Solvent Effects on Reactions of Coordination Complexes: Part IV† - Acid Catalysed Aquation of Oxygen Bonded (αβS)-(Sulphito)(tetraethylenepentamine)cobalt(III) in Aqueous Binary Mixtures of Protic & Dipolar Aprotic Cosolvents—A Flash Photolysis Study on Sulphur Bonded (αβS)(Sulphito)-(tetraethylenepentamine)cobalt(III) Ion

ANADI C DASH* & NEELAMADHAB DASH
Department of Chemistry, Utkal University, Bhubaneswar 751 004
and
SUKEUMAR ADITYA* & ANSUMAN ROY†
Department of Chemical Technology, University College of Science and Technology, 92, A P C Road, Calcutta 700 009

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Medium effects on the acid-catalysed aquation of oxygen-bonded (αβS)(sulphito)(tetren)cobalt(III) has been investigated at 25°C using dimethyl sulphoxide-water, acetonitrile-water and methanol-water media of varying compositions. The O-bonded sulphito species has been generated in situ from the corresponding stable S-bonded isomer as a transient by flash photolysis of the latter isomer in solution and the kinetics of its acid-catalysed decay to (αβS)(teten)CoOH+ and SO₂ (ms time scale) has been investigated by flash kinetics in the range of [H⁺]₀ = [1 to 20] × 10⁻⁴ mol dm⁻³. The protonation constant of (αβS)(teten)CoOSO₂⁺ and the rate constant of aquation of its protonated form have been evaluated at various compositions of the mixed solvent media. It turns out that the reaction medium plays dominant role in mediating the rate of elimination of SO₂ from the protonated O-bonded sulphito complex, although the process is totally intramolecular. The Brønsted correlation between log kᵣ and pH of (αβS)(teten)CoOSO₂⁺ is valid with a slope = −0.58 irrespective of the solvent media chosen except for acetonitrile-water mol fraction of acetonitrile > 0.25.

The acid-catalysed aquation of oxygen bonded (αβS)(sulphito)(tetraethylenepentamine)cobalt(III), (αβS)(teten)CoOSO₂⁺ involves fast protonation pre-equilibrium followed by slow elimination of SO₂ from the protonated substrate without heterolysis of Co – O bond as depicted in Eq. (1):

\[
\begin{align*}
\text{[teten]CoO}_2^+ & + H^+ \rightarrow K_H \text{[teten]CoO}_2H^+ \\
\text{[teten]COOH}_2^+ & \rightarrow H^+ + \text{[teten]COOH}_2^+
\end{align*}
\]

The rate-controlling step is presumed to involve a transition state (I) in which the proton attached to S-bound oxygen is transferred to the Co – O bond. This process may be totally intramolecular with or without solvent intervention.

In the light of these observations, it was considered worthwhile to examine the medium effect on the protonation equilibrium of the dipolar complex ion, (tetren)CoO₂⁺ – SO₂, a species in which the cobalt(III) centre is surrounded by the hydrophobic skeleton of tetren. Unfortunately the oxygen-bonded sulphito complex is highly unstable and has not yet been prepared in the solid state. On the contrary the corresponding sulphur-bonded isomer is highly stable and has been well characterized in the solid state and in solution. In an earlier paper, Aditya and coworkers demonstrated that flash photolysis of a solution of the S-bonded sulphito complex generated the corresponding O-bonded isomer as a transient intermediate which underwent fast acid-catalysed elimination of SO₂ without any other side reaction. We took advantage of this method of generating the O-bonded sulphito complex, (αβS)(teten)CoOSO₂⁺ from the corresponding stable S-bonded isomer. In this paper attempts have been made to elucidate the role of medium on the rate of acid-catalysed aquation and on the protonation equilibrium of (αβS)(teten)CoOSO₂⁺. The organic solvent components of the mixed solvent media chosen...
The rate data for the acid-catalysed decay of the transient in different solvent media of varying compositions are presented in Table 1. It is worth noting that at low acidities in methanol-water media, the formation of a stable species absorbing at 390 nm could be observed**. The reason for not getting any transient absorption at 390 nm in some of the acetonitrile-water and DMSO-water media at \([H^+]=0.01, 0.02\) mol dm\(^{-3}\) (see Table 1) may be due to high acid-catalysed decomposition rates of the transient or formation of no transient under these conditions. In accord with the rate and equilibrium steps shown in Eq. (1), the pseudo-first order rate constant is given by Eq. (2),

\[
\text{k}_{\text{obs}} = \frac{k_{H}^T \frac{f_s}{f_s CoOSO_2^2} \frac{f_s CoOSO_2^2}{f_s CoOSO_2^2 + f_s CoOSO_2 H^+}}{1 + k_{H}^T \frac{f_s}{f_s CoOSO_2^2} \frac{f_s CoOSO_2^2}{f_s CoOSO_2 H^+}} \tag{2}
\]

where \(k_{H}^T\) denotes the thermodynamic protonation constant of \((\alpha\beta S)[(tetren)CoOSO_2]^+\); \(f_s\) are the activity coefficients; and \(K_{H}\) is the SO\(_2\) elimination rate constant for the protonated O-bonded sulphito complex. Equation (2) further assumes that the activity coefficient of the transition state of the acid-catalysed path \(k_{H}\) path is equal to the activity coefficient of the initial state (i.e. \((\alpha\beta S)[(tetren)CoOSO_2 H]^2+\) species). This is reasonable considering the net charge of the initial state and the transition state and the low ionic strength of the media \((2.34 \times 10^{-4} \leq \text{l}, \text{mol dm}^{-3} \leq 4.4 \times 10^{-4})\).

** Further work is in progress to identify the species in methanol-water media at low acidities.
Further assuming \( f_H = f_{CoSO_3} = f_c \) and writing 
\( f_{CoSO_3,H} = f_c \), Eq. (2) is linearized to yield Eq. (3):

\[
k_{\text{obs}}^{-1} = k_H^{-1} + (k_H K_H^{-1}) f_c / [H^+ f_c^2] \tag{3}
\]

The activity coefficient \( f_c \) was calculated from the Debye-Hückel equation,

\[
\log f_c = -AZ_i^2 / (1 + B a) \tag{4}
\]

assuming \( a = 5 \) Å for both the solvated proton and the cobalt(III) species; the values of the parameters \( A = 1.8246 \times 10^6 / (D T)^{3/2} \) and \( B = 50.29 / (D T)^{1/2} \) were computed using the dielectric constant \( (D) \) data of DMSO-water and AN-water media. The values of \( A \) and \( B \) for MeOH-water were chosen from the compilation of Bates and Robinson. The rate data were fitted to Eq. (3) by weighted least squares procedure, the weight of \( k_{\text{obs}} \) being calculated from the error quoted for \( k_{\text{obs}} \) (\( w = (6 k_{\text{obs}} / k_{\text{obs}})^{-1} \)). Typical plots of \( k_{\text{obs}}^{-1} \) versus \( f_c / [H^+ f_c^2] \) are presented in Fig. 1 and the calculated values of \( k_H \) and \( K_H \) are presented in Table 2. The values of \( k_H \) and \( K_H \) for fully aqueous medium compare reasonably with those reported in our earlier preliminary communication \( (k_H = 1.2 \times 10^3 \text{ s}^{-1}, \ K_H = 2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}) \).

The plots of \( \log K_H \) versus \( X_{\text{org}} \) (\( X = \text{mol fraction of the organic solvent component} \)) clearly demonstrate the medium effect on the protonation equilibrium of the O-bonded sulphito complex. \( \log K_H \) decreases non-linearly with \( X_{\text{MeOH}} \) while for AN- and DMSO-water systems minimum in this plot occurs at \( X_{\text{AN}} = 0.038 \) and \( X_{\text{DMSO}} = 0.032 \). Beyond \( X_{\text{DMSO}} = 0.032, \ \log K_H \) increases steadily (see curve 3 of Fig. 2). On the other hand at \( X_{\text{AN}} > 0.038, \ \log K_H \) increases non-linearly and tends to attain limiting value at \( X_{\text{AN}} = 0.2 \) (see curve 2, Fig. 2). This behaviour reflects the differential propensity of the mixed solvents to transfer proton from the solvated state to the O-bonded sulphito complex as also the solvation interaction of the protonated and the unprotonated forms of the concerned cobalt(III) substrate in the mixed solvent media. The dielectric constants of the mixed solvent media for any value of \( X_{\text{org}} \) are comparable in magnitude. Hence the nature of variation of \( \log K_H \) with \( X_{\text{org}} \) is not entirely due to the electrostatics of the protonation reaction. Solvent structural changes also seem to influence \( K_H \).

Both DMSO and AN can not solvate the anionic oxygen site of \((\alpha\beta\delta)\text{tetren})CoO_2^2+ - SO_2\) while the dipolar protic MeOH can solvate it effectively by H-bonding. On the other hand the protonated form of the complex \((\alpha\beta\delta)\text{tetren})CoO_2(H)_2\) can be solvated by MeOH, DMSO and AN via H-bonding, e.g. CoOSOOH..., CoOSOOH...O=S(CH3)2, CoOSOOH...OHCH3, CoOSOOH...N=C(CH3). This differential solvation effect of the solvents is also responsible for the increased proton affinity of \((\alpha\beta\delta)\text{tetren})CoO_2(H)_2\) in DMSO-water and AN-water media relative to that in MeOH-water media. The minima in the \( \log K_H \) versus \( X_{\text{AN}} \) or \( X_{\text{DMSO}} \) plots presumably are consequences of the break down of normal water struc-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Vol \% of & \multicolumn{2}{c|}{MeOH/W} & \multicolumn{2}{c|}{AN/W} & \multicolumn{2}{c|}{DMSO/W} \\
O.S. & \(10^{-3} k_H\) & \(K_H\) & \(10^{-3} k_H\) & \(K_H\) & \(10^{-3} k_H\) & \(K_H\) \\
(\text{s}^{-1}) & (\text{dm}^3 \text{ mol}^{-1}) & (\text{dm}^3 \text{ mol}^{-1}) & (\text{dm}^3 \text{ mol}^{-1}) & (\text{dm}^3 \text{ mol}^{-1}) & (\text{dm}^3 \text{ mol}^{-1}) & (\text{dm}^3 \text{ mol}^{-1}) \\
\hline
0 & 3.11 \pm 0.73 & 573 \pm 136 & 3.11 \pm 0.73 & 573 \pm 136 & 3.11 \pm 0.73 & 573 \pm 136 \\
10.0 & 6.42 \pm 2.50 & 290 \pm 116 & 4.12 \pm 0.20 & 452 \pm 25 & 6.61 \pm 0.90 & 400 \pm 56 \\
30.0 & 7.45 \pm 0.86 & 215 \pm 25 & 4.98 \pm 0.40 & 876 \pm 90 & 5.81 \pm 1.50 & 475 \pm 130 \\
50.0 & 5.05 \pm 3.20 & 206 \pm 136 & 9.25 \pm 2.83 & 1078 \pm 369 & 3.23 \pm 0.25 & 937 \pm 81 \\
70.0 & 11.3 \pm 1.7 & 148 \pm 24 & - & - & 2.52 \pm 0.18 & 2016 \pm 621 \\
\hline
\end{tabular}
\caption{Calculated Values of \( k_H \) and \( K_H \) at 25°C}
\end{table}

(a) Vol \% refers to that of organic solvent component of the mixed solvent.

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**Fig. 1—Plot of \( 10^3 / (k_{\text{obs}} \text{ s}^{-1}) \) versus \( 10^3 f_c^2 / [H^+ f_c^2] \) (\text{dm}^3 \text{ mol}^{-1}) \) for acid-catalysed SO\(_2\) elimination reaction of \((\alpha\beta\delta)\text{tetren})CoO_2^2+\) : (1) 100% water; (2) 30% (v/v) MeOH; (3) 70% (v/v) DMSO; and (4) 30% (v/v) AN.**
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Fig. 2—Plots of log $K_H^T$ versus mol fraction of cosolvent ($X_{Org}$) [(1) MeOH; (2) AN; and (3) DMSO]

Fig. 3—Plot of log $k_H$ versus mol fraction of cosolvent ($X_{Org}$) [(1) MeOH; (2) AN; and (3) DMSO]

ture by DMSO and AN at low mol fractions which consequently leads to production of more of monomeric water so that the H-bonding equilibrium (5)

$$\text{III} \quad \text{(tetren)Co} - \text{O} - \text{SOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{III} \quad \text{(tetren)Co} - \text{OSOO}^...\text{HOH} \quad \ldots(5)$$

becomes the most favourable. The formation of the proton solvation bridge acts against protonation of the oxygen site of O-bonded sulphito complex so that log $K_H^T$ attains minimum around $X_{AN} = 0.038$ and $X_{DMSO} = 0.032$. Similar trends in the $pK$ of phenols in DMSO water media have also been reported. At higher mol fractions of AN and DMSO, however, both these cosolvents are involved in H-bonding with water molecules and DMSO can compete successfully with water for solvation of $H^+$ ion. Electrostatic forces also dominate. Hence it is not unusual to expect that the proton affinity of the O-bonded sulphito species increases with increase in mol fraction of DMSO or AN.

Strikingly enough, log $k_H$ versus $X_{Org}$ plots (see Fig. 3) display well developed maximum around $X_{DMSO} = 0.03$; a broad maximum around $X_{MeOH} = 0.12$ and a minimum at $X_{MeOH} = 0.3$. Only a weakly developed inflexion is observed around $X_{AN} = 0.12$. The trend in the reactivities of the protonated species, (αβS)[(tetren)CoOSO$_2$H]$^+$ (i.e. the rate of elimination of SO$_2$) in the mixed solvent media reflected in the log $k_H$ versus $X_{Org}$ plot leaves no doubt regarding the involvement of medium in the rate-determining process. It is likely
that the process of proton transfer from the S-O site to the Co-O site (see the transition state I) is strongly mediated by the medium although the process is totally intramolecular.

The medium effect on the rate of SO₂ elimination reaction can be better understood considering the transfer free energy data for the initial and the transition state (I). On the basis of the transition state equation, \( k_H = \frac{(kT/h)}{\exp(-\Delta G^\ddagger/RT)} \) and the thermodynamic cycle shown in Scheme 1,

\[
\Delta G^\ddagger_{\text{ts}} \quad \Delta G^\ddagger_{\text{i,s}} \quad \Delta G^\ddagger_{\text{t,s}}
\]

where i.s. and t.s. denote the initial state and transition state of the reactant \((\text{tptren})\text{CoO}_{2}\text{H}_2^+\) respectively; \(\Delta G^\ddagger_j\) is the activation free energy in the medium \(j\) (\(j = w\) for water and \(s\) for the mixed solvent) and \([\Delta G_i]\)\(_{\text{t,s}}\)\(_{\text{w}}\) is the standard free energy of transfer of the species \(i\) (i.e. i.s. or t.s.) from water to the mixed solvent, the transfer free energy change of the transition state relative to that for the initial state for the transfer of the species from water to the mixed solvents, can be stated as in Eq. (6).

\[
[\Delta G_{\text{t.s.}}] - [\Delta G_{\text{i.s.}}]_{\text{w}} = 2.303 \frac{RT}{\log k_H^w/k_H^s}
\]  

(6)

Figure (4) depicts the variation of the relative transfer free energy changes at 25°C as a function of \(X_{\text{Org}}\) from which the differential solvating behaviour of different media for the initial state and the transition state is clearly evident. Minima in such plots for MeOH-water (at \(X_{\text{MeOH}} = 0.15\)) and DMSO-water (at \(X_{\text{DMSO}} = 0.03\)) media with nonlinear variation of the relative transfer free energy term with \(X_{\text{Org}}\) indicate that structural perturbations in the mixed solvent media also control the solvation of the initial and transition states. The linear decrease of the relative transfer free energy term with \(X_{\text{AN}}\), however, would mean that the free energy changes associated with the structural perturbation in the medium is proportional to the variation of the relative transfer free energy function with increasing \(X_{\text{AN}}\). It is, however, evident that \([\Delta G_{\text{t,s.}}]_{\text{w}}\) is less than \([\Delta G_{\text{i.s.}}]_{\text{w}}\) at all solvent compositions except for \(X_{\text{DMSO}} > 0.2\). Hence relative to the initial state, the transition state is more stabilized in the mixed solvents. At \(X_{\text{DMSO}} = 0.2\) it appears that there is little difference between the solvational propensity of the initial and the transition states as the value of \([\Delta G_{\text{t.s.}}] - [\Delta G_{\text{i.s.}}]_{\text{w}}\) approaches zero. At \(X_{\text{DMSO}} > 0.2\) the transition state appears to be more destabilized relative to the initial state in DMSO-water medium. Hence it is clear that medium does participate during proton transfer and SO₂ elimination processes and most likely both the processes are solvent-mediated to different degrees.

The solvent effect on the protonation equilibriu is virtually proportional to the solvent effect on the rate process following it. This is evident in the observed Brønsted correlation between log \(k_H\) and log \(K_{iH}\) (see Fig. 5). The numerical value of the slope \((-0.58)\) of the plot is in keeping with the Marcus' theory for the rate-equilibrium relationship in proton transfer reactions. Data point at high \(X_{\text{AN}}\) shows positive deviation from the Brønsted plot indicating that such proportionality
between the rate and equilibrium parameters is adversely affected as the proportion of AN is increased.

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References