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Kinetics and Mechanism of the Acid Hydrolysis of Carbonatobis(ethylenediamine)cobalt(III) Ion[1]

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The kinetics and mechanism of the acid hydrolysis of $Co(en)_2CO_3^+$ at 25.0° has been studied spectrophotometrically at 347, 381, and 550 mμ, the isosbestic wave lengths of the products *cis*- and *trans*-$Co(en)_2(H_2O)_2^{3+}$, in aqueous solutions of unit ionic strength. The rate equation at (H^+) between about 2×10^{-4} and 4×10^{-3} M was $-d(Co(en)_2CO_3^+)/dt = 0.92(Co(en)_2CO_3^+)(H_3O^+)$ M sec.$^{-1}$.

Introduction

Lamb and Mysels[2] found qualitatively that the rate of acid hydrolysis of $Co(NH_3)_5CO_3^+$ varied with concentrations of the complex and of the hydrogen ion. Hunt, Rutenburg, and Taube[3] have shown that this reaction proceeded predominantly by a mechanism in which a C–O bond was broken. Posey and Taube[4] have shown that the acid hydrolysis of $Co(NH_3)_4CO_3^+$ involved the breaking of only one C–O bond. No direct study of the kinetics and mechanism of acid hydrolysis of $Co(en)_2CO_3^+$ has been reported.

The present work is a continuation of the studies of the chemistry of $Co(en)_2CO_3^+$ and related ions.[5–7] In the investigation of the kinetics and mechanism of the *cis–trans* isomerization of $Co(en)_2(H_2O)_2^{3+}$ and related ions,[6] the isosbestic wave lengths of the *cis*- and *trans*-$Co(en)_2(H_2O)_2^{3+}$ were determined. The use of these wave lengths in the present study greatly simplified the treatment of the kinetic data.

Experimental

The synthesis of $Co(en)_2CO_3ClO_4$, the water used, the preparation and standardization of sodium perchlorate and perchloric acid stock solutions, the cleaning of glassware and cells, and the spectrophotometer and accessories for maintaining constant temperature were similar to those used in an earlier paper[5] except that a newer Beckman DU spectrophotometer was used for the present work.

The ionic strengths of the reaction solutions were made 1.00 M with $NaClO_4$.

Kinetic Procedure.—A clean and dry 10.00-cm. quartz cylindrical spectrophotometric cell was placed in intimate contact with a thermostated cell block 30 min. before the zero time of the kinetic experiment. A 250-ml. erlenmeyer flask containing all the reagents except $Co(en)_2CO_3ClO_4$ was partially immersed in a constant temperature bath. At zero time a small volume of a stock solution of $Co(en)_2CO_3ClO_4$ was added by pipet with vigorous swirling of the contents of the flask. A sample of the reaction solution was transferred into the cell with a thermostated pipet. The first reading was taken 100–200 sec. from zero time. The infinity reading was taken 3 to 4 days from zero time.

The temperature of the constant temperature bath was measured with a N.B.S. certified thermometer to be 25.00 ± 0.02°. The temperature of the reaction solution in the spectrophotometric cell was estimated to be 25.0 ± 0.1° with a thermometer.

The absorbance of a solution and the cell was measured against air and an appropriate blank solution was measured in the same cell under the same conditions. A given slit width was used for a given wave length throughout the whole study.

Symbols

A	Observed absorbance of solution and cell against air
A_0	A at zero time
A_∞	A at infinite time
ϵ_1	Molar absorptivity of $Co(en)_2CO_3^+$
ϵ_2	Molar absorptivity of $Co(en)_2(H_2O)_2^{3+}$
c_0	Initial stoichiometric $(Co(en)_2CO_3ClO_4)$
$c_0 - c =$	$(Co(en)_2(H_2O)_2^{3+})$ at time t
h_0	Initial stoichiometric $(HClO_4)$
$h =$	$h_0 - 2c_0 + 2c$
k	Rate constants
K	Equilibrium constants
λ	Wave length
n	Number of values of A in a given experiment used in calculation
(Z)	Molar concentration of Z
σ	Sample standard deviation[8]
t	Time
$y =$	$y_0 + mt$, y is a function of t; y_0 and m are constants

Calculation

The net reaction studied was

$$Co(en)_2CO_3^+ + 2H_3O^+ = Co(en)_2(H_2O)_2^{3+} + CO_2 + H_2O \quad (1)$$

At (H_3O^+) greater than 2×10^{-4} M, the predominant products were the *cis*- and *trans*-$Co(en)_2(H_2O)_2^{3+}$ ions.[9] Since the isosbestic wave lengths of these two ions were used in the present study, the two products could be treated as one substance and the rate of their *cis–trans* isomerization reactions would not enter into the calculation. The differential and integrated equations for which rate constants were calculated with the present data are

$$-dc/dt = k_1c \quad (2)$$

$$\ln (A - A_\infty) = \ln (A_0 - A_\infty) - k_1t \quad (3)$$

$$-dc/dt = k_2ch \quad (4)$$

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[3] J. P. Hunt, A. C. Rutenburg, and H. Taube, *ibid.*, **74**, 268 (1952).

[4] F. A. Posey and H. Taube, *ibid.*, **75**, 4099 (1953).

[5] J. Y. Tong and P. E. Yankwich, *ibid.*, **80**, 2664 (1958).

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[7] J. Y. Tong and G. Hargis, paper presented before the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963; to be published.

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[9] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

TABLE I

DATA AND CALCULATED RATE CONSTANTS (TIME IN SECONDS)

Expt. no.	$h_0 \times 10^3$, M	$c_0 \times 10^3$, M	λ, mμ	n	$k_1 \times 10^3$	k_2	$k_3 \times 10^{-3}$	k'
1	4.00	0.794	381	30		0.991		1.076
5	4.00	0.794	550	36	2.39	0.874	0.313	0.933
7	4.00	0.794	347	39		0.889		0.963
10	4.00	0.799	381	32		0.873		0.934
2	2.00	0.794	381	49		0.858		1.165
3	2.00	0.794	550	48	0.807	0.978	1.19	1.294
8	2.00	0.799	381	60		0.972		1.297
9	2.00	0.799	550	32		0.988		1.429
6	2.00	0.397	347	46	1.18	0.810	0.530	0.893
4	1.00	0.397	381	55	0.461	0.871	2.05	1.220
11	1.00	0.400	381	28		1.018		1.454

$$\ln (h/c) = \ln (h_0/c_0) + (h_0 - 2c_0)k_2t \qquad (5)$$

$$-\mathrm{d}c/\mathrm{d}t = k_3ch^2 \qquad (6)$$

$$\ln (h/c) - (h_0 - 2c_0)/h = \ln (h_0/c_0) - (h_0 - 2c_0)/h_0 + (h_0 - 2c_0)^2k_3t \qquad (7)$$

$$-\mathrm{d}c/\mathrm{d}t = k'c(h - c) \qquad (8)$$

$$\ln [(h - c)/c] = \ln [(h_0 - c_0)/c_0] + (h_0 - 2c_0)k't \qquad (9)$$

The rate equations tested correspond to the following mechanisms: (1) The predominant carbonato species in solution is the unprotonated carbonato complex, $Co(en)_2CO_3^+$, with one or more molecules of water, and the rate-determining step is (a) (rate eq. 2)

$$Co(en)_2CO_3^+ \longrightarrow$$

or

$$Co(en)_2CO_3^+ + H_2O \longrightarrow$$

(b) (rate eq. 4)

$$Co(en)_2CO_3^+ + H_3O^+ \longrightarrow$$

or

$$Co(en)_2CO_3H^{2+} \longrightarrow$$

or

$$Co(en)_2CO_3H^{2+} + H_2O \longrightarrow$$

(c) (rate eq. 6)

$$Co(en)_2CO_3H^{2+} + H_3O^+ \longrightarrow$$

(2) The predominant carbonato species in solution is the protonated carbonato complex, $Co(en)_2CO_3H^{2+}$, with one or more molecules of water, and the rate-determining step is (a) (rate eq. 2)

or

$$Co(en)_2CO_3H^{2+} \longrightarrow$$

$$Co(en)_2CO_3H^{2+} + H_2O \longrightarrow$$

(b) (rate eq. 8)

$$Co(en)_2CO_3H^{2+} + H_3O^+ \longrightarrow$$

Equations 3, 5, 7, and 9 were all of the type $y = y_0 + mt$. The function y and the parameters y_0 and m of each equation were calculated (the parameters by least-square method) with a digital computer LGP-30. Some of the experimental data and the rate constants calculated from the parameters are given in Table I.

The experiment number in first column of Table I indicates the chronological order in which the experiments were done. Two different cobalt stock solutions made in a similar manner were used, experiments 8, 9, 10, and 11 having been done with the second stock solution.

Calculations were also made with the quantities h_0, a_1, and a_2 changed by 1% or more to determine the change produced in the calculated rate constants. Samples of such calculation are given in Table II. Such calculation showed that the rate constants are most sensitive to errors in a_2 (or A_∞). Since a_2 was observed at seven wave lengths for all but one experiment, the average values of a_2 given in Table III were used in the calculation of k_2 and k'.

TABLE II

$(\Delta k/k)/(\Delta q/q)$

	k_2, expt. 4	k', expt. 4
h_0	−2.15	−2.96
a_1	1.06	0.75
a_2	4.13	3.67

TABLE III

AVERAGE MOLAR ABSORPTIVITY OF EQUILIBRIUM MIXTURES OF *cis*- AND *trans*-$Co(en)_2(H_2O)_2^{3+}$ IONS AT 25.0°, UNIT IONIC STRENGTH

λ, mμ	347	348	381	382	492	550	551
Slit width, mm.	0.08	0.08	0.055	0.055	0.02	0.02	0.02
Av. ε	55.3	56.3	41.1	40.0	77.4	32.4	31.6
σ	0.70	0.68	0.56	0.57	0.36	0.35	0.30

The values of the molar absorptivity of the carbonato complex, a_1, at 347, 381, and 550 mμ were 101.9, 87.2, and 75.7, respectively.

Discussion

It was obvious from the large variations in the values of k_1 and k_3 with compositions of solutions that eq. 2, 3, 6, and 7 could not account for the data and that the mechanisms (1a), (1c), and (2a) were not valid for the reaction.

The choice between the remaining sets of equations is not as distinct. The average k_2 is 0.92 with a sample standard deviation of 0.070 or 7.6% while the average k' is 1.15 with a sample standard deviation of 0.20 or 18%. The agreement between calculated and experimental $\ln (h/c)$ for eq. 5 was approximately three times better than that of $\ln (h - c)/c$ for eq. 9. The average difference for 455 pairs of calculated and experimental $\ln (h/c)$ values was 0.33%. One may attribute these differences between k_2 and k' in part to the greater sensitivity of the quantity $(h - c)$ of eq. 9 to experimental errors than the quantity h of eq. 5. On the other hand, the differences between $(h - c)$ and h are not great enough in the present experiments to produce the observed effects. Calculations of the types given in Table II showed that a given error in h_0, a_1, and a_2 produced about the same per cent errors in calculated k_2 and k'. If eq. 5 is the correct equation, under the experimental conditions, one could not expect the use of eq. 9 to produce very much greater scattering of k' values. The facts that calculated k' values did scatter more than k_2 values did and that such difference could not be produced by introducing errors from various possible sources into calculations support the choice of eq. 4 and 5 as being able to account for the data better than eq. 8 and 9. Consequently, mechanism (1b) may be more plausible than mechanism (2b).

If one considers certain trends in k_2 and k' as significant, one may use this as a clue to postulate a different mechanism which may account for the data better than either mechanisms (1b) and (2b). Mechanism (1b) assumes that the carbonato complex species is practically all $Co(en)_2CO_3^+$ while mechanism (2b) assumes that the species is practically all $Co(en)_2CO_3H^{2+}$. If one assumes that both $Co(en)_2CO_3^+$ and $Co(en)_2CO_3H^{2+}$ are present at significant concentrations, that they are in rapid equilibrium with one another according to eq. 10 and equilibrium constant K, and that the rate-determining reaction is (with rate constant k)

$$Co(en)_2CO_3^+ + H_3O^+ = Co(en)_2CO_3H^{2+} + H_2O \quad (10)$$

$$Co(en)_2CO_3H^{2+} \longrightarrow$$

or

$$Co(en)_2CO_3H^{2+} + H_2O \longrightarrow$$

one obtains the rate equation

$$-dc/dt = kK(H_3O^+)c/[K(H_3O^+) + 1] \quad (11)$$

The concentration (H_3O^+) is less than h but greater than $(h - c)$. If eq. 11 is the correct equation and eq. 5 and 9 are used to calculate the respective rate constants, the k_2 and k' calculated are approximately $kK/[K(H_3O^+) + 1]$. This will account for increasing k_2 and k' with decreasing h_0 at constant c_0 as well as for decreasing k_2 and k' with decreasing c_0 at constant h_0 in Table I (if one ignores experiments 1 and 2).

The present data are not useful in testing the last mechanism. The most direct approach is to determine the protonation constant independently.

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Semiempirical Molecular Orbital Theory. I. Permanganate and Related Anions[1]

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Although the Wolfsberg and Helmholz approach to molecular orbital theory for transition metal complexes is receiving increased attention, the results obtained in its prototype calculation on permanganate have been challenged by several authors. An alternative assignment of the energy levels, proposed by Ballhausen and Liehr, has gained acceptance through its use in the interpretation of e.s.r. measurements on manganate. Since the worth of a semiempirical method rests on its ability to correlate experimental results, this discrepancy casts some doubt on the usefulness of the method. This work consists of a systematic investigation of the modified Wolfsberg and Helmholz approach with particular attention to the effects of the parameters on the calculated energy levels. The method is applied to the series of complexes, MnO_4^-, MnO_4^{-2}, and MnO_4^{-3}. In addition to a study of the sensitivity of calculated energy levels to parameter choices, an attempt has been made to correlate the two alternative assignments with the absorption spectra of the complexes. The results indicate that the order of the energy levels is very dependent upon the amount of s and p character in the hybrid ligand orbitals. Use of the criterion proposed by Ballhausen and Gray to establish the degree of hybridization does not result in energy levels in accord with the e.s.r. results. By adjustment of the H_{ij} terms in the secular determinant, it is possible to obtain *either* set of energy levels and to rationalize the results with reasonable transition assignments for the three complexes. In fact, within the framework of the method employed, the Wolfsberg and Helmholz assignment would appear to yield better correlation with the experimental values. This is particularly true of the calculated transition intensities. In general, it appears that the results one obtains by the semiempirical method are strongly dependent upon the initial assumptions employed in the calculations.

Introduction

In an attempt to interpret the absorption spectra of the permanganate and chromate ions, Wolfsberg and Helmholz[2] proposed a semiempirical molecular orbital calculation of the energy levels of the complexes. However, the energy level assignment obtained by the approach was seriously questioned by Ballhausen and Liehr[3] on the basis of absorption intensity calculations and an alternative assignment was proposed by these authors. The Wolfsberg and Helmholz ordering

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