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Acid-Catalyzed Hydrolysis of the $[Co(en)_2CO_3]^+$ Ion Revisited

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Introduction

Although there have been a number of studies on the acid-catalyzed aquation of the $[Co(en)_2CO_3]^+$ ion,[1-3] a rigorous mechanistic description is still lacking. This is indeed a pity, since this reaction should provide the basis for understanding one of the most important processes undertaken by metal ions—the mediated hydrolysis of CO_3^{2-}. The present difficulties arise partly from the failure of investigators to follow the reaction at a wavelength where its biphasic nature is fully disclosed (k_1, k_2 in Scheme I) and partly from a lack of appreciation for the acidity of the protonated reactant $[Co(en)_2CO_3H]^{2+}$ (K_a, Scheme I). The expectation has been that K_a is very large ($\sim 10^6$),[2-4] and this assumption has not been tested. Further, the apparent inability of this rapid hydrolytic reaction to yield readily analyzable absorbance–time traces at H^+ concentrations in the range 0.05–1.00 M has led to considerable simplification of the kinetic analysis. Harris and Hyde[2] collected data at 512 and 360 nm but discarded the crucial first 1 s of the data and treated the remainder as if it arose from a single exponential. A further simplification was made through the approximation of the extinction coefficient of the critical *cis*-$[Co(en)_2(OH_2)OCO_2H]^{2+}$ intermediate.[2] Such features would be expected to create problems in the interpretation of this important consecutive first-order process,[5] and indeed the picture that has emerged is one of distorted kinetic parameters, which in turn has led to an incomplete view of the mechanism. It is the purpose of this note to correct these deficiencies.

Experimental Section

The complex $[Co(en)_2CO_3](ClO_4)$ was obtained from $[Co(en)_2CO_3]Cl$[6] by addition of $NaClO_4$ to a warm aqueous solution and recrystallization from water. λ_{max} (ϵ) = 510 nm (133), 360 nm (122).

Rapid-scan spectra (300–600 nm) were obtained using a Durrum D-110 stopped-flow spectrophotometer equipped with a Harrick rapid-scan monochromator. The Durrum instrument was used for conventional kinetic measurements at a fixed wavelength and for measurement of the acidity constant of $[Co(en)_2CO_3H]^{2+}$. Data storage and manipulation were carried out using a North Star Horizon computing system with OLIS software.[7] Reactions followed at 477 nm were normally monitored to 97–98% of the total absorbance change.

All solutions were maintained at I = 1.0 M ($NaClO_4$) and 25.0 °C, unless otherwise specified, and were filtered through Celite prior to use.

The two rate constants k_{fast} and k_{slow} appropriate to the consecutive first-order kinetic scheme $A \rightarrow B \rightarrow C$ were obtained from data collected at 477 nm by use of the OLIS nonlinear least-squares-fitting routine V-DataFit.[7] These rate parameters and the absorbance changes associated with each (ΔA_1 increase, followed by a ΔA_2 decrease) were initially treated as variables and approximate values obtained. The starting absorbance of the reaction mixture was strongly dependent on the hydrogen ion concentration (vide infra),[8] as were both absorbance changes, and better fits were achieved by reducing the number of variables. This was done by setting the rate constant for the faster of the two processes (k_{fast}) to a value of 0.93 s^{-1} independent of hydrogen ion concentration[9] and by maintaining a constant final absorbance (i.e., A_∞ was not treated as a variable and its value was also independent of $[H^+]$). The above approximate values for the absorbance changes and for the smaller of the two rate constants (k_{slow}) were then entered into the routine as estimates, and these were refined to convergence. In some cases, a further small improvement to the fit (as judged from the sum of squares of residuals) could be made by minor manual adjustments to the computed values for the absorbance changes (i.e., these modified values were inserted as fixed parameters). Such adjustments never amounted to more than ±3% of the observed changes and did not significantly alter the value of either rate constant.

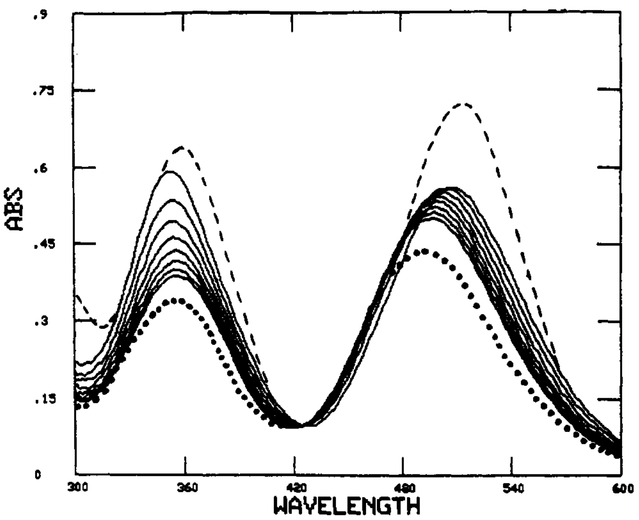
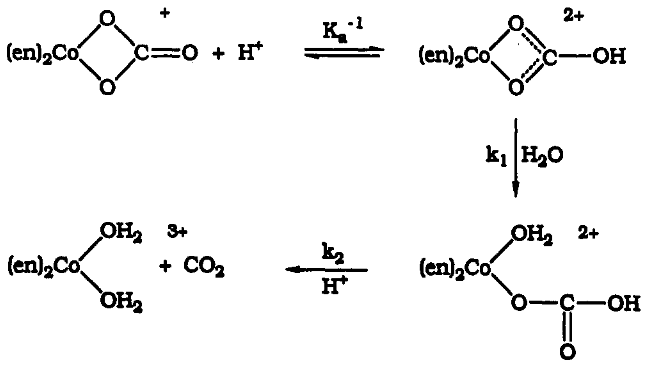


Figure 1. Rapid-scan spectra (path length 2 cm) obtained on mixing $[Co(en)_2CO_3]_{aq}^+$ with $HClO_4$ and recorded over the range 300–600 nm. $[Co]_T$ = 2.86 mM; $[H^+]$ = 2.70 M (eight spectra recorded over 3 s following an initial time delay following mixing of 50 ms). Also shown is the spectrum of the final product *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ recorded after 13-s reaction (•••) and the spectrum of $[Co(en)_2CO_3]^+$ (2.86 mM) in 2.70 M $NaClO_4$ (- - -).

Scheme I



Results and Discussion

Figure 1 shows a series of eight rapid-scan spectra (scan interval 0.43 s) recorded over the range 300–600 nm following mixing a solution of $[Co(en)_2CO_3]^+$ with aqueous $HClO_4$ ($[Co]_T$ = 2.86 mM, $[H^+]$ = 2.70 M). The final spectrum, obtained after a further delay of 10 s (λ_{max} (ϵ) = 493 nm (75), 357 nm (59)), corresponds to that of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$,[6] and the initial spectrum (λ_{max} (ϵ) = 508 nm (98), 352 nm (103)) is markedly

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[1] Harris, G. M.; Sastri, V. S. *Inorg. Chem.* **1965**, *4*, 263. Sastri, V. S.; Harris, G. M. *J. Am. Chem. Soc.* **1970**, *92*, 2943.

[2] Harris, G. M.; Hyde, K. E. *Inorg. Chem.* **1978**, *17*, 1892.

[3] van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* **1983**, *70*, 147.

[4] Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

[5] Jackson, W. G.; Harrowfield, J. M.; Vowles, P. D. *Int. J. Chem. Kinet.* **1977**, *9*, 535.

[6] Springborg, J.; Schaffer, C. E. *Inorg. Synth.* **1973**, *14*, 63. Absorption maxima (λ_{max}, nm) and extinction coefficients (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$) are reported as follows: $[Co(en)_2CO_3]^+$ in water, 511.5 (133), 359.5 (121); *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ in dilute $HClO_4$, 492 (76), 358 (61).

[7] Olis, V-DataFit, On Line Instrument Systems Inc., Jefferson, GA 30549.

[8] This was also the case for measurement at 512 or 360 nm.

[9] In preliminary computations the fit consistently converged to this value irrespective of $[H^+]$ (k_{fast} = 0.93 ± 0.03 s^{-1}), while values for k_{slow} were always within 15% of those obtained finally.

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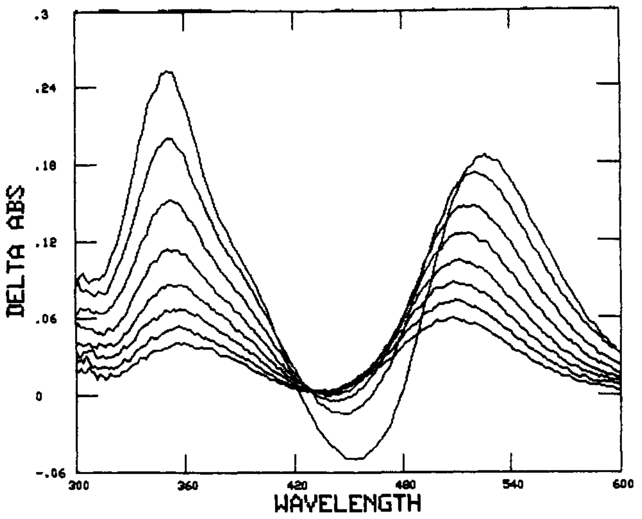

Figure 2. Difference spectra for the traces given in Figure 1, referenced to the final spectrum after 13 s.

Table I. First-Order Rate Constants for the Acid-Catalyzed Aquation of $[Co(en)_2CO_3]^+$ at 25 °C and $I = 1.0$ M ($NaClO_4$)[a]

$[H^+]$/M	k_{fast}^{obs}/s^{-1}	k_{slow}^{obs}/s^{-1}	k_{slow}^{calc}/s^{-1} [b]	k^{obs}/s^{-1} [c]
0.10	0.93	0.0830	0.0897	0.0820
0.20	0.93	0.160	0.162	0.163
0.35	0.93	0.247	0.248	0.245
0.50	0.93	0.327	0.315	0.324
0.60	0.93	0.360	0.352	0.360
0.75	0.93	0.387	0.399	0.386
0.90	0.93	0.440	0.438	0.440
1.00	0.93	0.467	0.460	0.450 (0.362)
2.70[d]	0.93	0.560	–	

[a] Obtained at 477 nm unless otherwise stated. [b] Calculated using eq 1, with $k' = 0.85$ s^{-1} and $K = 1.18$ M^{-1}. [c] Observed rate constants (512-nm data) obtained from plots of $\ln(A_t - A_\infty)$ vs time but using only the last 25–15% of the data. The value in parentheses (1.00 M H^+) represents the "best-fit" rate constant obtained using the last 80% of the data. This corresponds to a 1-s delay before data acquisition and reproduces the conditions used by Harris and Hyde,[2] who reported a rate constant of 0.37 s^{-1}. We also obtained a rate constant of 0.38 s^{-1} from data at 360 nm using all the absorbance–time trace for reaction at this acidity. However, as with the 512-nm data, large departures from true first-order behavior were apparent at early times. [d] $I = 2.70$ M.

different from that of $[Co(en)_2CO_3]^+$ in the presence of 2.70 M $NaClO_4$ (λ_{max} (ϵ) = 512 nm (130), 358 nm (116)). Hydrolysis of $[Co(en)_2CO_3]^+$ in 2.70 M $HClO_4$ involves progressively decreasing absorbances above 500 and below 420 nm, but a more complex behavior is shown in the intermediate region. Difference spectra also obtained under the 2.70 M H^+ condition (Figure 2) show that in the range 460–500 nm the reaction initially gives rise to an absorbance increase, followed by a decrease after approximately 1 s.[10] This result was confirmed by detailed rate measurements at 477 nm over a range of H^+ concentrations (0.1–1.0 M, 25.0 °C, $I = 1.0$ M ($NaClO_4$)), and additional measurements were also made at 512 and 360 nm.

The 477-nm data were chosen for detailed analysis in terms of a consecutive first-order reaction scheme, $A \rightarrow B \rightarrow C$,[5] using an OLIS fitting routine.[7] This wavelength was chosen because it gave the maximum differentiation in absorbance changes for the two reactions (Figure 2). This analysis furnished values for k_{fast} and k_{slow} as well as the calculated absorbance change associated with each (ΔA_1, ΔA_2). Rate constants are listed in Table I (k_{fast}^{obs}, k_{slow}^{obs}). The quality of the fit can be judged from Figure 3, which gives observed and calculated absorbance–time traces for the reaction in 1.0 M $HClO_4$.

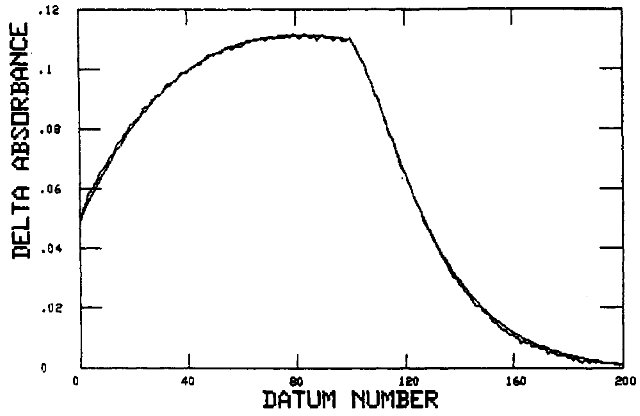

Figure 3. Observed and calculated absorbance–time traces (477 nm) for reaction of 6.94 mM $[Co(en)_2CO_3]^+$ in 1.00 M $HClO_4$. The time axis is split, with the first 100 data points being collected over 1.5 s and the remaining 100 being collected over the next 8 s. The fit uses $k_{fast} = 0.93$ s^{-1}, $\Delta A_{fast} = 0.290$ and $k_{slow} = 0.467$ s^{-1}, $\Delta A_{slow} = -0.340$.

Major features to come out of this analysis were (1) the independence of k_{fast} on $[H^+]$ ($k_{fast} = 0.93 \pm 0.03$ s^{-1}) and (2) the substantial acid dependence of k_{slow}, which fits the rate expression

$$k_{slow} = \frac{k'K[H^+]}{1 + K[H^+]} \tag{1}$$

Calculated values (using $k' = 0.85 \pm 0.04$ s^{-1} and $K = 1.18 \pm 0.10$ M^{-1}) of k_{slow} are given in Table I, and excellent agreement is found. It will be noted that k_{slow} approaches k_{fast} with increasing $[H^+]$. Similar treatment of the 512-nm (or 360-nm) data, where the absorbance changes for the two processes are in the same sense (cf. Figure 2), failed to give unique solutions.[11] In an attempt to duplicate the analytical method of Harris and Hyde,[2] we found that good, and meaningful (Table I), fits to a single exponential could only be obtained by using the final 15–25% of the 512-nm (or 360-nm) absorption traces. If more extensive data were used, increasing distortion from first-order behavior was found, and the "best fit" observed rate constants showed increasing variation.[12] The fact that k_{slow} approaches k_{fast} as $[H^+]$ increases required great care in data choice and treatment, as well as the collection of data over extensive time periods of both reactions.

We attribute the **first observed** reaction ($k_{fast} = 0.93$ s^{-1}) to the **second mechanistic** process,[13] i.e. to the spontaneous hydrolysis of the monodentate *cis*-$[Co(en)_2(OH_2)(OCO_2H)]^{2+}$ intermediate (Scheme I; $k_{fast} = k_2$).[14] This is consistent with the known pH independence of other reactions of monodentate carbonates in

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(10) Rapid-scan spectra over the range 345–586 nm reported previously[3] for reaction in 2.0 M $HClO_4$ failed to show this feature.

(11) Various combinations of k_{fast}, k_{slow} and ΔA_1, ΔA_2 gave fits of comparable quality. This emphasizes the need for discriminating absorption data in this type of analysis.[5] For the present reaction a unique solution could not be obtained since the extinction coefficients of **both** B and A were not known with certainty at these wavelengths and because both reactions involved absorbance decreases.

(12) For example, in 1.0 M $HClO_4$ best-fit values for k_{slow} ($k^{obs,c}$, Table I) were 0.310 s^{-1} (50-ms delay following mixing, 100% data treated), 0.362 s^{-1} (1 s, final 80%), 0.410 s^{-1} (2.5 s, final 48%), and 0.450 s^{-1} (5.0 s, final 16%).

(13) Changes in absorbance for the consecutive first-order scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ follow the time course $A_t - A_\infty = Me^{-k_1t} + Ne^{-k_1t}$ where M and N are complex functions of k_1, k_2 and extinction coefficients for A, B, and C. At long reaction times one of the exponentials will normally dominate (provided $k_1 \neq k_2$),[5] but which of k_1 or k_2 corresponds to k_{slow} depends on which is the smaller.

(14) In an early and closely related study of the $[Co(tren)CO_3]^+$ system, spectral observation at 504 nm revealed two phases for reaction in 2.0 M H^+. These were similarly attributed to chelated ring opening and hydrolysis of the resultant mondentate complex: Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1971**, *93*, 91.

acid media,[15,16] and the magnitude of k_2 (0.93 s^{-1}) agrees well with those found for such reactions (e.g. 1.10 s^{-1} for $[Co(NH_3)_5OCO_2H]^{2+}$.[16] The second observed reaction at 477 nm (k_{slow}) is attributed to the first mechanistic process, viz. to be opening of the four-membered bicarbonato chelate $[Co(en)_2CO_3H]^{2+}$ for which $k' = 0.85$ s^{-1} equates with k_1. Thus K_a (Scheme I) = $1/K$ (eq 1) = 0.9 ± 0.1 M. This value suggests that some 50% of the chelate should exist in the protonated form in 1 M acid.

We therefore set about to directly observe the protonated chelate and to measure K_a at $I = 1.0$ M ($NaClO_4$) by using zero-time absorbance data. It is clear from Figure 1 that the first observed spectrum of $[Co(en)_2CO_3]^+$ at high acid concentration differs appreciably from that observed in $NaClO_4$. This difference is significant in the range 500–530 nm, and 512 nm was chosen as the wavelength of maximum differentiation. Spectral observation was made over a 0.1–0.3-s time period (following a 5-ms time delay after mixing), and accurate (±0.003 absorbance unit) zero-time absorbances (A_{obs}) were obtained by extrapolation. These data are given in Figure 4 as a plot of ΔA vs $[H^+]$ where $\Delta A = A_1 - A_{obs}$ and where A_1 represents the absorbance of $[Co(en)_2CO_3]^+$ in the absence of acid (i.e. in 1.0 M $NaClO_4$). If A_2 represents the absorbance of the bicarbonate chelate $[Co(en)_2(CO_3H)]^{2+}$, then K_a may be obtained from the relationship

$$\Delta A = \frac{(A_1 - A_2)[H^+]}{K_a + [H^+]} \qquad (2)$$

Least-squares fitting of the data gave K_a = 1.1 ± 0.1 M,[17] and a comparison between the experimentally obtained ΔA values and the computer-generated fit is shown in Figure 4. The value of K_a is in good agreement with that found kinetically (0.9 ± 0.1 M).

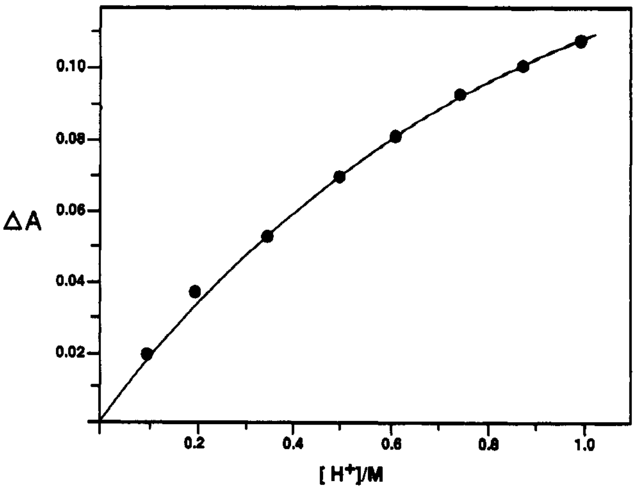

Figure 4. Plot of zero-time absorbance differences, ΔA (see text), versus $[H^+]$ for $[Co(en)_2CO_3]^+$ in $HClO_4/NaClO_4$ mixtures ($\lambda = 512$ nm, $[Co]_T = 2.61$ mM, 25.0 °C). Each point represents the average (±0.003) of five absorbance determinations. The solid line is drawn using eq 2, with $K_a = 1.1$ M^{-1} and $A_1 - A_2 = 0.226$.

So, in summary, the acid-catalyzed hydrolysis of $[Co(en)_2CO_3]^+$ follows the biphasic process given by Scheme I (k_1 = 0.85 ± 0.04 s^{-1}, k_2 = 0.93 ± 0.03 s^{-1}) following rapid preprotonation (K_a = 1.0 ± 0.1 M). We have found that similar preprotonation occurs with other bidentate carbonato complexes and that the differences in the observed rate constants for ring opening resides largely in the rates of Co–O bond cleavage in the protonated reactants.[18]

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[15] Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1968**, *90*, 6360. van Eldik, R.; Palmer, D. A.; Kelm, H.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 3679. van Eldik, R.; Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 3673.

[16] Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965.

[17] Since $[Co(en)_2CO_3H]^{2+}$ is never fully formed in the concentration range $0.1 \le [H^+] \le 1.0$ M, A_2 was also treated as a variable in the fitting routine (cf. Figure 4).

[18] Clark, C. R.; Buckingham, D. A. To be published.