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Mechanistic Information on Fast Reactions of Transition Metal Complexes Using Rapid Scan Spectrophotometry.
III. The Acid-Catalyzed Aquation of a Series of Co(III) Carbonato Complexes in Aqueous Solution [1]

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The acid-catalyzed aquation reactions of $Co(NH_3)_5OCO_2^+$, β-cis-$Co(edda)CO_3^-$ *and* $Co(nta)CO_3^{2-}$ *were re-investigated using rapid scan spectrophotometry. Direct spectral evidence for the participation of protonated and ring-opened carbonato species is now provided. The observations underline the validity of the earlier suggested decarboxylation mechanisms, and enable a comparison of the spectral data for unstable carbonato intermediates.*

Introduction

In a series of papers [2–10] Harris and co-workers used kinetic evidence to show that the acid-catalyzed decarboxylation of monodentate carbonato complexes in general follows the mechanism outlined in Scheme I

$$ML_5OCO_2^{n+} + H^+ \rightleftharpoons ML_5OCO_2H^{(n+1)+} \qquad 1/K_1$$

$$ML_5OCO_2H^{(n+1)+} \longrightarrow ML_5OH^{(n+1)+} + CO_2 \qquad k_2$$

$$ML_5OH^{(n+1)+} + H^+ \rightleftharpoons ML_5OH_2^{(n+2)+} \qquad 1/K_3$$

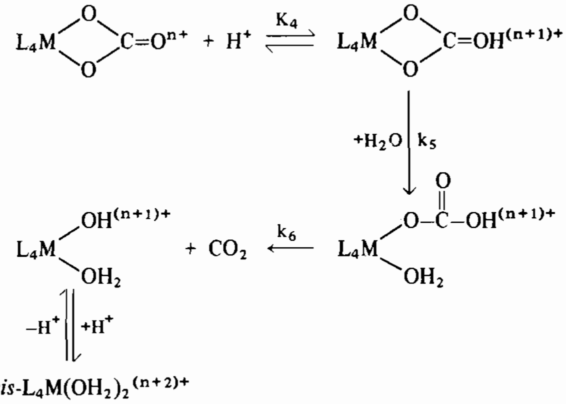
Scheme I. M = Co(III), Rh(III), Ir(III); L_5 = ligands with nitrogen, oxygen or halide donor atoms.

In this mechanism only the protonated carbonato intermediate undergoes decarboxylation via O–C bond breakage (k_2), such that

$$k_{obs} = k_2[H^+]/([H^+] + K_1) \qquad (1)$$

Plots of k_{obs} *versus* pH result in typical sigmoid-shaped curves from which it follows that pK_1 approx. equals the pK_a value of $CO_2(aq)$, and $k_{obs} = k_2 \sim 1\ sec^{-1}$ at $[H^+] \gg K_1$ and 25 °C.

The decarboxylation of bidentate carbonato complexes occurs according to a different mechanism [8, 11–17], as indicated in Scheme II. During the first step a ring-opened (M–O bond breakage) bicarbonato complex is produced, which undergoes rapid decarboxylation in the second step to produce the diaquo species.



Scheme II

Under these conditions

$$k_{obs} = k_5K_4[H^+]/\{1 + K_4[H^+]\} \qquad (2)$$

which in general simplifies to eqn. (3) since K_4 is usually very small.

$$k_{obs} = k_5K_4[H^+] \qquad (3)$$

For a number of systems [11, 13, 14, 17] it was found that a limiting value of k_{obs} is reached at high $[H^+]$ and this was ascribed to the situation where the ring-opening rate ($k_5K_4[H^+]$) had been increased to such an extent that decarboxylation (k_6), which is independent of $[H^+]$, became rate-determining.

In an earlier study in this series [18], rapid scan spectrophotometry was employed to detect the ring-opened protonated carbonato intermediate during the acid-catalyzed decarboxylation of $Co(en)_2CO_3^+$ [12, 17], such that direct spectral evidence for the earlier suggested change over in rate-determining step at high $[H^+]$ was provided. Accordingly, we have now re-investigated the acid-catalyzed decarboxylation of $Co(NH_3)_5OCO_2^+$ [2], β-*cis*-$Co(edda)CO_3^-$

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[14] and Co(nta)CO_3^{2-} [13] in an effort to obtain spectral information on the reaction intermediates and the rate-determining steps.

Experimental

[Co$(NH_3)_5OCO_2$]$(ClO_4)_2$ [19, 20], β-KCo(edda)$CO_3 \cdot H_2O$ [21, 22] and K_2Co(nta)$CO_3 \cdot H_2O$ [23] were prepared and recrystallized as described in the literature. Chemical analyses [24] and UV-visible absorption spectra were in good agreement with the theoretically expected values and with those reported in the literature, [2, 25, 14, 22, 13], respectively. Chemicals of analytical reagent grade and doubly-distilled water were used throughout this investigation.

Rapid scan spectra were recorded on an OMA II (Princeton Applied Research) instrument combined with a Durrum Model 110 stopped-flow assembly [1]. All measurements were performed at 25.0 ± 0.1 °C. UV-visible spectra were recorded on a Perkin Elmer 555 spectrophotometer.

The acidification kinetics of these carbonato complexes were repeated using a conventional stopped-flow system. The results were in close agreement with the data reported earlier [2, 13, 14].

Results and Discussion

Acidification of Co$(NH_3)_5OCO_2^+$

In the earlier study [2] of the acid-catalyzed decarboxylation of Co$(NH_3)_5OCO_2^+$ it was found that $pK_1 = 6.4$ and $k_2 = 1.25$ sec^{-1} at 25 °C (Scheme I). This means that at pH $\leqslant$ 5, eqn. (1) reduces to $k_{obs} = k_2$ and the carbonato complex should be present in the protonated form.

The reaction was, therefore, followed under these conditions in the rapid scan spectrophotometer. A typical recording is presented in Fig. 1. On mixing the carbonato complex with perchloric acid to give a final [H^+] of 0.05 *M*, the first recorded spectrum (b) differs significantly from (a), which was obtained in a similar way by mixing the complex solution with water instead of acid in the stopped-flow instrument. Spectrum (a) is in good agreement with that recorded on a conventional spectrophotometer ($\lambda_{max} = 505$ nm, $\epsilon = 94$ M^{-1} cm^{-1} [2, 25]). The difference between spectra (a) and (b) can only be ascribed to the protonation equilibration step in Scheme I (diffusion controlled), such that spectrum (b) is that for the bicarbonato species, *viz.* Co$(NH_3)_5OCO_2H^{2+}$. In these measurements the delay time was approx. 150 msec, which is short in comparison with the half-life of the decarboxylation process (k_2) of ~550 msec under the present conditions. Faster scan rates demonstrated that Co$(NH_3)_5OCO_2H^{2+}$ has a maximum absorbance at 485 nm with $\epsilon \sim 65$ M^{-1} cm^{-1}. The very significant decrease in absorbance at $\lambda \leqslant 400$ nm, where the carbonato complex has no absorbance maximum [26] during protonation of the ligand has been observed for a number of systems [1, 27]. Such strong charge-transfer bands have been ascribed to intramolecular hydrogen bonding between the ligand and a N–H proton of the coordinated amines. The subsequent spectral changes (b to c in Fig. 1) are in agreement with the decarboxylation process during which Co$(NH_3)_5OH_2^{3+}$ is produced.

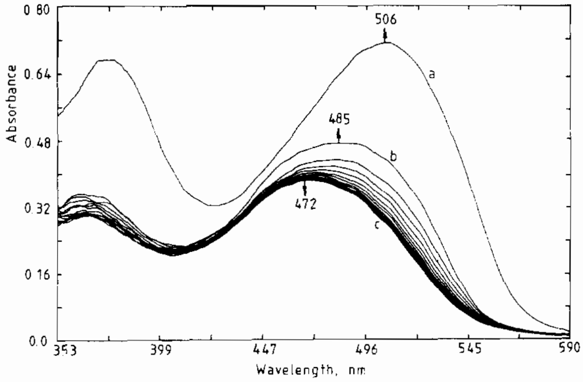

Fig. 1. Rapid scan spectral recordings for the acid-catalyzed aquation of Co$(NH_3)_5OCO_2^+$. [Co(III)] = 4×10^{-3} *M*, [H^+] = 0.05 *M*, ionic strength = 1.0 *M*, optical pathlength = 2 cm, scan rate = 20 msec/track a: spectrum of Co$(NH_3)_5OCO_2^+$ obtained by mixing with water instead of acid; b to c: spectra recorded during aquation with Δt ~ 0.15 sec.

*Acidification of β-*cis*-Co(edda)CO_3^-*

Earlier studies [14, 22] indicated that acidification of β-*cis*-Co(edda)CO_3^- results in the formation of β-*cis*-Co(edda)$(OH_2)_2^+$. At lower acid concentrations the ring opening process in Scheme II, *i.e.* k_5, is rate determining [14, 22], and $k_5K_4 = 2.4 \pm 0.1$ M^{-1} sec^{-1} at 25 °C. A limiting rate constant was observed at high acid concentrations, and it was suggested that decarboxylation became rate-determining under such conditions [14], $k_6 = 2.3$ sec^{-1} at 25 °C. Rapid scan spectra were therefore recorded at various [H^+], and the results are summarized in Figs. 2 to 4.

The repetitive scan spectra in Fig. 2 show a good correlation with those recorded at lower [H^+] on a conventional spectrophotometer. The absorbance maximum at $\lambda \leqslant 400$ nm is blue-shifted by 10 nm due to the 'cut-off' effect [26]. Two clean isosbestic points at 443 and 505 nm characterize the acidification process under these conditions. These differ to some extent from those recorded at lower [H^+], *viz.* 450 and 500 nm. At first we could not account for this difference, but the comparison of spectra in Fig. 3 resolved the discrepancy. In Fig. 3 the spectrum of β-*cis*-Co(edda)CO_3^- (c) is recorded along with the first (a) and last (b) spectra of Fig. 2. It is obvious that spectrum (c), which was measured in the same way as the others (see footnote to Fig. 3), does not

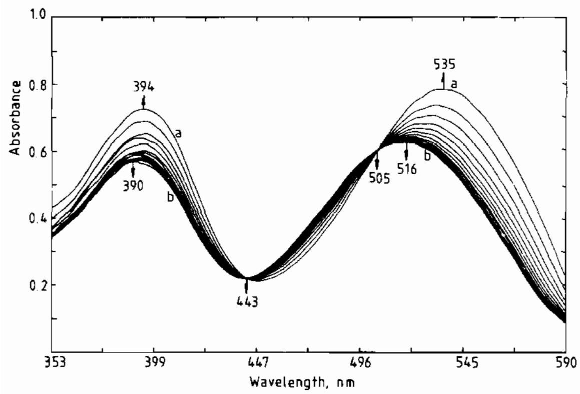

Fig. 2. Rapid scan spectral recordings for the acid-catalyzed aquation of β-*cis*-Co(edda)CO_3^-. [Co(III)] = 2 × 10^{-3} *M*, [H^+] = 0.05 *M*, optical pathlength = 2 cm, scan rate = 30 msec/track, Δt ~ 2 sec.

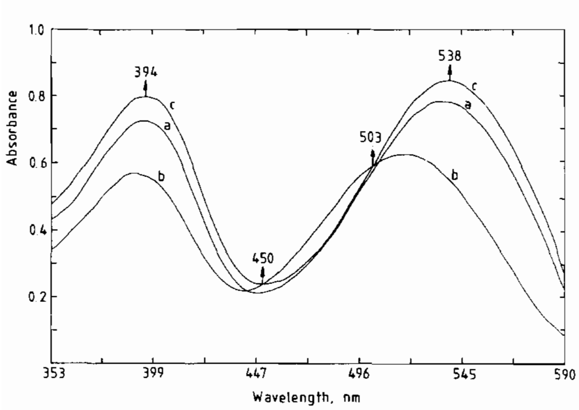

Fig. 3. Accumulation of spectra; a, b: taken from Fig. 2; c: spectrum of β-*cis*-Co(edda)CO_3^- recorded under similar conditions as for Fig. 2, but mixing with water instead of acid solution in the stopped-flow instrument.

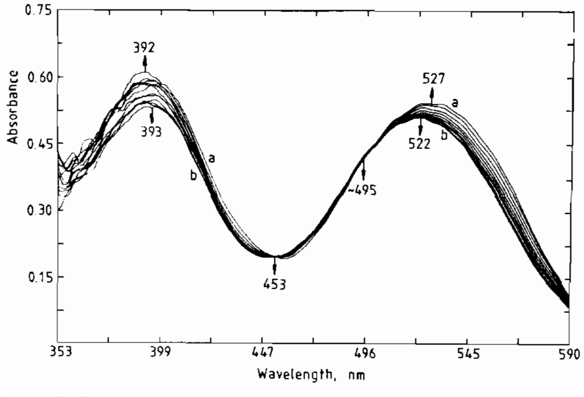

Fig. 4. Rapid scan spectral recordings for the acid-catalyzed aquation of β-*cis*-Co(edda)CO_3^-. [Co(III)] = 2 × 10^{-3} *M*, [H^+] = 2.0 *M*, ionic strength = 2.0 *M*, optical pathlength = 2 cm, scan rate = 10 msec/track, Δt ~ 70 msec.

pass through the isosbestic points of Fig. 2, but intersects with product spectrum (b) at 450 and 503 nm, in close agreement with the isosbestic points observed at lower [H^+]. From this we conclude that the different intersections of spectra (a) and (c) with (b) must be due to the formation of the protonated intermediate, β-*cis*-Co(edda)CO_3H, at higher [H^+] (see Scheme II).

Repetitive scan spectra recorded at [H^+] = 2.0 *M* (Fig. 4) differ again from those reported in Fig. 2. The different time scale (scan rate) on which these spectra were recorded partially accounts for the differences in λ_{max} and the associated extinctions of the product spectrum (b) (Fig. 4). The first spectrum (a) differs significantly from that recorded in Figs. 2 and 3, and is associated with the ring-opened bicarbonato species, β-*cis*-Co(edda)(OH_2)OCO_2H. In addition a clear isosbestic point is observed at 453 nm, and a second less clear one around 495 nm. We conclude that the spectra in Fig. 4 underline the earlier suggested change over in rate-determining step at high [H^+]. Very similar tendencies were recently observed [18] for the acidification of the *cis*-Co(en)$_2$-CO_3^+ species.

Some preliminary experiments were also performed on the acidification of α-*cis*-Co(edda)CO_3^-. Unfortunately the latter species undergoes a fairly rapid isomerization reaction [14] to the β-species, such that no clean isosbestic points could be observed. In addition, the α complex has a limiting rate constant at high [H^+] of 55 sec^{-1} at 25 °C, which makes it almost impossible to record spectra under such conditions with the present instrumentation.

Acidification of Co(nta)CO_3^{2-}

This complex undergoes acid-catalyzed aquation to produce *cis*-Co(nta)(OH_2)$_2$ [13]. Very similar kinetic behaviour to that described in the previous section for the acidification of β-*cis*-Co(edda)CO_3^- was reported for this complex [13]. The ring-opening rate constant (k_5K_4) was found to be 42 M^{-1} sec^{-1} at 25 °C, compared to a value of 57 sec^{-1} for the decarboxylation step (k_6). Rapid scan spectra could only be recorded under conditions where ring-opening is rate-determining, due to the rapidity of the decarboxylation step.

Figure 5 is a typical example of the type of spectral recordings obtained at lower [H^+] where ring-opening is rate-determining. Isosbestic points were observed at 436 and 482 nm. These differ significantly from those expected on the basis of the spectra of Co(nta)CO_3^{2-} and *cis*-Co(nta)(OH_2)$_2$, which intersect at 450, 492 and 580 nm (this work and ref. [13]). The spectrum (c) of the Co(nta)-CO_3^{2-} species was recorded on the rapid scan spectrometer in a similar way as those in Fig. 5 (by mixing with water instead of acid), and is compared with the latter in Fig. 6. We note that spectrum (c) does not pass through the isosbestic points observed in Fig. 5, but intersects with spectrum (b) at 448, 489 and 580 nm. These are in close agreement with

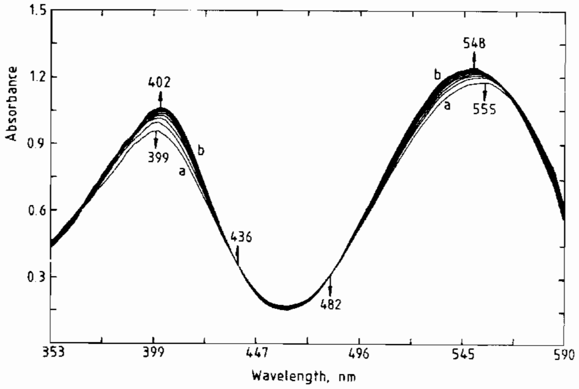

Fig. 5. Rapid scan spectral recordings for the acid-catalyzed aquation of $Co(nta)CO_3^{2-}$. $[Co(III)] = 4 \times 10^{-3}$ *M*, $[H^+] =$ 0.05 *M*, ionic strength = 1.0 *M*, optical pathlength = 2 cm, scan rate = 10 msec/track, $\Delta t \sim 0.15$ sec.

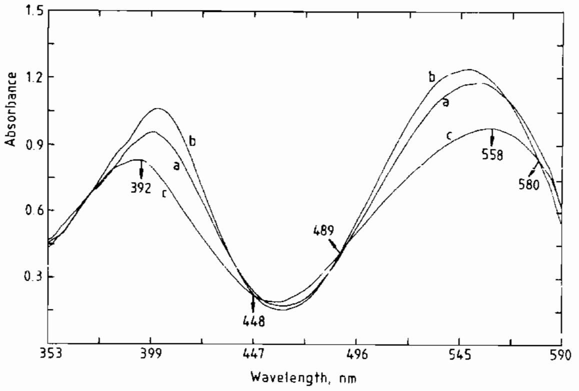

Fig. 6. Accumulation of spectra; a, b: taken from Fig. 5; c: spectrum of $Co(nta)CO_3^{2-}$ recorded under similar conditions as for Fig. 5, but mixing with water instead of acid solution in the stopped-flow instrument.

those recorded on a conventional spectrophotometer as mentioned above. Furthermore, spectra (a) and (c) in Fig. 6 are significantly different, indicating that protonation of the carbonate ligand has occurred under these conditions and spectrum (a) must be associated with the $Co(nta)CO_3H^-$ species. The subsequent spectral changes (a to b in Fig. 5) are ascribed to the ring-opening reaction which is followed by the rapid decarboxylation step (Scheme II).

Finally, the results of this and an earlier study [18] allow an overall comparison of the visible spectra of protonated and ring-opened carbonato intermediates. In all investigated systems, protonation of a mono- or bidentate carbonate ligand causes the visible absorption spectrum to change in the direction towards the corresponding aquo complex (aquation product). This change is very prominent for the monodentate $Co(NH_3)_5OCO_2^+$ species (Fig. 1) and smaller for the bidentate complexes increasing in the order $Co(en)_2CO_3^+$ (ref. [18]) < β-*cis*-$Co(edda)CO_3^-$ (Fig. 3) < $Co(nta)CO_3^{2-}$ (Fig. 6). The latter tendency can probably be correlated with the charge on the complex, which will determine the proton affinity of the carbonate ligand. The spectra of the protonated ring-opened intermediates β-*cis*-$Co(edda)(OH_2)OCO_2H$ (Fig. 4 curve a) and *cis*-$Co(en)_2(OH_2)(OCO_2H^{2+}$ (ref. [18] - Fig. 2) are close to those of the corresponding aquo species, and in good agreement with the observations for the $Co(NH_3)_5OCO_2H^{2+}$ species (Fig. 1 curve b).

The rather significant spectral changes observed immediately on the acidification of β-*cis*-$Co(edda)CO_3^-$ and especially $Co(nta)CO_3^{2-}$, indicates that K_4 may not be small in these cases. It was previously argued [17] that K_4 for the protonation of the carbonyl group could be of the order of 10^{-6} M^{-1} for the $Co(en)_2CO_3^+$ species. However, in the case of anionic carbonato species, protonation may play a larger role and K_4 values in the order of unity may be expected. This would be in line with the spectral changes observed at $[H^+] = 0.05$ *M*, but requires that the limiting rate reached at high $[H^+]$ (see Introduction) be ascribed to the ring-opening rate constant k_5 due to saturation of the preprotonation step. In addition, this could also account for the significantly higher decarboxylation rate constants (k_6) reported for β-*cis*-$Co(edda)CO_3^-$ and $Co(nta)CO_3^{2-}$ [13, 14] than for α-*cis*-$Co(edda)CO_3^-$ [14] and some cationic carbonato species [11].

We conclude that the results of this investigation not only underline the general validity of the previously suggested reaction mechanism, but also furnish spectral information on unstable carbonato intermediates.

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