Mechanistic Information on Fast Reactions of Transition Metal Complexes using Rapid Scan Spectrophotometry. II. The Base Hydrolysis of (αβS)-(Salicylato)(tetraethylenepentamine)cobalt(III) in Aqueous Solution*

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In a recent paper Dash and Harris [2] reported on the kinetics and mechanism of the base hydrolysis of Co(tetren)(salicylato)$^{2+}$ (tetren ≡ tetraethylenepentamine) as part of a series of studies dealing with the hydrolysis of some Co(III) salicylato complexes [3–5]. In general, the phenoxide form of such complexes aquates $\sim 10^3$ faster than the corresponding phenol form. It was suggested that the unbound phenoxide group generates the amine conjugate base in an intramolecular acid-base equilibrium step to account for this reactivity pattern. The tetren phenoxide complex [2] undergoes aquation and base hydrolysis within the stopped-flow time scale, very much faster than any of the other studied salicylato complexes [3–5]. As a result, no spectral parameters of the phenoxide species, which was suggested to account for the instantaneous orange to yellow colour change on addition of base to Co(tetren)-$(OCOC_6H_4OH)^{2+}$, could be determined.

In part I of this series [1] it was demonstrated how rapid scan spectrophotometry could be employed to determine spectral characteristics of unstable intermediates and to provide direct spectral evidence for a changeover in the rate-determining step. We now report our findings on the base hydrolysis of Co-(tetren)$(OCOC_6H_4OH)^{2+}$ using this technique.

Experimental Section

(αβS)-[Co(tetren)$(OCOC_6H_4OH)](ClO_4)_2$ was prepared from the corresponding chloro complex as outlined previously [2]. The UV-visible spectrum of this complex, recorded on a Perkin Elmer 555 spectrophotometer, was in excellent agreement with that found before [2]. Chemicals of analytical reagent grade and doubly-distilled water were used throughout this study. Rapid scan spectra were recorded on an OMA II (Princeton Applied Research) instrument combined with a Durrum Model 110 stopped-flow assembly. This set-up is capable of recording spectra over 250 nm at a rate of 10 msec/track. All measurements were performed at 25.0 ± 0.1 °C.

Results and Discussion

The instantaneous colour change on addition of base to the salicylato complex has been attributed to the formation of the phenoxide species [2].

$$\mathrm{Co(tetren)(OCOC_6H_4OH)^{2+} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} Co(tetren)(OCOC_6H_4O)^+ + H_2O} \qquad (1)$$

Similar changes were observed for $Co(NH_3)_5(OCOC_6H_4OH)^{2+}$ and *cis*-$Co(en)_2(NH_3)(OCOC_6H_4OH)^{2+}$ [6, 7]. The phenoxide species is believed [2] to undergo aquation and base hydrolysis according to the reactions

$$\mathrm{Co(tetren)(OCOC_6H_4O)^+ + H_2O \xrightarrow{k_1} Co(tetren)OH^{2+} + OCOC_6H_4OH^-} \qquad (2)$$

$$\mathrm{Co(tetren)(OCOC_6H_4O)^+ + OH^- \xrightarrow{k_2} Co(tetren)OH^{2+} + OCOC_6H_4O^{2-}} \qquad (3)$$

for which

$$k_{obs} = k_1 + k_2[OH^-] \qquad (4)$$

in the range $[OH^-] = 0.026$–0.9 *M*. At $[OH^-] < 0.026$ *M*, deviations from the straight-line plot of k_{obs} *versus* $[OH^-]$ occurred, from which it was possible to calculate the value for K_1 as 520 ± 160 M^{-1} at 30 °C. It follows that the salicylato complex exists exclusively in the phenoxide form at $[OH^-] \geqslant 0.026$ *M*. Typical values [2] for k_1 and k_2 are 0.116 sec^{-1} and 3.32 M^{-1} sec^{-1} at 25 °C, respectively, from which it follows that $k_{obs} = 1.77$ sec^{-1} (*i.e.* a half-life of 400 msec) at $[OH^-] = 0.5$ *M*. Under these

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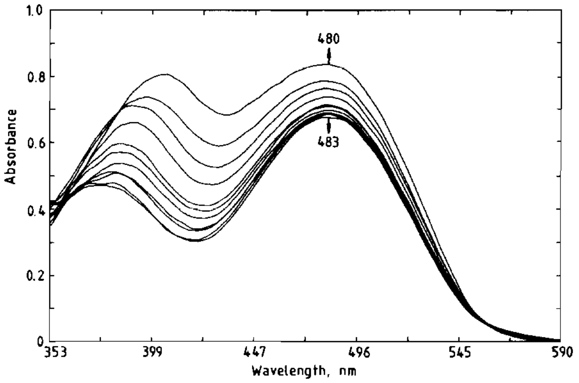

Fig. 1. Repetitive scan spectra recorded during the base hydrolysis of Co(tetren)($OCOC_6H_4OH$)$^{2+}$. [Co(III)] = 3 × 10^{-3} *M*, [OH^-] = 0.5 *M*, Δt ~ 0.1 sec, spectra recorded at 30 msec/scan, optical pathlength = 2 cm.

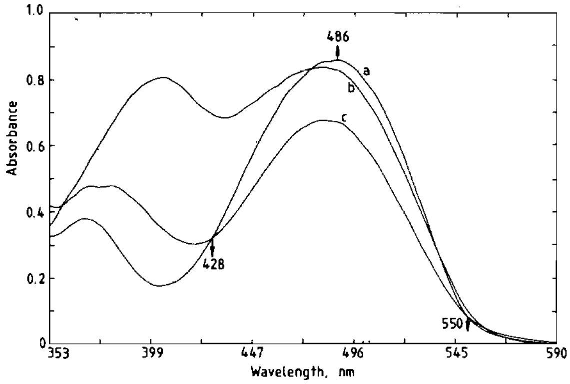

Fig. 2. Accumulation of spectra. (a) Spectrum of Co(tetren)($OCOC_6H_4OH$)$^{2+}$ recorded under similar conditions as for Fig. 1, but mixing with H_2O instead of base in the stopped-flow instrument. (b, c) First and last spectra of Fig. 1 respectively.

conditions the rate of the aquation/hydrolysis process is such that it should be possible to record a spectrum of the phenoxide intermediate using the rapid scan spectrophotometer.

For the interpretation of Figs. 1 and 2 it must be kept in mind that the absorbance maxima at $\lambda \leqslant$ 400 nm is an artificial 'cut-off' effect [1], since the studied species all show strong absorptions in the ultraviolet spectral region [2]. Nevertheless, the repetitive scan spectra in Fig. 1 clearly illustrate that the base hydrolysis process is accompanied by a large spectral change in the UV region. In addition the first spectrum recorded immediately after mixing differs completely from that for the Co(tetren)($OCOC_6H_4OH$)$^{2+}$ species. This is seen more clearly in Fig. 2 where the spectrum of Co(tetren)($OCOC_6H_4OH$)$^{2+}$ is compared with the first and last spectra in Fig. 1, all recorded in the same manner. The significant increase in absorbance around 400 nm on the addition of base to Co(tetren)($OCOC_6H_4OH$)$^{2+}$ is ascribed to the formation of the Co(tetren)($OCOC_6H_4O$)$^+$ species. The subsequent spectral changes in Fig. 1 (b to c in Fig. 2) are due to the base hydrolysis process (reactions (2) and (3)), and do not exhibit any characteristic isosbestic points. Spectra a and c in Fig. 2 intersect at 428 and 550 nm, close to the point observed in kinetic runs with a conventional spectrophotometer, *viz.* 421 and 548 nm, respectively.

The Co(tetren)($OCOC_6H_4O$)$^+$ species has a maximum absorption at 480 nm for which $\epsilon \approx 150\ M^{-1}\ cm^{-1}$, which is very similar to that for the protonated salicylato species [2]. The increase in absorption at $\lambda \leqslant 400$ nm on deprotonation of the salicylato ligand can be interpreted as evidence for the suggested [2] internal acid–base equilibration through hydrogen bonding of the type

$$\text{–}NH_2\text{———}OC_6H_4OCO\text{–} \rightleftharpoons \text{–}NH\text{———}HOC_6H_4OCO\text{–}$$

during which the more reactive conjugate base complex is generated. The deprotonation of the ammine group, *i.e.* tetren ligand, is expected to influence the d–d transitions of the metal center significantly more than the deprotonation of the salicylate ligand, since the former is bound directly to the metal atom. This internal acid–base equilibration not only accounts for the observed kinetic effects [2], but also for the large absorbance changes in the UV region and the almost constant absorbance in the visible region. We observed very similar spectral changes when base was added to Co(NH_3)$_5$($OCOC_6H_4OH$)$^{2+}$ [6, 8]: a very large increase in absorbance at $\lambda \leqslant 450$ nm and hardly any change at the maximum of the salicylato species. In line with the above arguments this change could also be interpreted as evidence for an internal acid–base equilibration. Similar effects may account for the spectral changes [7] on adding base to a series of salicylato complexes of the type *cis*-Co(en)$_2$(NH_3)($OCOC_6H_3$(X)OH)$^{2+}$ where X = H, 5-Br, 5-SO_3^-, 5-NO_2 and 3-NO_2.

Finally, it should be mentioned that Ogino [9] reported the formation of a strong-charge tranfer band at $\lambda \leqslant 350$ nm during the deprotonation of a series of Co(NH_3)$_5$$NH_2$($CH_2$)$_n$$NH_3^{4+}$ (n = 2 to 8 and 10) complexes. The spectral changes are ascribed to intramolecular hydrogen bonding between the free amino group and a N–H proton of the coordinated ammines or amino group. This probably also plays a significant role in the above reported observations and the suggested internal acid–base equilibration.

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References

1 R. van Eldik and G. M. Harris, *Inorg. Chim. Acta, 70,* 147 (1983).

2 A. C. Dash and G. M. Harris, *Inorg. Chem., 20,* 4011 (1981).

3 A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem., 39,* 1179 (1977).

4 A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem., 40,* 309 (1978).

5 A. C. Dash and B. Mohanty, *Transition Met. Chem., 5,* 183 (1980).

6 E. S. Gould and H. Taube, *J. Am. Chem. Soc., 86* , 1318 (1964).

7 M. S. Dash and A. C. Dash, *J. Inorg. Nucl. Chem., 38,* 571 (1976).

8 A. C. Dash and G. M. Harris, *Inorg. Chem., 21,* 2336 (1982).

9 H. Ogino, *Inorg. Chem., 19,* 1619 (1980).