ligand for a given charge type cobalt(III) substrate, is $\leqslant 10^{-5}$ dm^3 mol^{-1} s^{-1} at 25°C with substantially high activation enthalpy and low positive, zero or low negative activation entropy. Moreover, the hydroxide is a much weaker leaving group than OH_2. Hence, the value of the uncatalysed (or water catalysed) rate constant k_1 ($\sim 10^{-3}$ dm^3 mol^{-1} s^{-1}) is too high to be reconciled with the dissociative interchange mechanism. Contrastingly, the inverse $[OH^-]$ dependence for the reaction, *trans*-Co(en)$_2$(SO$_3$) OH + SO$_3^{2-} \xrightarrow{k}$ *trans*-Co(en)$_2$(SO$_3$)$_2^-$, was taken to be indicative of the dissociative activation process (D) passing through a five-coordinate intermediate, Co(en)$_2$ SO$_3^+$ (Stranks and Yandell 1970), the rate constant and the activation enthalpy and entropy for the formation of the

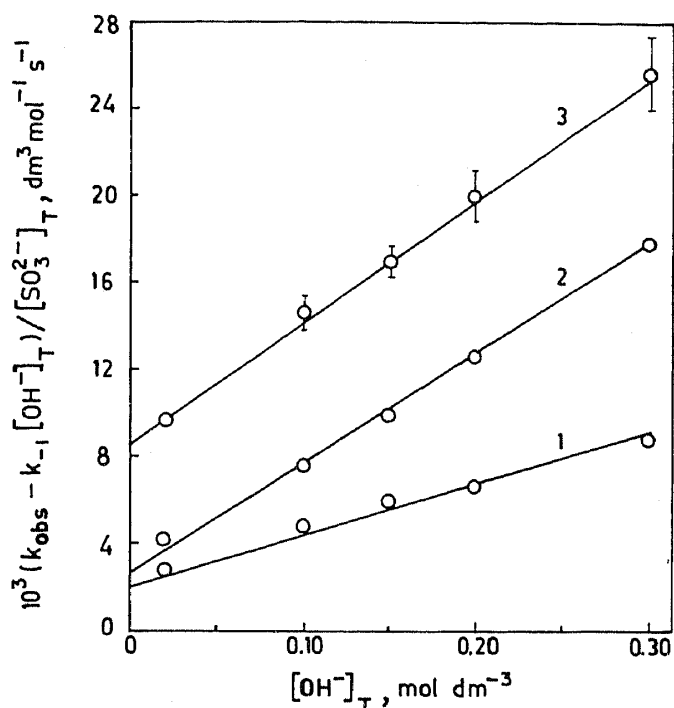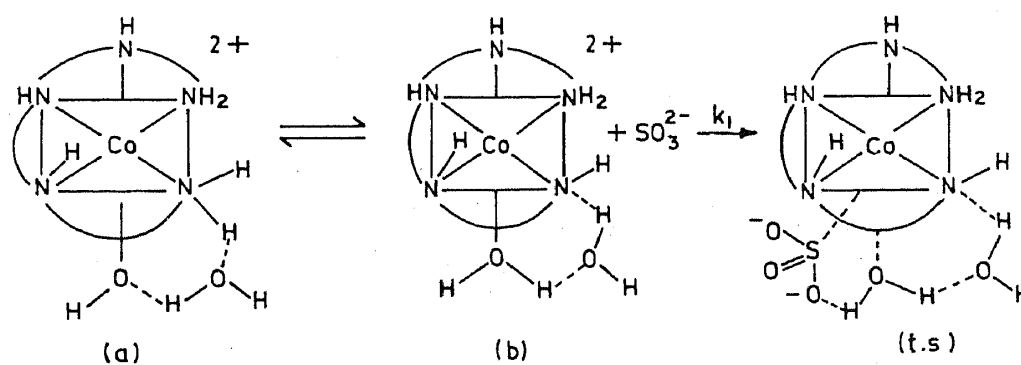**Figure 2.** Successive scans of the spectral change during the reaction of (α, β)S-(tetren)CoOH^{2+} with SO$_3^{2-}$: [complex]$_T = 2.5 \times 10^{-3}$, [SO$_3^{2-}$]$_T = 0.06$, [OH$^-$] $= 0.02$, $I = 1.0 \, \text{mol dm}^{-3}$, pH $= 12.06$, temp. $= 30°$C. 1 – after 5 min, 2 – 15 min, 3 – 30 min, 4 – 60 min, 5 – 90 min, 6 – 120 min, 7 – 180 min, 8 – 240 min, 9 – 300 min; dotted line – after 24 h. Bold line represents the complex with [SO$_3^{2-}$]$_T = 0$ and [OH] $= 0.02 \, \text{mol dm}^{-3}$ (scanned for 4 h).

Scheme 2.

five coordinate intermediate, Co(en)$_2$(SO$_3$)$^+$ being $\sim 3 \, \text{s}^{-1}$ (25°C), $88 \pm 8 \, \text{kJ mol}^{-1}$, and $\cong 17 \pm 32 \, \text{JK}^{-1} \text{mol}^{-1}$ respectively. Moderately fast SO$_3^{2-}$ substitution for (tetren) CoOH^{2+} without any evidence for ion pairing of the reactants may be visualised in terms of internal conjugate base mechanism (ICB) in which the Co$^{\text{III}}$-OH is transformed to Co$^{\text{III}}$-OH$_2$ by internal proton transfer from the Co$^{\text{III}}$-NH function generating reactive conjugate base (scheme 2, b). This is very similar to the internal conjugate base mechanism postulated by us in the base hydrolysis of (substituted

salicylato)-(tetren)cobalt(III) complexes (Dash and Harris 1981; Dash and Nayak 1986; Dash and Das 1992). The high rate of aquation of $N_4Co(OH)Cl^+$, where the N_4 moiety is not bereft of an N–H proton, has also been accounted for in terms of such a mechanism (Tobe 1983). Although the high value of k_1 might be the reflection of the reactivity of the amido conjugate base (b in scheme 2) and H_2O (rather than OH^-) as the leaving group, the substantially low values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are indicative of a rigid transition state which is presumably achieved due to its I_a character, i.e., Co^{III}–S bond formation is significant in the transition state. This is quite likely as the nucleophilicity of S in SO_3^{2-} $(N^+ = 7{\cdot}90)$ is substantially higher than that of OH^- $(N^+ = 4{\cdot}78)$ and H_2O $(N^+ = 0)$ (Ritchie 1976).

The OH^- dependent path arises due to the conjugate base equilibrium, (tetren)$CoOH^{2+}$ + OH^- ⇌ (tetren-H)$CoOH^+$, preceding the substitution reaction of the conjugate base, (tetren-H)$CoOH^+$; the high pK_{NH} $(\gg 15)$ of the coordinated tetren does not permit substantial amounts of the conjugate base to be formed under the experimental condition but such a species is kinetically significant due to its high reactivity. Substantially low values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ might indicate that the transition state for the OH^- dependent path is very similar to that for the OH^- independent path.
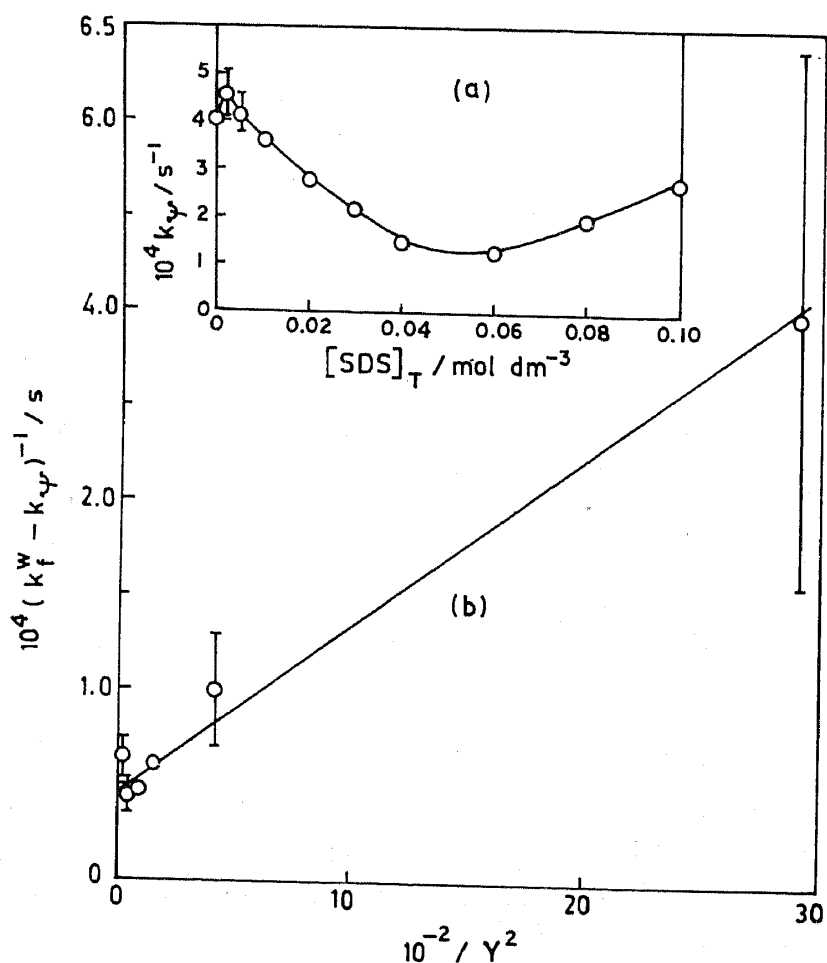

Figure 3. (a) k_{obs}/s^{-1} versus $[SDS]_T/mol\,dm^{-3}$ plot at $35{\cdot}0°C$; $[complex]_T = 3{\cdot}6 \times 10^{-4}$, $[SO_3^{2-}]_T = 0{\cdot}06$ and $[OH^-]_T = 0{\cdot}10\,mol\,dm^{-3}$. (b) $(k_f^W - k_\psi)^{-1}$(s) versus Y^{-2} plot.

3.2 *Effect of SDS micelles*

SDS beyond CMC retarded the rate. Variation of k_{obs} with $[SDS]_T$ at $[SO_3^{2-}]_T = 0.06$, $[OH^-] = 0.10 \, mol \, dm^{-3} (0 \leqslant [SDS]_T \leqslant 0.10 \, mol \, dm^{-3}, 35°C)$ displays a minimum at $[SDS]_T = 0.06 \, mol \, dm^{-3}$ (see figure 3a). The rate retardation is a consequence of selective partitioning of $Co(tetren)OH^{2+}$ into the anionic micellar pseudo-phase. Also our earlier study (Dash and Prusti 1990) has shown that $(tetren)CoSO_3^+$ bound to SDS micelles does not undergo base hydrolysis. The pseudo-phase ion-exchange equilibria were assumed to interpret the rate data (see scheme 3). In accord with scheme 3, and at constant $[SO_3^{2-}]_T$ and $[OH^-]_T$ but varying $[SDS]_T$, k_{obs} is given by

$$k_{obs} = \frac{k_f^W + k_f^M K_{ex}' \, Y^2}{1 + K_{ex}' Y^2} + \frac{k_r^W}{1 + K_{ex} Y} \tag{2}$$

where K_{ex} and K_{ex}' are the equilibrium constants as defined in scheme 3; k_f^W, k_f^M denote the pseudo-first order rate constants for SO_3^{2-} anation for $(tetren)CoOH^{2+}$ in aqueous (W) and micellar (M) pseudo-phases respectively, $k_r^W = k_{-1}[OH^-]_W$ (see (1)) and $Y = [Na_M^+]/[Na_W^+]$. All concentrations were expressed in terms of total solution volume. The charge compensated micellar binding parameters, β, $(= m_{Na}^s + 2m_{CoOH}^s)$ (Dash and Nayak 1987; Dash *et al* 1990) and $[Dn] = [SDS]_T - CMC$ define Y as

$$Y = (\beta - 2m_{CoOH}^s)[Dn]/\{[Na^+]_T - (\beta - 2m_{CoOH}^s)[Dn]\}. \tag{3}$$
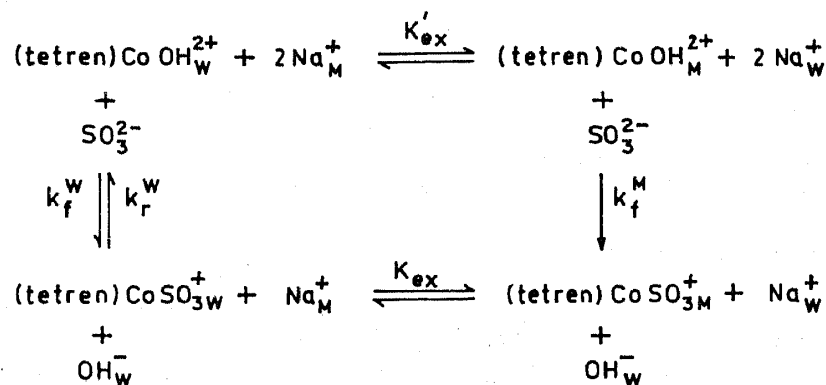
To evaluate Y, β was assumed to be constant $= 0.7$ and the further assumption that $m_{CoOH}^s = [(tetren)CoOH^{2+}]_T/[Dn]$, and $CMC = 0.003 \, mol \, dm^{-3}$ (Dash and Nayak 1987; Dash and Prusti 1990; Dash *et al* 1990), was made. The ionic strength of the aqueous pseudo-phase was calculated from known solution compositions. With the ionic strength, corrected value of $k_r^W (= 0.66 \times 10^{-4} \, s^{-1})$ and $K_{ex} = 12.0$ obtained from our earlier work (Dash and Prusti 1990) and $k_f^W (= k_{obs}$ (at $[SDS] = 0) - k_r^W) = 3.36 \times 10^{-4} \, s^{-1}$, the rate data were fitted to (4), the rearranged form of (2) (see figure 3b).

$$(k_f^W - k_\psi)^{-1} = (k_f^W - k_f^M)^{-1} + |(k_f^W - k_f^M)K_{ex}'|^{-1} Y^{-2}, \tag{4}$$

where

$$k_\psi = k_{obs} - k_r^W/(1 + K_{ex} Y). \tag{5}$$

Values of k_f^M and K_{ex}' calculated from the intercept and gradient of $(k_f^W - k_\psi)^{-1}$ versus Y^{-2} plot (see figure 3b) are $(0.66 \pm 0.27) \times 10^{-4} \, s^{-1}$ and 219 ± 60 respectively. Thus the

$(tetren)Co\,OH_W^{2+}$ $+$ $2\,Na_M^+$ $\underset{}{\overset{K_{ex}'}{\rightleftharpoons}}$ $(tetren)\,Co\,OH_M^{2+}$ $+$ $2\,Na_W^+$

$+$ $\qquad\qquad\qquad\qquad\qquad\qquad$ $+$

SO_3^{2-} $\qquad\qquad\qquad\qquad\qquad\qquad\quad$ SO_3^{2-}

$k_f^W \,\Vert\, k_r^W$ $\qquad\qquad\qquad\qquad\qquad\qquad\quad$ $\Big| k_f^M$

$(tetren)Co\,SO_{3W}^+$ $+$ Na_M^+ $\underset{}{\overset{K_{ex}}{\rightleftharpoons}}$ $(tetren)\,Co\,SO_{3M}^+$ $+$ Na_W^+

$+$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $+$

OH_W^- $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ OH_W^-

Scheme 3.

rate retardation by a factor $\sim 5 (k_f^W/k_f^M \simeq 5)$ was observed when the hydroxo complex was fully partitioned into the anionic micellar pseudo phase. This small retardation clearly points out that the reaction occurred in the water-rich zone of the micellar bulk aqueous interface or in other words, the cobalt(III) substrate, $(tetren)CoOH^{2+}$, is not incorporated in the inner surface layer of the anionic micelle. This further substantiates the fact that the mechanism is interchange type (I_a) where the sequence of events controlling the Co–S bond formation involves dominantly Co–O bond breaking.

The substantially high value of K'_{ex} is indicative of strong binding of the dipositive complex, with the anionic micelles, by both coulombic and hydrophobic interactions; the coulombic interaction is reduced by the shielding of the charge on the substrate by the hydrophobic tetren ligand. Presumably the hydrophobic interaction between the tetren skeleton of the substrate and the hydrocarbon tail of the surfactant anion, which is believed to be temporarily exposed to the aqueous environment as conceived by Menger (1979), accentuated the driving force for micellar binding.

Acknowledgements

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