

## Mechanistic Information on the Acid-catalyzed Decarboxylation of the Carbonatobis(ethylenediamine)cobalt(III) Ion in Aqueous Solution Using Rapid Scan Spectrophotometry

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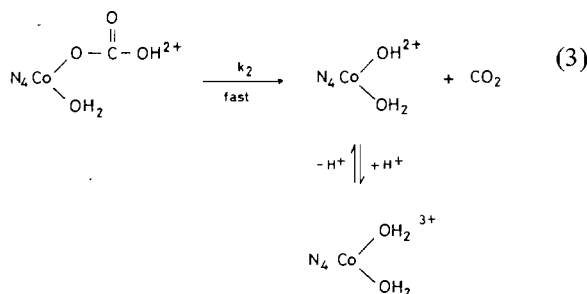
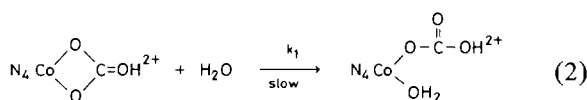
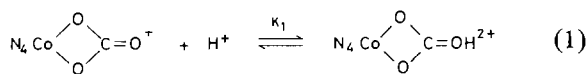
Rapid scan spectrophotometry was employed to detect the ring-opened protonated carbonate intermediate during the acid-catalyzed decarboxylation of  $\text{Co(en)}_2\text{CO}_3^+$  in aqueous solution. Direct spectral evidence for the suggested changeover in the rate-determining step at high acid concentrations is now provided.

### Introduction

In a series of papers Harris and co-workers [1–6] used kinetic evidence to show that the acid-catalyzed decarboxylation of complexes of the type  $\text{CoN}_4\text{CO}_3^+$  ( $\text{N}_4 \equiv$  various tetramine ligand groupings of uni-, bi- or quadridentate type) proceeds in two steps. During the first a ring-opened bicarbonato complex  $\text{cis-CoN}_4(\text{OCO}_2\text{H})\text{OH}_2^{2+}$  is produced, which undergoes rapid decarboxylation (loss of  $\text{CO}_2$ ) in the second step to produce  $\text{cis-CoN}_4(\text{OH}_2)_2^{3+}$ . The first reaction is acid-catalyzed and results in a linear dependence of  $k_{\text{obs}}$  on  $[\text{H}^+]$ . In some cases a small intercept is observed in such plots, which is ascribed to the water-promoted ring-opening process. In general, the first step is rate-determining, whereas the second step is comparatively fast with a rate constant in the order of  $1 \text{ sec}^{-1}$  at  $25^\circ\text{C}$  – a value typical for the decarboxylation of a series of bicarbonato complexes [7].

In a recent mechanistic re-appraisal of the decarboxylation of  $\text{Co(en)}_2\text{CO}_3^+$  ( $\text{en} \equiv$  ethylenediamine), Harris and Hyde [8] considered two alternative mechanisms to account for the first-order hydrogen ion concentration dependence of the ring opening

process, *viz.* a carbonyl preprotonation step followed by rate-determining ring-opening, or a concerted proton-promoted carbonate dechelation process. On the basis of deuterium solvent isotope effects they [8] concluded that the former mechanism is the more acceptable one, formulated as follows



Since  $K_1$  is expected to be small,  $k_{\text{obs}} = k_1 K_1 [\text{H}^+]$  and in general is significantly smaller than  $k_2$ . However, in a number of systems [3–5, 8] it was found that plots of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  reach a limiting value at high  $[\text{H}^+]$  and this was ascribed to the situation that under such extreme conditions reaction (3) becomes the rate-determining step. Since the latter reaction involves decarboxylation of a protonated monodentate carbonate complex,  $k_{\text{obs}}$  will be independent of  $[\text{H}^+]$  [7], and so account for the limiting value of  $k_{\text{obs}}$  at high  $[\text{H}^+]$ . An alternative explanation involv-

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TABLE I. Absorption Spectra of  $\text{Co}(\text{en})_2\text{CO}_3^+$  recorded on a Rapid-scan Spectrophotometer.<sup>a</sup>

$[\text{H}^+]$ $M$	$\lambda_{\text{max}}$ nm	Absorbance <sup>b</sup>	Remarks
0.0	508	$1.139 \pm 0.017$	mean value of all 15 tracks
	509	$1.144 \pm 0.019$	mean value of all 15 tracks
0.1	507	$1.070 \pm 0.008$	mean value of first 7 tracks
	507	$1.083 \pm 0.017$	mean value of first 7 tracks
1.0	499	$0.914 \pm 0.016$	mean value of first 3 tracks
	499	$0.910 \pm 0.015$	mean value of first 3 tracks

<sup>a</sup> $[\text{Co}(\text{III})] = 4.5 \times 10^{-3} M$ , track time = 30 msec, delay = 0.    <sup>b</sup>Optical pathlength = 2 cm.

ing only the protonation equilibrium (1) and reaction (2) as the rate-determining step cannot account [8] for the strong curvature observed in the  $k_{\text{obs}}$  versus  $[\text{H}^+]$  plots.

Up to the present time, the validity of the suggested mechanism has not been supported by direct spectral evidence for the existence of the proposed intermediate species. In this paper we report our observations using rapid scanning spectrophotometry, by means of which we have obtained such evidence.

## Experimental

$[\text{Co}(\text{en})_2\text{CO}_3]\text{ClO}_4$  was prepared by recrystallizing  $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$  [9] from a  $\text{NaClO}_4$  solution. Chemical analyses [10] are in good agreement with the theoretically expected values. The visible absorption spectra, recorded on a Perkin Elmer 555 spectrophotometer, of  $\text{Co}(\text{en})_2\text{CO}_3^+$  ( $\lambda_{\text{max}}$  ( $\epsilon$ ) 510 (131), 357 (120)) and *cis*- $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$  ( $\lambda_{\text{max}}$  ( $\epsilon$ ) 490 (78), 355 (61)) are in good agreement with those reported elsewhere [8, 11]. Chemicals of analytical reagent grade and doubly-distilled water were used in the preparation of all solutions.

Rapid scan spectra were recorded on an OMA II instrument (Princeton Applied Research) combined with a Durrum Model 110 stopped-flow assembly. This set-up is capable of recording spectra over a 250 nm range at a rate of 10 msec/track. All measurements were performed at 25 °C.

## Results and Discussion

In some preliminary measurements we scanned the spectrum of  $\text{Co}(\text{en})_2\text{CO}_3^+$  fifteen times immediately after mixing with water and with diluted acid in the stopped-flow apparatus. The spectrum obtained in the absence of acid (Table I) is very similar to that measured on the conventional spectrophotometer. The absorption around 360 nm could not be measured accurately, since the energy of the tungsten

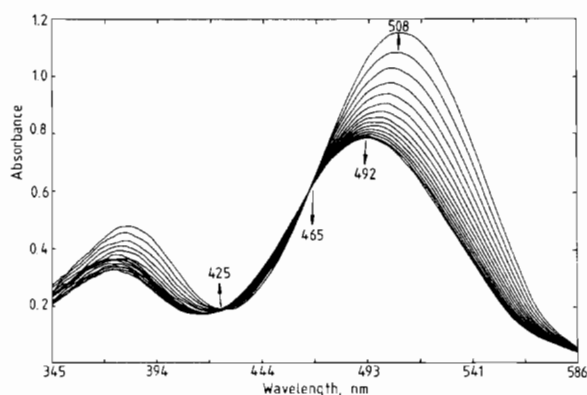


Fig. 1. Rapid scan spectral recordings for the aquation of  $\text{Co}(\text{en})_2\text{CO}_3^+$  in acidic medium.  $[\text{H}^+] = 0.1 M$ ;  $[\text{Co}(\text{III})] = 4.5 \times 10^{-3} M$ ; each spectrum is the average of five scans recorded at 30 ms/scan; delay = 3.6 sec; optical pathlength = 2 cm.

light source falls off rapidly at shorter wavelengths\*. Similarly recorded spectra in the presence of acid show shifts in  $\lambda_{\text{max}}$ , accompanied by decreases in absorbance. At low acid concentration, where reaction (2) is too slow to cause spectral changes during the scanning time over the first 7 tracks, the observed changes can be ascribed to the influence of the protonation step (1). At higher acid concentrations the observed changes are even more drastic, although interference from reactions (2) and (3) cannot be completely ruled out under the conditions concerned. It follows that at least in the low acid con-

\*The resolution of the instrument can be improved significantly in the lower wavelength region by using a Xenon lamp. However, deviations at higher wavelengths then occur due to deviations in the light intensity in this region. The latter can be resolved when the high voltage on the detector target is reduced, but this simultaneously causes an energy cut off at lower wavelengths, such that very similar spectra to those obtained with the tungsten lamp, are recorded.

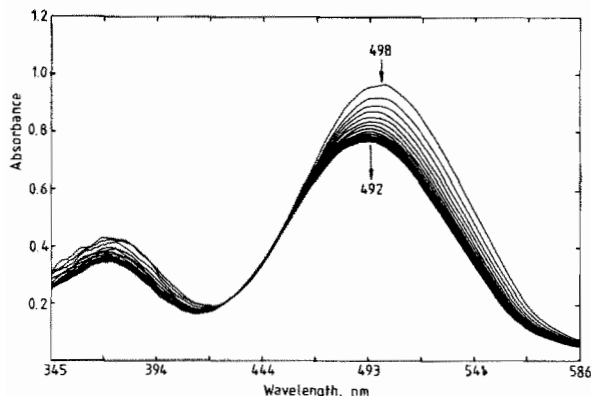


Fig. 2. Rapid scan spectral recordings for the aquation of  $\text{Co(en)}_2\text{CO}_3^+$  in strongly acidic medium.  $[\text{H}^+] = 2.0 \text{ M}$ ;  $[\text{Co(III)}] = 4.5 \times 10^{-3} \text{ M}$ ; each spectrum is the average of five scans recorded at 20 ms/scan; delay = 0.4 sec; optical pathlength = 2 cm.

centration region, the spectral measurements do suggest the presence of a protonated bidentate carbonato species.

According to the earlier reported data [8], plots of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  are linear for  $[\text{H}^+] \leq 0.2 \text{ M}$  and reach a limiting value at  $[\text{H}^+] \geq 1.5 \text{ M}$  during the decarboxylation reaction of  $\text{Co(en)}_2\text{CO}_3^+$ . Similar tendencies were reported for the other mentioned systems [3–5]. We therefore performed rapid-scan measurements at 0.1 and 2.0 M acid, in order to observe the suggested switch over in the rate-determining step and the corresponding spectral changes. The results are recorded in Figs. 1 and 2, respectively. At  $[\text{H}^+] = 0.1 \text{ M}$  (Fig. 1), two clean isosbestic points at 425 and 465 nm are observed, which are in close agreement with those measured at pH = 3 on conventional spectrophotometers, viz. 421 and 465 nm, and 422 and 468 nm\*\*, respectively. Rapid scan recordings at  $[\text{H}^+] = 1.0 \text{ M}$  exhibited similar isosbestic points for the first couple of traces, but deviations occurred at longer reaction times, probably due to the interference of reaction (3) under these conditions. Spectral recordings at  $[\text{H}^+] = 2.0 \text{ M}$  (Fig. 2) showed no distinct isosbestic points and the spectra all coincide at 430 to 450 nm†. It follows that a different mechanistic step is observed under these conditions, which verifies the suggested shift in rate-determining step at high acid

\*\*Recorded on a Cary 118 spectrophotometer.

†Experiments using a Xenon lamp gave almost identical results to those shown in Figs. 1 and 2. A very distinct isosbestic point at 425 nm (for Fig. 1) could be observed in this way.

concentrations. In addition, the first spectrum recorded in Fig. 2 is in close agreement with that reported in Table I at high acid concentration, and which can now be ascribed to the species  $\text{cis-Co(en)}_2(\text{OCO}_2\text{H})\text{OH}_2^{2+}$ . The final spectra recorded in Figs. 1 and 2 are in line with those for the species  $\text{cis-Co(en)}_2(\text{OH}_2)_2^{3+}$ .

The spectral changes in Fig. 2 also enable the estimation of the magnitude of the decarboxylation rate constant  $k_2$ , which is found to be  $0.58 \text{ sec}^{-1}$  at 25 °C. This is in close agreement with the limiting rate constant found by Harris and Hyde [8], and with earlier data reported [12, 13] for the decarboxylation of  $\text{cis-Co(en)}_2(\text{OH}_2)\text{OCO}_2^+$  under similar experimental conditions.

Our rapid scan spectral measurements have provided direct evidence for the earlier suggested reaction mechanism, and have unequivocally clarified the remaining uncertainties. This technique will also be applied to other systems involving rapid uptake and loss of  $\text{CO}_2$  and  $\text{SO}_2$ .

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