J. Chem. Research (S),
1997, 136–137
J. Chem. Research (M),
1997, 0925–0950

Effect of Solvent on the Reactions of Coordination Complexes. Part 22.[1] Kinetics of Base Hydrolysis of Some (Aminomonocarboxylato)(tetraethylenepentamine)cobalt(III) Complexes in Acetonitrile–Water Media: the Role of Solvent Basicity and Solvent Structure

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The base of hydrolysis of $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$ {R = NH_2CH_2—, $NH_2[CH_2]_2$—, pyridine-2- ($\alpha\beta S$ isomer), $NH_2CH(CH_3)$— ($\alpha\beta S$ and $\alpha\beta R$ isomers); tetren = tetraethylenepentamine} is accelerated by acetonitrile + water media ($0 \leq X_{AN} \leq 0.578$, X_{AN} = mole fraction of acetonitrile) owing to the combined effects of destabilisation of OH^-, relatively greater destabilisation of the transition state of the amido conjugate base $[((\text{tetren})\text{-H})\text{Co}^{2+}\cdots{}^-\text{O}_2\text{CR}]^{+*}$ as compared to that of the initial state $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$, and solvent structure; the activation enthalpies and entropies are also sensitive to solvent structure and conformational arrangement of the tetren ligand.

In connection with our studies[1] to understand the role of solvent on the reactivities of coordination complexes, we report here the effects of acetonitrile (AN) + water media on the kinetics of base hydrolysis of some $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$ where RCO_2^- denotes glycinate, β-alaninate, pyridine-2-carboxylate ($\alpha\beta S$ isomer) and α-alaninate ($\alpha\beta S$ and $\alpha\beta R$ isomers) and tetren stands for tetraethylenepentamine. The rate constants were determined at 20.0–40.0 °C, $0 \leq X_{AN} \leq 0.578$ (X_{AN} = mole fraction of AN) and $I = 0.02$ mol dm^{-3}.

The second-order rate constants at zero ionic strength ($k_{OH}^{0,s}$, the superscript s denoting mixed solvent) increased with increasing X_{AN}. A multiparameter regression, $\log k_{OH}^{0,s} = C + A_1\alpha^s + A_2\beta^s + A_3\pi^{*s}$, where α^s, β^s and π^{*s} denote the solvent acidity, basicity and polarizability[18] respectively and $C = \log k_{OH}^{0,s}$ at $\alpha^s = \beta^s = \pi^{*s} = 0$ was satisfactory. The values of A_i (the coefficients of α^s and β^s in particular, see Table 5) are sensitive to the nature of the substrates indicating the importance of specific solute–solvent interactions on reactivity. The basicity of the mixed solvent increases with increasing X_{AN} (see values of β in footnote *b* of Table 5). The positive correlation between $\log k_{OH}^{0,s}$ and β (except for the pyridine-2-carboxylato complex) indicates that solvent acceleration is predominantly due to enhanced basicity of the mixed solvent media.

The solvent effect on the stability of the transition state of the amido conjugate base $[((\text{tetren})\text{-H})\text{Co}^{2+}\cdots\text{O}_2\text{CR}]^{+*}$ relative to that of the initial state $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$ was judged from the relative transfer free energy data, $Y = [\Delta_tG(\text{t.s.}) - \Delta_tG^\circ(\text{i.s.})]_{(s\leftarrow w)}(25\ °\text{C})$, calculated by the relationship $Y = RT \ln (k_{OH}^{0,w}/k_{OH}^{0,s}) + [\Delta_tG^\circ(OH^-)]_{(s\leftarrow w)}$. The values of $[\Delta_tG^\circ(OH^-)]_{(s\leftarrow w)}$ (molar scale, 25 °C) were taken from the literature.[31] These data fitted $Y = aX_{AN} + cG^E$, where G^E is the excess Gibbs free energy of mixing of AN–water media, satisfactorily (see Table 6). As G^E is positive,[30] the negative values of c indicated that the solvent structural perturbations have a greater stabilising effect on the transition state relative to that on the initial state of the complexes

Table 5 Calculated values of C, A_1, A_2 and A_3 for $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$ complexes^{a,b}

R	C^c	A_1	A_2	A_3
$CH(CH_3)NH_2$	5.8	2.2 ± 0.5	3.9 ± 0.2	-7.7 ± 0.5
$CH(CH_3)NH_2$	$(2.3)^d$	$(1.0 \pm 0.4)^d$	$(6.7 \pm 0.2)^d$	$(-3.9 \pm 0.4)^d$
CH_2NH_2	6.0	1.7 ± 0.5	3.9 ± 0.2	-7.2 ± 0.5
$CH_2CH_2NH_2$	7.4	0.6 ± 0.6	1.9 ± 0.3	-6.4 ± 0.6
2-pyridyl	10.9	-1.2 ± 0.6	-1.2 ± 0.3	-5.9 ± 0.6

$^a \log k_{OH}^{0,s} = C + A_1\alpha^s + A_2\beta^s + A_3\pi^{*s}$. ^{b}Values of α^s, β^s and π^{*s} at (X_{AN}) respectively are: 1.13, 0.52, 1.14 (0); 1.11, 0.535, 1.125 (0.018); 1.075, 0.555, 1.105 (0.037); 1.105, 0.59, 1.09 (0.078); 0.955, 0.61, 1.05 (0.127); 0.91, 0.61, 0.99 (0.185); 0.90, 0.61, 0.94 (0.254); 0.90, 0.605, 0.90 (0.338); 0.90, 0.595, 0.86 (0.442); 0.875, 0.59, 0.82 (0.578) (ref. 18). ^{c}Held fixed at the best values to calculate errors in A_1, A_2 and A_3. ^{d}For $\alpha\beta R$; all other values are for $\alpha\beta S$.

Table 6 Calculated values of a and c for $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$ complexes at 25.0 °C^a

R	Isomer	a/kJ mol^{-1}	c	Corr. coeff.
$CH(CH_3)NH_2$	$\alpha\beta R$	56.6 ± 2.7	-9.5 ± 0.7	0.98
$CH(CH_3)NH_2$	$\alpha\beta S$	35.1 ± 1.4	-5.0 ± 0.5	0.98
CH_2NH_2	$\alpha\beta S$	36.5 ± 1.0	-5.3 ± 0.3	0.99
$CH_2CH_2NH_2$	$\alpha\beta S$	36.3 ± 1.1	-4.6 ± 0.4	0.99
2-pyridyl	$\alpha\beta S$	34.9 ± 0.9	-4.5 ± 0.3	0.99

$^a Y = aX_{AN} + cG^E$.

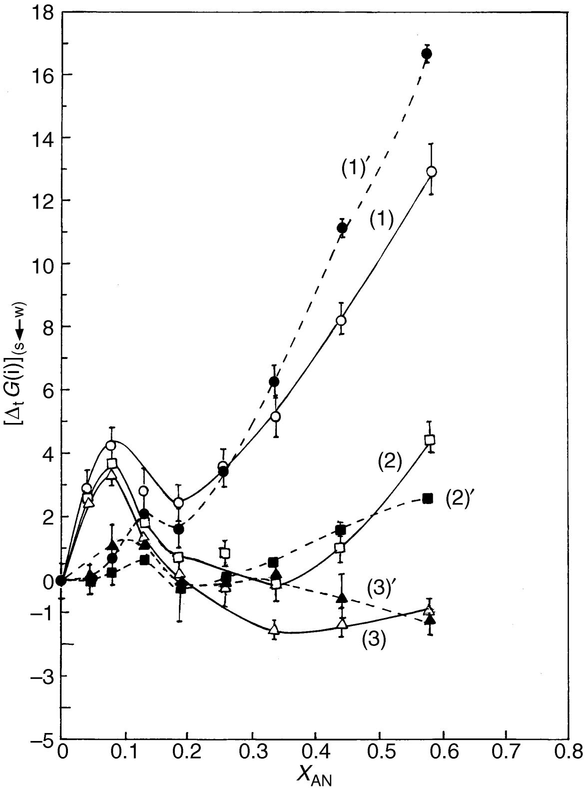

Fig. 1 $[\Delta_tG^\circ(i)]_{(s\leftarrow w)}$/kJ mol^{-1} *vs.* X_{AN} plots at 25 °C: i = $[((\text{tetren})\text{-H})\text{Co}^{2+}\cdots{}^-\text{O}_2\text{CR}]^{+*}$ (1,1′), $[(\text{tetren})\text{CoO}_2\text{CRH}]^{3+}$ (2,2′), $[(\text{tetren})\text{CoO}_2\text{CR}]^{2+}$ (3,3′); R = 2-pyridyl (1,2,3) and NH_2CH_2 (1′,2′,3′)

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(C^{2+}). However, this is largely overshadowed by the preferential solvation effect as indicated by the large positive values of *a*.

The solubility data for the picrate salts of the *N*-protonated glycinato complex and unprotonated pyridine-2-carboxylato complex, the dissociation constants of their *N*-protonated forms ($pK_{NH}{}^{0,s}$)($0 \leq X_{AN} \leq 0.578$, 25.0 °C), the rate constants ($k_{OH}{}^{0,s}$), $[\Delta_t G°(H^+)]_{(s \leftarrow w)}$, $[\Delta_t G°(OH^-)]_{(s \leftarrow w)}$ and $[\Delta_t G°(Pic^-)]_{(s \leftarrow w)}$ data[31,34] were combined to calculate the $[\Delta_t G°(i)]_{(s \leftarrow w)}$ where i = unprotonated (C^{2+}), *N*-protonated species (CH^{3+}) and the transition state, $[((tetren)\text{-}H)Co^{2+} \cdots {}^{-}O_2CR]^{+*}$. Fig. 1 depicts the non-linear variation of $[\Delta_t G°(i)]_{(s \leftarrow w)}$ with X_{AN}; maxima are discernible at $X_{AN} = 0.08$ *ca*. 0.13 (weak) for the pyridine-2-carboxylato and glycinato complexes respectively. It is also evident that the transition state is destabilised relative to the initial state (*i.e.*, C^{2+} species) when the transfer occurs from water to AN–water media and this effect increases as the cosolvent content increases beyond X_{AN} *ca*. 0.13. The destabilising effect of AN–water media increases in the order $C^{2+} < CH^{3+} <$ t.s. (species with +1 charge). The observed variation of $[\Delta_\tau G°(i)]_{(s \leftarrow w)}$ with X_{AN} (see Fig. 1) further suggests that both electrostatic and non-electrostatic effects, the latter relating to the solvent structure and substrate hydrophobicity, contribute to the stabilisation of the species in the mixed solvent media.

The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values show non-linear variation with the solvent composition. Those for the *αβR* isomer of $[(tetren)CoO_2CCH(CH_3)NH_2]^{2+}$ decreased with X_{AN} in contrast to the increasing trend exhibited by the rest of the other complexes. This is taken to indicate that the solvent structure and the conformational arrangement of the tetren skeleton affects the solvation components of these thermodynamic parameters. However, the solvent dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$, irrespective of the substrates, is mutually compensatory, thus supporting no gross change in the mechanism of the reaction.

This work was supported by the Council of Scientific and Industrial Research, New Delhi. S.D. is thankful to the Education Department, Government of Orissa, for granting study leave and to Dr P. Pradhan, Bio-organic Chemistry Division (BARC), for NMR measurements.

Techniques used: UV–visible and stopped-flow spectrophotometry

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Table 1: Analytical data for $[(tetren)CoO_2CRH](ClO_4)_3$

Table 2: Solubility (*s*) and $pK_{NH}{}°$ data at 25.0 °C in acetonitrile + water media

Table 3: Rate constants for base hydrolysis of $[(tetren)CoO_2CR]^{2+}$ in acetonitrile + water media at $I = 0$ and $20.0 \leq T/°C \leq 40.0$

Table 4: Activation parameters for base hydrolysis of $[(tetren)CoO_2CR]^{2+}$ in acetonitrile + water media

Table 7: Gibbs energies of transfer, $[\Delta_t G°(i)]_{(s \leftarrow w)}$ (i = C^{2+}, CH^{3+}, t.s., Pic^-, H^+ and OH^-), at 25.0 °C

Fig. 2: $\Delta H^\ddagger$ *vs*. X_{AN} plots

Fig. 3: $\Delta S^\ddagger$ *vs*. X_{AN} plots

Structure I: (*αβR*)-(α-alaninato)(tetren)cobalt(III) ion

Structure II: (*αβS*)-(α-alaninato)(tetren)cobalt(III) ion

Received, 9th September 1996; Accepted, 2nd January 1997
Paper E/6/06176A

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