transfer between the sulfite moiety and the reducible metal than is metal–sulfur bonding. This is probably to be expected in view of the greater electronegativity of the O^{2-} species as compared to the S^{IV} species.

RG 114.81, to R.v.E. and G.M.H.

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Mechanistic Information from the Micellar Effect on the Base Hydrolysis of (αβS)-(3-Nitrosalicylato)(tetraethylenepentamine)cobalt(III) Ion

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The kinetics of base hydrolysis of the (αβS)-(tetren)(3NO$_2$-salicylato)Co(III) ion has been investigated in the presence and absence of cationic (CTAB) and anionic (SDS) surfactants at 30.0 ± 0.1 °C. The phenoxide form of the complex undergoes aquation in the micellar pseudophase of the surfactants much faster than in the aqueous pseudophase, the effect being much more pronounced for SDS. This supports the internal conjugate base mechanism, the reactive amine conjugate base being generated by the intramolecular proton-transfer equilibrium [(tetren)CoO$_2$CC$_6$H$_3$(3NO$_2$)O]$^+$ ⇌ [(tetrenN-H)CoO$_2$CC$_6$H$_3$(3NO$_2$)OH]$^+$. The CTAB micelle, however, retards the second-order base hydrolysis of the micelle-bound phenoxide species. The dipositive phenol form of the complex binds strongly to the anionic micelle of SDS, but this does not lead to detectable enhancement of its rate of aquation.

Introduction

A recent study by A.C.D.[1] elucidated that the base hydrolysis of the phenoxide species of (αβS)-(salicylato)(tetren)Co(III) involved two pathways, namely, the pseudo-first-order OH$^-$-independent aquation and the second-order OH$^-$-catalyzed base hydrolysis. The rate and activation parameters for the OH$^-$-independent path, in comparison to the relevant data for the corresponding species of *cis*-(salicylato)(NH$_3$)(en)$_2$Co(III) and α-*cis*-(NH$_3$)(salicylato)(trien)Co(III) and related systems (see Table II of ref 1), provided evidence in favor of the internal conjugate base mechanism (ICB) involving the intramolecular phenoxide-assisted generation of the reactive amine conjugate base.[2] A detailed understanding of the ICB mechanism in cobalt(III) and other related systems is at present a rather difficult task due to the lack of data on sufficient number of representative systems.

This paper presents a study of the base hydrolysis of (αβS)-(3NO$_2$-salicylato)(tetren)Co(III) in buffered aqueous media in the presence and absence of cationic and anionic surfactants. The purpose was to generate the phenoxide species of the substrate in an aqueous medium and then partition it to the micellar pseudophase of the surfactants so that its reactivity in this phase can be assessed to support the ICB mechanism cited above. A preliminary report on the effect of CTAB on the base hydrolysis of *cis*-(5-nitrosalicylato)(ammine)bis(ethylenediamine)cobalt(III)[3] indicated that this dipolar substrate (phenoxide form) exchanged into the micellar pseudophase of CTAB in which it underwent base hydrolysis at a rate slightly faster than in the aqueous phase. However, the binding of this substrate with the CTAB micelle was observed to be weak, and the corresponding rate effect was also small. We chose the (3NO$_2$-salicylato)(tetren)Co(III) complex in the present work with the hope of observing enhanced micellar binding of this substrate and hence higher rate effects of the micelles.

Experimental Section

Tetraethylenepentamine was used as obtained from BDH. The bromide analysis of CTAB indicated that the sample has a purity of

99.8%. Sodium dodecyl sulfate (SDS) (Fluka, AG) was purified by repeated crystallization from ethanol and checked for purity by cmc determination (cmc = 0.008 M).[4] All other chemicals were of AR grade. Sodium perchlorate used for ionic strength adjustment was prepared by neutralizing HClO$_4$ with NaOH solution.

(αβS)-(3-Nitrosalicylato)(tetraethylenepentamine)cobalt(III) perchlorate was prepared from (αβ)-chloro(tetraethylenepentamine)cobalt(III) perchlorate as described earlier for the preparation of the corresponding salicylato complex.[1] Anal. Calcd for [Co(C$_8$N$_5$H$_{23}$)-(CO$_2$C$_6$H$_3$)(NO$_2$)OH](ClO$_4$)$_2$: Co, 9.36; N, 13.35. Found: Co, 9.3; N, 13.2. The spectral parameters of the complex measured by a Varian-Cary UV–visible recording spectrophotometer, Model 634S, are as follows [λ$_{max}$, nm (ϵ, M^{-1} cm^{-1})]: 492 (181), 310 (9512), and 228 (29368) in 0.01 M HClO$_4$ medium. These may be compared with corresponding data for the (αβS)-(salicylato)(tetren)Co(III) ion [λ$_{max}$, nm (ϵ, M^{-1} cm^{-1}): 491 (170) and 298 (4318)][1] and for *cis*-(ammine)(3-nitrosalicylato)bis(ethylenediamine)cobalt(III) ion [λ$_{max}$, nm (ϵ, M^{-1} cm^{-1})]: 500 (109) and 312 (6689)].[5]

The pH measurements were made with an Elico digital pH meter, Model LI 120; the reference electrode was filled with saturated NaCl instead of KCl in order to avoid precipitation of KClO$_4$ and KDS during pH measurements.

The kinetics of hydrolysis of the cobalt(III) substrate was investigated at 30.0 ± 0.1 °C in the pH range 7.32 ⩽ pH ⩽ 10.1. The reaction was initiated by injecting 0.15 mL of stock solution of the complex into the preequilibrated reaction mixture (3 mL) taken in a 10-mm quartz cell placed in the thermostated cell compartment of the spectrophotometer. The mixing time was <15 s. The rate of decrease of absorbance (measured against solvent blank) at 400 or 450 nm was monitored manually or by a Varian 9176 strip chart recorder. Runs were made under pseudo-first-order conditions with [complex]$_T$ = (0.29–3.20) × 10^{-4} M.

Results and Discussion

The complex ion is remarkably stable to aquation but it undergoes base hydrolysis quite rapidly. In mild alkaline medium, it dissociates to the highly absorbing phenoxide species, [Co(tetren)(O$_2$CC$_6$H$_3$(3NO$_2$)O]$^+$, which exhibits λ$_{max}$ at 400 nm with ϵ = 8054 M^{-1} cm^{-1} (see Figure 1).

(1) Dash, A. C.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 4011.
(2) Dash, A. C.; Mohanty, B. *J. Inorg. Nucl. Chem.* **1978**, *40*, 309.
(3) Dash, A. C. *Indian J. Chem., Sect. A* **1984**, *23A*, 421.

(4) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic: New York, 1975; p 20.
(5) Dash, M. S.; Dash, A. C. *J. Inorg. Nucl. Chem.* **1976**, *38*, 571.
(6) Dash, A. C.; Khatoon, S.; Nanda, R. K. *Indian J. Chem., Sect. A* **1984**, *23A*, 997.

Figure 1. Spectral changes during the base hydrolysis of [(tetren)-CoO$_2$CC$_6$H$_3$(3NO$_2$)OH]$^{2+}$ ([complex]$_T$ = 1.022 × 10^{-4} M, 28 °C: (1) 0–140 s, (2) 340–465 s, (3) 900–1050 s, (4) 1845–1977 s, (5) 2460–2590 s, (6) 24 h (pH 8.39 for curves 1–6). (a) Spectrum for hydrolysis in 0.006 M HClO$_4$.

Figure 2. Typical ln $(A_t - A_\infty)$ vs. 10^{-2}t (s) plot showing the biphasic nature of base hydrolysis (pH 7.6, 30 °C, λ = 400 nm).

The pseudo-first-order kinetic plots exhibit an initial curvature (Figure 2) that is attributed to the presence of a more reactive isomer, presumably the ($\alpha\beta R$) isomer in the sample. Resolution of the kinetic plots could be achieved in the pH range 7.32 ≤ pH ≤ 8.70. At pH >8.7, the fast-reacting isomer decays too fast and the initial curvature of the rate plots virtually disappears. k_{obsd} for the slow second phase of the reaction could be obtained from the gradients of the plots of ln $(A_t - A_\infty)$ against t (s). k_{obsd} values for the fast initial phase of the reaction were obtained by the method of Brown and Fletcher.[7]

Acid Dissociation Constant (K_1) of the Unbound Phenol Group. The extrapolated zero-time absorbance data (ϵ_{obsd}, M^{-1} cm^{-1}) for the complex at 400 nm obtained from the fast phase of the reaction at 7.32 < pH < 8.7 were interpreted in terms of the acid dissociation equilibrium

$$\text{ROCOC}_6\text{H}_3(3\text{NO}_2)\text{OH}^{2+} \overset{K_1}{\rightleftharpoons} \text{ROCOC}_6\text{H}_3(3\text{NO}_2)\text{O}^+ + \text{H}^+ \tag{1}$$

where R denotes (tetren)Co^{3+}. The phenoxide species was observed to be due to a relatively stronger absorbing species at the wavelength of measurement. Assuming that the value of K_1 is

(7) Brown, H. C.; Fletcher, R. S. *J. Am. Chem. Soc.* **1949**, *71*, 1845.

Figure 3. Determination of dissociation constant of the unbound phenol group: 10^5($\epsilon_{obsd} - a$)[H$^+$] (cm^{-1}) vs. 10$^{-4}\epsilon_{obsd}$ (M^{-1} cm^{-1}) plot.

Scheme I

$$\text{R}=(\alpha\beta S)\text{- or } (\alpha\beta R)\text{-(tetren)Co}^{III}$$

not influenced by the isomer distribution, ϵ_{obsd} can be easily represented as

$$\epsilon_{obsd} = \{(\epsilon_s A + \epsilon_r)/(1 + A) + [(\epsilon_s' A + \epsilon_r')/(1 + A)]K_1/[\text{H}^+]\}/(1 + K_1/[\text{H}^+]) \tag{2}$$

where A = ratio of the concentration of the two isomers in the sample = $[\alpha\beta S]_T/[\alpha\beta R]_T$, ϵ_s and ϵ_r (ϵ_s' and ϵ_r') denote the molar extinction coefficients of the phenol form (phenoxide form) of the ($\alpha\beta S$) and ($\alpha\beta R$) isomers, respectively. Equation 2 on linearization yields eq 3, where $a = (\epsilon_s A + \epsilon_r)/(1 + A) = \epsilon_{obsd}$ in the

$$(\epsilon_{obsd} - a)[\text{H}^+] = b - K_1\epsilon_{obsd} \tag{3}$$

acidic medium and $b = K_1(\epsilon_s' A + \epsilon_r')/(1 + A)$. With $a = 132 \pm 2$ M^{-1} cm^{-1} (pH 3) ϵ_{obsd} data were fitted to eq 3 by a least-squares program adopted to an IBM 1130 computer (see Figure 3), and we obtained $b = (19.7 \pm 0.3) \times 10^{-5}$ cm^{-1} and $K_1 = (1.2 \pm 0.3) \times 10^{-8}$ M (30 °C, $I = 0.3$ M). The value of K_1 agrees well with that of *cis*-(ammine)(3-nitrosalicylato)bis(ethylenediamine)cobalt(III) (p$K_1 = 7.9$, 28 °C, $I = 1.0$ M).[5]

Rate Data in the Absence of Surfactants. k_{obsd} data for both slow ($\alpha\beta S$) and fast ($\alpha\beta R$) reacting isomers are strongly sensitive to pH (see Table I). Scheme I presents the possible reaction pathways for which k_{obsd} is given by eq 4, where K_w denotes the

$$k_{obsd} = \frac{(k_0 K_1 + k_1 K_w) + k_2 K_1 K_w/[\text{H}^+]}{[\text{H}^+] + K_1} \tag{4}$$

ionic product of water, k_i's are the rate constants (see Scheme

Table I. Rate Data for Base Hydrolysis of [(tetren)CoO$_2$CC$_6$H$_3$(3NO$_2$)OH]$^{2+}$ at I = 0.3 M and 30.0 ± 0.1 °C

pH[a]	$10^2 k_{obsd}(\alpha\beta R)$, s^{-1}	$10^2 k_{calcd}$,[b] s^{-1}	$10^3 k_{obsd}(\alpha\beta S)$, s^{-1}	$10^3 k_{calcd}$,[b] s^{-1}	pH[a]	$10^3 k_{obsd}(\alpha\beta S)$, s^{-1}	$10^3 k_{obsd}$,[b] s^{-1}
7.32	0.72 ± 0.03	0.74	0.23 ± 0.01	0.23	9.20	1.46 ± 0.02	1.57
7.60	1.36 ± 0.03	1.16	0.36 ± 0.01	0.36	9.27	1.64 ± 0.02	1.71
7.86	1.45 ± 0.04	1.60	0.48 ± 0.01	0.49	9.28	1.52 ± 0.04	1.74
7.90	1.82 ± 0.06	1.68	0.55 ± 0.01	0.52	9.49	2.14 ± 0.04	2.32
8.06	2.02 ± 0.08	1.96	0.56 ± 0.01	0.60	9.59	2.64 ± 0.05	2.72
8.14	2.26 ± 0.09	2.10	0.67 ± 0.01	0.65	9.55	2.91 ± 0.03	2.55
8.20	2.85 ± 0.15	2.21	0.80 ± 0.02	0.69	9.73	2.85 ± 0.07	3.44
8.32	2.19 ± 0.07	2.40	0.73 ± 0.01	0.75	9.76	3.92 ± 0.05	3.63
8.45	2.60 ± 0.09	2.62	0.80 ± 0.01	0.83	9.77	4.46 ± 0.13	3.70
8.55	3.01 ± 0.14	2.80	0.90 ± 0.01	0.89	9.86	3.73 ± 0.11	4.35
8.61	3.03 ± 0.14	2.91	0.95 ± 0.01	0.93	9.89	5.26 ± 0.10	4.61
8.73	3.08 ± 0.12	3.14	1.00 ± 0.01	1.01	9.97	4.43 ± 0.13	5.37
8.75			1.32 ± 0.02	1.03	10.01	6.29 ± 0.10	5.81
8.87			1.18 ± 0.02	1.14	10.07	6.11 ± 0.10	6.55
9.08			1.30 ± 0.02	1.38	10.12	6.59 ± 0.18	7.25

param	$(\alpha\beta R)$ isomer	$(\alpha\beta S)$ isomer	param	$(\alpha\beta R)$ isomer	$(\alpha\beta S)$ isomer
$10^{11}(k_0 K_1 + k_1 K_w)$, s^{-1} M	47.5 ± 2.3	1.46 ± 0.23	k_0,[d] s^{-1}	(2.84 ± 0.13) × 10^{-2}	(8.6 ± 2.2) × 10^{-4}
$10^{20}(k_2 K_1 K_M)$, s^{-1} M^2	20.2 ± 10.4	0.82 ± 0.19	k_1,[e] s^{-1} M^{-1}	(1.89 ± 0.09) × 10^4	(5.8 ± 1.9) × 10^2
$10^9 K_1$, M	16.7[c]	16.9 ± 3.5	k_2, s^{-1} M^{-1}	(4.7 ± 2.4) × 10^2	(18.8 ± 5.8)

[a] 2-Methylimidazole–HClO$_4$ buffer for pH 8.4–9.1, Tris base–HClO$_4$ buffer for pH 7.32–8.73; borate buffer for pH 7.86–9.59, and 2-amino-ethanol–HClO$_4$ buffer for pH 9.77–10.12. [b] See eq 3. [c] K_1 was held fixed at this value to calculate errors of other parameters. [d] k_1 path is assumed to be nonexistent. [e] k_0 path is assumed to be nonexistent and K_w = 2.58 × 10^{-14} M^2: Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., Reinhold: New York, 1958; p 485.

I), and K_1 is as defined earlier (eq 1). The rate data were fitted to eq 4 by a computer program that varied the parameters ($k_0 K_1$ + $k_1 K_w$), $k_2 K_1 K_w$, and K_1 and minimized the sum of the weighted residuals $\sum[(k_{calcd} - k_{obsd})/\sigma(k_{obsd})]^2$. K_1 being known, the approximate values of other parameters were judged from the $k_{obsd}([H^+] + K_1)$ against $[H^+]^{-1}$ plots. The calculated values of the parameters of eq 4 and the optimized values of k_0 and k_1 are given in Table I. It is of interest to note that the fast reacting isomer is ≃ 30 times more reactive than the slow reacting isomer (k_{fast}/k_{slow} = 32.5, 32.8, and 25 for k_0, k_1, and k_2 paths, respectively). A similar reactivity difference is exhibited by $(\alpha\beta R)$ and $(\alpha\beta S)$ isomers of [(tetren)CoCl]$^{2+}$ ($(\alpha\beta R) > (\alpha\beta S)$) in the base hydrolysis path (see Table II of ref 1). The observed trend in the reactivity of the isomers is presumably associated with their strain energies.[8] A comparison of the values of k_0 and k_2 for the slow-reacting isomer with the corresponding data for $(\alpha\beta S)$-(salicylato)(tetren)Co(III) (k_0 = 0.3 s^{-1}, k_2 = 5.5 s^{-1} M^{-1} at 30.1 °C, I = 1.0 M)[1] reveals a 30 times rate enhancement in the k_0 path with a comparable rate in the k_2 path when 3-nitrosalicylate is replaced by salicylate. The reactivity trend in the k_0 path parallels the basicity of the unbound phenoxide group; K_1 = 16.9 × 10^{-9} M (I = 0.3 M, 30 °C) and 13 × 10^{-12} M (I = 1.0 M, 30 °C)[9] for 3-nitrosalicylato and salicylato complexes, respectively, in agreement with the operation of an internal conjugate base mechanism, the reactive amine conjugate base being generated by the pendant phenoxide group:

[Co(tetren)O$_2$CC$_6$H$_3$(3NO$_2$)O]$^+$ ⇌

[Co(tetren-H)O$_2$CC$_6$H$_3$(3NO$_2$)OH]$^+$ (5)
ICB
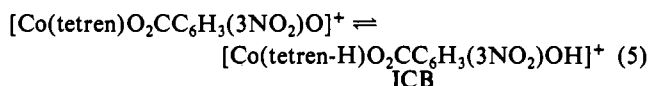
Effect of CTAB on the Rate of Base Hydrolysis. Rate data in Table II (Figure 4) demonstrate the rate accelerating effect of [CTAB] in contrast with retardation by [KBr]. The biphasic nature of the kinetic plots virtually disappeared at all concentrations of CTAB used at pH 9. At pH 8, however, such plots did exhibit initial curvature; but sufficient data points were not available for the initial fast phase of the reaction to resolve the

(8) $(\alpha\beta R)$-[(tetren)CoCl]$^{2+}$ is 2.6 kcal mol^{-1} higher in strain energy than its $(\alpha\beta S)$ analogue: Snow, M. R. *J. Chem. Soc. Dalton Trans.* **1972**, 1627.

(9) Calculated from the relationship[1] K_1 = $Q_1 K_w$ for K_w = 2.5 × 10^{-14} M^2 and Q_1 = 523 M^{-1} at I = 1.0 M, 30 °C, where Q_1 is the forward equilibrium constant of the reaction

$(\alpha\beta S)$-[(tetren)CoO$_2$CC$_6$H$_4$OH]$^{2+}$ + OH$^-$ $\xrightarrow{Q_1}$
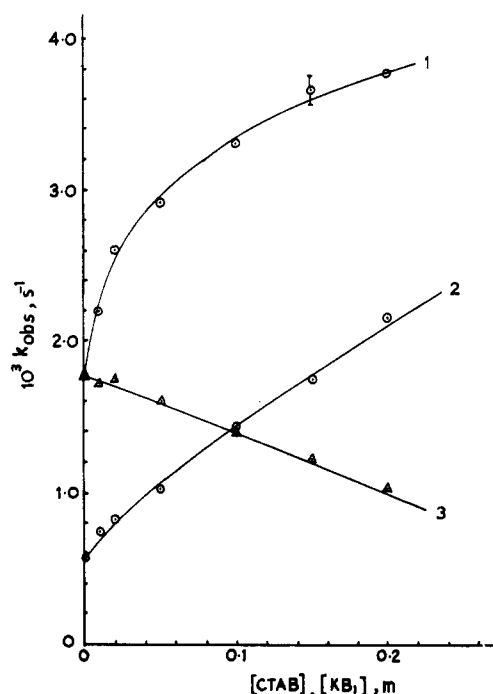
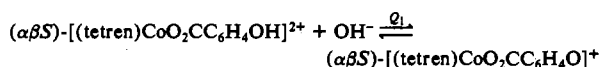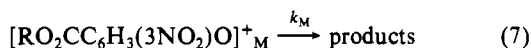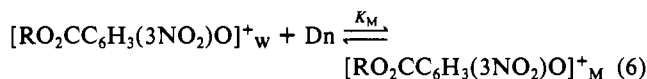$(\alpha\beta S)$-[(tetren)CoO$_2$CC$_6$H$_4$O]$^+$

Figure 4. Effect of [CTAB] (O) and [KBR] (△) on the rate of base hydrolysis of the slow reacting isomer: (1) pH 9.10 ± 0.02; (2) pH 8.03 ± 0.01; (3) pH 9.05 ± 0.05.

Table II. Effect of [CTAB] and [KBr] on the Rate of Base Hydrolysis of $(\alpha\beta S)$-[(tetren)CoO$_2$CC$_6$H$_3$(3NO$_2$)OH]$^{2+}$ at 30.0 ± 0.1 °C

[CTAB]$_T$, M	$10^3 k_{obsd}$,[c] s^{-1} pH 8.03 ± 0.01[a]	pH 9.10 ± 0.02[b]	[KBr]$_T$, M	pH	$10^3 k_{obsd}$, s^{-1}
0.00	0.56 ± 0.01	1.76 ± 0.02			
0.01	0.755 ± 0.004	2.20 ± 0.02	0.01	9.13	1.72 ± 0.02
0.02	0.923 ± 0.006	2.50 ± 0.02	0.02	9.11	1.74 ± 0.02
0.05	1.22 ± 0.01	2.90 ± 0.02	0.05	9.08	1.59 ± 0.01
0.10	1.42 ± 0.01	3.30 ± 0.02	0.10	9.02	1.39 ± 0.01
0.15	1.75 ± 0.05	3.67 ± 0.08	0.15	9.00	1.22 ± 0.01
0.20	2.17 ± 0.01	3.77 ± 0.13	0.20	8.98	1.04 ± 0.01

[a] Tris base/Tris–HCl = 0.02 M/0.02 M. [b] [NaH$_2$BO$_3$]/[H$_3$BO$_3$] = 0.02 M/0.02 M. [c] 0.02 ≤ I_{calcd} ≤ 0.04 M based on cmc = 5.0 × 10^{-4} M and α (degree of dissociation of the CTAB micelle)[12] = 0.2.

kinetics with good precision. A qualitative estimate of the effect of [CTAB] on the k_{obsd}(fast) value at pH 8.03 ± 0.01 is, however, as follows: $10^2 k_{obsd}$(fast) = 0.021, 0.03, 0.038, and 0.042 s^{-1} at $[CTAB]_T$ = 0, 0.01, 0.02, and 0.05 M, respectively. Nevertheless, these data do indicate the rate-accelerating effect of CTAB for the fast-reacting isomer also. Reasonable assumptions to interpret the rate data are as follows: (i) the phenoxide species being dipolar in nature ($R^{2+}XO^-$) can be reversibly bound to the cationic micellar pseudophase of the surfactant; (ii) the dipositive phenol form ($RXOH^{2+}$) exists exclusively in the aqueous pseudophase in equilibrium with its phenoxide form; (iii) the micellar binding equilibrium for the phenoxide species is established rapidly;[10] (iv) the phenoxide species hydrolyzes in the micellar pseudophase much faster than in the aqueous pseudophase. Another very important and useful assumption is that the buffer equilibria in aqueous phase is not appreciably perturbed by the surfactant. This is supported by the constancy of the intermicellar pH of Tris (pH 8) and borate buffers (pH 9).[11,12] A reasonable reaction scheme, therefore, will involve micelle-mediated paths 6 and 7 in addition to those presented in Scheme I.

$$[RO_2CC_6H_3(3NO_2)O]^+_W + Dn \xrightleftharpoons{K_M} $$
$$[RO_2CC_6H_3(3NO_2)O]^+_M \quad (6)$$

$$[RO_2CC_6H_3(3NO_2)O]^+_M \xrightarrow{k_M} products \quad (7)$$

In reactions 6 and 7, the subscripts W and M stand for the aqueous and micellar pseudophases, respectively, and Dn denotes the micellized surfactant. The spectral measurement indicated that one of the products is 3-nitrosalicylate ion reversibly bound to the micellar pseudophase. The other product was assumed to be $(\alpha\beta S)$-[(tetren)CoOH]$^{2+}$ since no other cobalt(III) product was obtained in the base hydrolysis reaction in the presence of KBr. At constant pH and under pseudo-first-order conditions of $[CTAB]_T$, k_{obsd} takes the form

$$k_{obsd} = \frac{k^W_{obsd}([H^+]_W + K_1) + k^M K_1 K_M[Dn]}{[H^+]_W + K_1 + K_1 K_M[Dn]} \quad (8)$$

where $k_{obsd} = k^W_{obsd}$ at $[CTAB]_T = 0$, $[Dn] = [CTAB]_T - cmc$, and k^M denotes the pseudo-first-order hydrolysis rate constant for the micellar-bound phenoxide species. The ionic strength of the aqueous pseudophase for both borate and Tris buffer media based on α (the degree of ionization of the micelle)[12] = 0.2 varies to a small extent ($I = 0.03 ± 0.01$ M) in the range of $[CTAB]_T$ used. But the rate data under varying [KBr] indicate that the effect of ionic strength on k_{obsd} is negligible at $I < 0.04$ M once pH is held constant. The effect of ionic strength variation was neglected, and the rate data in the presence of CTAB were fitted to eq 9 obtained from eq 8. Cmc was taken to be $5.0 × 10^{-4}$ M

$$(k_{obsd} - k^W_{obsd})^{-1} = $$
$$(k^M - k^W_{obsd})^{-1} + [(k^M - k^W_{obsd})K_1 K_M]^{-1}([H^+]_W + K_1)[Dn]^{-1} \quad (9)$$

for both buffer systems.[13] The least-squares gradients and intercepts of the double reciprocal plots of $(k_{obsd} - k^W_{obsd})^{-1}$ against $[Dn]^{-1}$ yielded $k_M = (2.3 ± 0.2) × 10^{-3}$ s^{-1} and $K_M = 17.4 ± 1.9$ M^{-1} at pH 8.03 and $k_M = (4.0 ± 0.4) × 10^{-3}$ s^{-1} and $K_M = 26.6 ± 1.9$ M^{-1} at pH 9.10 ± 0.02, using an ionic strength corrected value of $K_1 = 2.9 × 10^{-8}$ M ($I = 0.03$ M).[14] Relatively weaker micellar binding in tris buffer system (pH 8.03) might result from

efficient competition of Cl$^-$ (see footnote a in Table II) with the dipolar complex ion for micellar binding. Values of K_M for binding of substituted phenoxide ions with the CTAB micelle are $>10^3$ M.[15] In the present case the low value of K_M is due to electrostatic repulsion between the bipositive charge center of the substrate and the cationic micelle, which does not allow the hydrophobic part of the tetren complex (unlike that of the substituted phenoxide ions) to penetrate into the interior of the micelle.

It is, however, worth noting that k_M is slightly sensitive to pH, indicating thereby that the OH$^-$-catalyzed path is also available to the dipolar complex ion in the micellar pseudophase. The validity of eq 9 also suggests that intramicellar [OH$^-$] ([OH$^-$]$_M$) is not appreciably altered in the range of $[CTAB]_T$ used for both buffer systems and pH conditions. Assuming [OH$^-$]$_M \propto$ [OH$^-$]$_W$ an empirical correction is applied as is shown in eq 10, which yields

$$k_M = (k_0)_M + (k_2)_M[OH^-]_M = (k_0)_M + C(k_2)_M K_W/[H^+]_W \quad (10)$$

$(k_0)_M = (2.2 ± 0.2) × 10^{-3}$ s^{-1} and $C(k_2)_M K_W = 1.44 × 10^{-12}$ s^{-1} M, where K_W is the ionic product of water in the aqueous pseudophase and the constant C^{16} may be given by

$$C = (1/\bar{V})K_M K_{OH/Br}[Br^-]_M/[Br^-]_W$$

It is to be noted that $(k_0)_M = k_M$ at pH 8.03; $(k_2)_M$ turns out to be 3.5 M^{-1} s^{-1}, taking the selectivity parameter $K_{OH/Br} = 0.08$, $K_M = 26.6$ M^{-1} $K_W = 2 × 10^{-14}$ M^2 ($I = 0.03$ M),[17] $\bar{V}$ ($\equiv$partial molar volume of the micellized surfactant) = 0.37 L mol^{-1} (calculated),[16] and the mean value of [Br$^-$]$_M$/[Br$^-$]$_W$ = 3.6 in borate buffer system. Bunton and co-workers,[18] however, estimated the molar volume of the Stern layer of the micelle of CTAB, in which the exchangeable ions are likely to be present, as 0.14 L. Using this value of $\bar{V}$, we obtain $(k_2)_M = 1.3$ M^{-1} s^{-1}. The calculated value of $(k_2)_M/(k_2)_W$ (=0.19 or 0.07 for $\bar{V} = 0.37$ or 0.14 L mol^{-1}, respectively) reflects the rate-decelerating effect of the cationic micelle of CTAB on the second-order base hydrolysis path. However, a comparison of the values of $(k_2)_M$ for the tetren–3NO$_2$-salicylato complex with that of cis-(NH$_3$)-(5NO$_2$-salicylato)(en)$_2$Co(III) (($k_2)_M = 3.1 × 10^{-3}$ M^{-1} s^{-1} at 35 °C)[20] presumably indicates a relatively stronger micellar effect for the former.

The spontaneous aquation rate constant of $(\alpha\beta S)$[(tetren)-CoO$_2$C$_6$H$_3$(3NO$_2$)OH]$^{2+}$ is expected to be comparable to that of the corresponding salicylato complex, which is $(2.0 ± 0.4) × 10^{-6}$ s^{-1} at 75 °C ($I = 1.0$ M).[6] In the absence of the *ICB* mechanism the aquation rate constant of the tetren–phenoxide species is also expected to be less than that of its phenol form since the former will involve displacement of 3-nitrosalicylate dianion and the latter the corresponding univalent anion from the same cobalt(III) center.[19]

The phenoxide species aquates in the micellar pseudophase of CTAB twice as fast as in the aqueous phase ($(k_0)_M/(k_0)_W = 2$, taking the optimized value of $(k_0)_W = 8.6 × 10^{-4}$ s^{-1}). The

(10) Stilbs, P.; Jermer, J.; Lindman, B. *J. Colloid Interface Sci.* **1977**, *60*, 232.

(11) Bunton, C. A.; Minch, M. J. *J. Phys. Chem.* **1974**, *78*, 1490.

(12) Quina, F. H.; Politi, M. J.; Cuccovia, I. M.; Bumgarten, E.; Martins-Franchetti, S. M.; Caimovich, H. *J. Phys. Chem.* **1980**, *84*, 361.

(13) 0.02 M borate buffer has been reported[12] to reduce the cmc of CTAB from 9.4 × 10^{-4} to 5.0 × 10^{-4} M. A small departure from this value of cmc will not affect the analysis since $[CTAB]_T \gg$ cmc was maintained.

(14) $K_1(I = 0.03$ M) = $K_1(I = 0.3$ M)$[(f'/f'')_{(I=0.3M)}(f''/f')_{(I=0.03M)}]$ where f' and f'' are the activity coefficients of the phenoxide and phenol forms of the complex respectively. f values were calculated by using the Davies equation: Davies, C. W. *J. Chem. Soc.* **1938**, 2093.

(15) Hirose, C.; Sepulveda, L. *J. Phys. Chem.* **1981**, *85*. 3689. Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* **1979**, *83*, 680.

(16) See eq 3 of ref 12. Calculations, using eq 4–7 of ref 12, indicate [Br$^-$]$_M$/[Br$^-$]$_W$ (=3.2–3.95) and I (=0.021–0.04 M) do not vary significantly in a borate-buffered medium of varying $[CTAB]_T$ used (see Table II) to seriously affect the constancy of [OH$^-$]$_M$.

(17) $K_W = 1.47 × 10^{-14}$ M^2 at 30 °C, $I = 0$, was ionic strength corrected by using $f_{H^+} = f_{OH^-} = 0.85$ at $I = 0.03$ M (the mean value of ionic strength (see Table II).

(18) Ai-Lohedan, H.; Bunton, C. A.; Romsted, L. S. *J. Phys. Chem.* **1981**, *85*, 2123.

(19) Unlike the tetren complex, the k_0 path for cis-[(NH$_3$)-(en)$_2$CoO$_2$CC$_6$H$_3$(5NO$_2$)O]$^+$ in the micellar pseudophase of CTAB was too slow to be detected at comparable temperature.[3] This argues against the pendant phenoxide group assisted hydration of the ester carbonyl followed by the acyl cleavage mechanism usually applicable to organic esters since for both systems comparable rates are expected in the micellar phase. Earlier, we also discounted such a possibility from consideration of the activation parameters.[1]

(20) Note that the rate constant in CTAB micelle for the bis(ethylenediamine) complex was reduced to the second-order form[18] (($k_2)_m = k_M × 0.14$ M^{-1} s^{-1}).
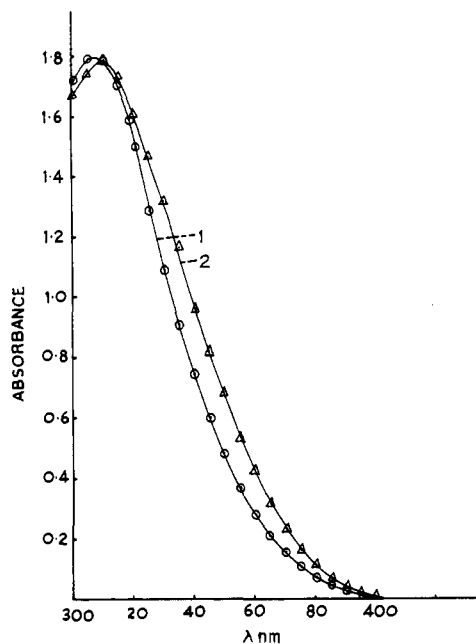
Figure 5. Effect of SDS on the absorption spectrum of [(tetren)-CoO$_2$CC$_6$H$_3$(3NO$_2$)OH]$^{2+}$ at 30 °C; (1) [SDS] = 0.1, [HClO$_4$] = 0.01 M; (2) [SDS] = 0, [HClO$_4$] = 0.01 M; [complex]$_T$ = 2 × 10^{-4} M.

Figure 6. 10$^{-2}\epsilon_{obsd}$ (M^{-1} cm^{-1}) vs. 10^{-2}/[SDS]$_T$ (M^{-1}) plots. [HClO$_4$]$_T$ = 0.005 M; λ_{nm} = 340 (1), 350 (2), and 360 (3).

rate-accelerating effect may be ascribed to (i) a favorable internal conjugate base equilibrium and (ii) easy expulsion of the positively charged cobalt(III) moiety from the dissociative transition state of the internal conjugate base in the cationic micellar pseudophase of CTAB. In both these processes it is likely that polarity of the microenvironment at the binding site of the micelle plays an important role.

Binding of [(tetren)CoO$_2$CC$_6$H$_3$(3NO$_2$)OH]$^{2+}$ with the Anionic Micelle of SDS and Its Effect on the Hydrolysis Rate. Micellar binding of the dipositive complex ion is indicated by the observed spectral changes (see Figure 5). No significant enhancement of the rate of aquation of the phenol species by SDS is indicated. For the micellar binding equilibrium (11), ϵ_{obsd} for the complex is given by eq 12, where ϵ_W and ϵ_M denote the molar extinction

$$(ROXH)^{2+}_W + Dn \underset{\longleftarrow}{\overset{K_M}{\rightleftharpoons}} (ROXH)^{2+}_M \qquad (11)$$
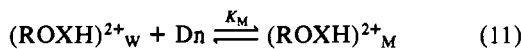
$$\epsilon_{obsd} = \frac{\epsilon_W + \epsilon_M K_M[Dn]}{1 + K_M[Dn]} \qquad (12)$$

coefficients of the phenol species in the aqueous and micellar pseudophases, respectively. Equation 12 can be transformed to eq 13 if $K_M[Dn] \gg 1$ is satisfied. ϵ_{obsd} data at 340, 350, and 360

$$\epsilon_{obsd} = \epsilon_W/K_M[Dn]^{-1} + \epsilon_M \qquad (13)$$

nm fit eq 13 satisfactorily (Figure 6) in the range [SDS]$_T$ = 0.002–0.01 M, taking [Dn] = [SDS]$_t$.[21] ϵ_{obsd} leveled off to a constant value at each of these wavelengths in the range 0.015 < [SDS]$_T$ < 0.1 M. An average value of K_M = (5.2 ± 0.5) × 10^3 M^{-1} was obtained from the slopes of the plots of ϵ_{obsd} against [SDS]$_T^{-1}$ at 340, 350, and 360 nm. The value of (ϵ_W/ϵ_M) was found to be 1.36, 1.45, and 1.56 at 340, 350, and 360 nm, respectively. The value of the binding constant, which is significantly higher than the same for substituted phenols,[22] depicts a strong Coulombic interaction between the anionic micelle and the dipositive complex ion.

The effect of SDS on the rate of base hydrolysis of the complex was examined at 30 °C at constant [OH$^-$]$_T$ = 0.0182 and varying
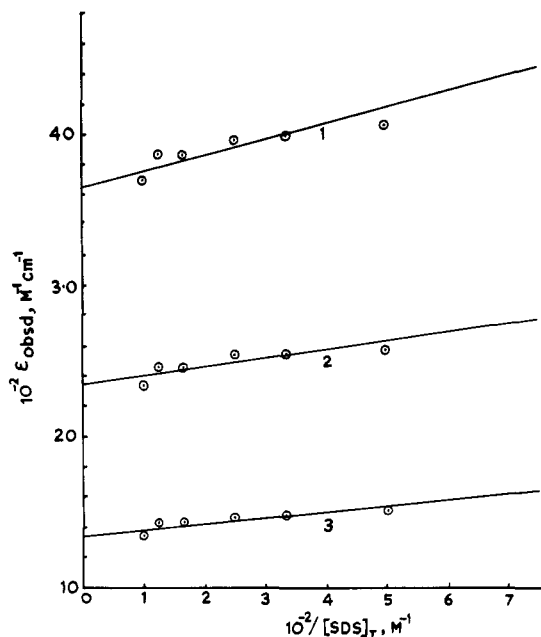
[SDS]$_T$ = 0.0112, 0.04, 0.06, and 0.12 M ([complex]$_T$ = 3.8 × 10^{-5} M). The rate of formation of the highly absorbing 3-nitrosalicylate dianion was followed at 420 nm. At [SDS]$_T$ = 0.0112 M, the rate was immeasurably fast. Absorbance–time data at [SDS]$_T$ = 0.04, 0.06, and 0.12 M yielded good pseudo-first-order kinetic plots from which we obtained SDS-independent k_{obsd} = (4.2 ± 0.1) × 10^{-2} s^{-1}. Hence complete micellar binding is indicated under this condition. For the slow-reacting isomer k_{obsd} at [OH$^-$]$_T$ = 0.0182 M and [SDS]$_T$ = 0 is calculated to be 0.24 s^{-1} (calculated k_{obsd} = k_0 + k_2[OH$^-$]$_T$).[23] Thus unlike CTAB, the anionic surfactant retards the base hydrolysis rate of the complex. This is attributed to the nonavailability of the OH$^-$-catalyzed path for the phenoxide species in the anionic micellar pseudophase of SDS. The spontaneous aquation of the phenoxide species in the anionic micellar pseudophase is 20 times faster than in the cationic micelle of CTAB. This is in complete agreement with the ICB mechanism since the unbound phenoxide ion is expected to be a stronger base in the anionic micelle than in the cationic one. The electrostatic effect of the anionic micelle will also favor separation of the anionic species, $^-$O$_2$CC$_6$H$_3$(3NO$_2$)OH, from the cobalt(III) center in the dissociative transition state of the ICB mechanism to cause rate enhancement.

It is, however, of interest to note that the acid dissociation equilibrium of the complex (eq 1) is strongly favored in the direction of the phenol species in the presence of SDS. This is indicated by the disappearance of the absorption maximum of the phenoxide species at 400 nm and appearance of the absorption maximum of the phenol species at 310 nm in the presence of SDS (0.0112–01.12 M) at pH 9.1. The rate constants (k_{obsd}) for the slow phase of the reaction measured by following the rate of decrease of absorbance at 310 nm averaged to (1.0 ± 0.1) × 10^{-3} s^{-1} at 0.0112 ≤ [SDS]$_T$ ≤ 0.12 M, (pH 9.10 ± 0.01, 30 °C). k_{obsd} may be taken to be the rate constant in the micellar pseudophase. The apparent retardation of base hydrolysis rate by SDS under mildly alkaline pH conditions (k_{obsd} = (1.76 ± 0.02) × 10^{-3} s^{-1} at [SDS]$_T$ = 0, pH 9.11 ± 0.01, 30 °C) indicates that a significant proportion of the complex exists in the micellar pseudophase as the unreactive phenol species in equilibrium with its more reactive phenoxide analogue.

(21) This assumption becomes valid if cmc ≪ 0.002 M. Added salts have been reported to diminish the cmc value of SDS significantly: Cordes, E. H.; Gitter, C. *Prog. Bioorg. Chem.* **1973**, *2*, 1.

(22) For SDS micelle, the binding constants of a series of para-substituted phenols are 5 (H), 13 (*p*-Me), 34 (*p*-Et), 76 (*p*-*n*-Pr), 120 (*p*-*t*-Bu), and 520 M^{-1} (*p*-*t*-Am).[15]

(23) The rate retarding effect of ionic strength on k_2 was neglected in this qualitative comparison.