complexes is remarkably fast, and any mixed complexes which are produced by the oxidation reactions may be entirely dissociated in less than 3 min. Although the reaction studied in the present work is surprisingly fast for the oxidation of a metal center by a molecular oxidizing agent (see Table III), it is not fast enough to be classified as an outer-sphere reaction on the basis of speed.[26] The rate constant for the loss of coordinated water by $Fe^{2+}(aq)$ is 3×10^6 sec^{-1} [27] and the outer-sphere association constant expected for an ion and a neutral molecule is approximately 0.1 M^{-1}. This leads to a maximum predicted substitution-limited rate for the reaction of $Fe^{2+}(aq)$ with I_2 of 3×10^5 M^{-1} sec^{-1}, which is slower than the observed rate for the iodine oxidation reported here. What effect, however, coordination with CyDTA might have upon the water-exchange rate is not known. The nature of the reactants does not preclude an inner-sphere mechanism.[23,24,28] The values of the entropies of activation indicate that displacement of a coordinated group by the oxidant probably occurs.

In contrast to the speed of the reaction between $Fe^{II}CyDTA^{2-}$ and iodine, preliminary results show that the oxidations of $Co^{II}CyDTA^{2-}$ by iodine and bromine are slow. The observed rate constant for the oxidation by total bromine species is 3.6×10^{-2} M^{-1} sec^{-1} at pH 7.0 and $[Br_2]_T = 0.05$ M. The iodine oxidation of $Co^{II}CyDTA^{2-}$ is slower than that of bromine, by about two orders of magnitude. Although it is expected that electron-transfer reactions of cobalt will be slower than analogous reactions of iron, the magnitude of the difference in rate in this instance is perhaps surprising. A study of similar reactions with analogous complexes of iron and other transition elements is in progress.

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[26] P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).

[27] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[28] D. H. Huchital and R. G. Wilkins, *Inorg. Chem.*, **6**, 1022 (1967).

Contribution from the Department of Chemistry,
The Catholic University of America, Washington, D. C. 20017

Kinetics of the Acid Cleavage of the Di-μ-hydroxo-tetrakis(ethylenediamine)dicobalt(III) Ion in the Presence of Various Anions

By M. M. deMaine and J. B. Hunt*

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The acid cleavage of the binuclear ion $(en)_2Co(OH)_2Co(en)_2{}^{4+}$ has been followed by spectrophotometry at 525 mμ and by uptake of hydrogen ion in $HClO_4$, HNO_3, HCl, and H_2SO_4 solutions. In $HClO_4$ and HNO_3 solutions the sole reaction product is *cis*-$Co(en)_2(H_2O)_2{}^{3+}$, but *cis*-$Co(en)_2SO_4{}^{2+}$ is also a product in H_2SO_4 solutions and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2{}^+$ are also products in HCl solutions. In $HClO_4$ and HNO_3 solutions the cleavage follows the rate law $-d \ln [\text{dimer}]/dt = k_0 + a[H^+]/(1 + b[H^+])$, where $k_0 = (5.0 \pm 0.2) \times 10^{-5}$ sec^{-1} for both $HClO_4$ and HNO_3, $a = (3.8 \pm 0.3) \times 10^{-2}$ M^{-1} sec^{-1} and $b = 1.9 \pm 0.2$ M^{-1} in HNO_3, and $a = (8.4 \pm 0.3) \times 10^{-3}$ M^{-1} sec^{-1} and $b = 0.77 \pm 0.08$ M^{-1} in $HClO_4$, all at 35° and $\mu = 1.0$. In $HCl-HClO_4$ solutions an additional rate term of the form $k_{Cl}[H^+][Cl^-]$ is observed, where $k_{Cl} = (2.8 \pm 0.1) \times 10^{-2}$ M^{-2} sec^{-1} at 25° and $\mu = 1.0$. In 1 M $HClO_4$ or 1 M HCl the absorbance at 635 mμ first increases and then decreases at the beginning of the reaction, which is interpreted as evidence for the involvement of single-bridged intermediates.

Introduction

Rasmussen and Bjerrum[1] reported that the double-bridged binuclear complex ion $(en)_2Co(OH)_2Co(en)_2{}^{4+}$, where en = ethylenediamine, cleaves in nitric acid solution to form the monomeric diaquo species *cis*-$(en)_2Co(OH_2)_2{}^{3+}$. These authors also measured the kinetics of the cleavage of the dimer by nitric acid, and a rate law of the form $-d[\text{dimer}]/dt = (k_1 + k_2[H^-])[\text{dimer}]$ describes their data. A reinvestigation of this reaction was prompted by the observation that the cleavage of the analogous chromium(III) complex, $(en)_2Cr(OH)_2Cr(en)_2{}^{4+}$, obeys entirely different rate laws in nitric and perchloric acids.[2] The form of the rate law given above for the cobalt(III) complex is identical with that found for the chromium(III) complex in nitric acid at constant nitrate ion concentration. In the present study the kinetics of the cleavage of the cobalt(III) dimer by perchloric acid have been measured to determine whether the complex behaves differently in the presence of perchlorate and nitrate ions, as does the chromium(III) complex.

Since the completion of most of the work reported here, Hoffman and Taube[3] have reported that the cleavage of the analogous ammonia complex, $(NH_3)_4Co(OH)_2Co(NH_3)_4{}^{4+}$, obeys the rate law $-d \ln [\text{dimer}]/dt = a[H^+]/(1 + b[H^+])$ in $HClO_4-NaClO_4$ solutions. Taube and Hoffman noted that the very different rate laws reported for the very similar ammonia and ethylenediamine complexes both reduce to an approximately first-order dependence on hydrogen ion concentration at the low acidities used by Rasmussen and Bjerrum. It will be seen that our kinetic data over a wider range of acidities than used by Rasmussen and Bjerrum show the behavior of the ethylenediamine complex to be qualitatively similar to

[1] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

[2] D. Wolcott and J. B. Hunt, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, No. O-88.

[3] A. B. Hoffman and H. Taube, *Inorg. Chem.*, **7**, 903 (1968).

that of the ammonia complex. Further, we will present direct evidence for the formation and subsequent disappearance of the single-bridged intermediate.

The present investigation has been extended also to solutions containing chloride and sulfate ions to test the effect of ambient ligands on the rate, stoichiometry, and stereochemistry of the cleavage reaction. Since the dimer has a charge of +4 and is expected therefore to be highly associated in solution, the effects of changes in ionic strength have been investigated also.

Experimental Section

Preparation of $[(en)_2Co(OH)_2Co(en)_2](ClO_4)_4$.—Carbonatobis(ethylenediamine)cobalt(III) chloride (27.5 g), prepared by the method outlined by Dwyer, Sargeson, and Reid,[4] was dissolved in a mixture of 17 ml of 70% $HClO_4$ and 40 ml of H_2O to give a solution of diaquobis(ethylenediamine)cobalt(III) chloride. To this mixture were added in turn 125 ml of pyridine and 125 ml of a saturated sodium dithionate solution.[5] Scratching the sides of the beaker induced precipitation of the $[Co(en)_2(H_2O)(OH)](S_2O_6)$, which was separated by filtration and washed with 95% alcohol and ether (yield 22.5 g). A 5-g portion of $[Co(en)_2(H_2O)(OH)](S_2O_6)$ was refluxed with 50 ml of acetic anhydride for 2 hr to yield $[(en)_2Co(OH)_2Co(en)_2](S_2O_6)_2$ which was filtered from the colorless liquid and then washed with alcohol and ether.[5] A 4.7-g sample of $[(en)_2Co(OH)_2Co(en)_2](S_2O_6)_2$ was ground with 10 g of NH_4Br and 25 ml of water. After 10 min a further 10 ml of water was added, whereupon the NH_4Br dissolved. The red-violet residue was collected on a filter and was then washed with alcohol and ether. This solid was dissolved in 150 ml of water and any undissolved dithionate was removed by filtration. The addition of 5 g of NH_4Br to the clear solution precipitated the $[(en)_2Co(OH)_2Co(en)_2]Br_4 \cdot 4H_2O$ as dark violet crystals which were filtered off, washed with alcohol, and dried with ether. The diol bromide was dissolved in the minimum amount of water and an equal volume of a saturated solution of $NaClO_4$ was added. The $[(en)_2Co(OH)_2Co(en)_2](ClO_4)_4$ precipitate was filtered off and washed with alcohol and ether.

Anal. (Spang Microanalytical Laboratory, Ann Arbor, Mich.) Calcd for $[Co_2(C_2H_8N_2)_4(OH)_2](ClO_4)_4$: C, 12.16; H, 4.34; N, 14.18; Cl, 17.94. Found: C, 12.89; H, 4.67; N, 14.02; Cl, 17.78. The compound exploded violently during combustion for CH.

Kinetic Measurements.—Generally the progress of the cleavage reaction was followed spectrophotometrically as the decrease in absorbance at 525 mμ. To begin kinetic runs under conditions such that half-times were long, weighed portions of $[(en)_2Co(OH)_2Co(en)_2](ClO_4)_4$ were dissolved quickly in an aqueous solution already containing the other reactants (*e.g.*, $NaClO_4$ and $HClO_4$) at the temperature of the run. The resulting solution was transferred quickly to a cuvette and placed in the thermostated cell compartment of a Cary Model 15 spectrophotometer. The reaction vessel used under conditions such that half-times were short was a Pyrex cuvette onto which a side arm had been sealed. Measured volumes of a solution of the dimer in very dilute (*ca.* 0.001 *M*) acid and of the appropriate acid were brought to temperature separately in the two compartments of the cuvette, which was immersed in a water bath suspended in the cell compartment of the spectrophotometer. Reaction was initiated by inverting and shaking the cuvette to mix the reactants.

In most experiments the acid was present in large excess with respect to the dimer. Pseudo-first-order rate constants were obtained either graphically from the slope of the log $(A_t - A_\infty)$ *vs.* time plot or from a nonlinear least-squares computer fit of the absorbance–time data to the equation $A_t = (A_0 - A_\infty)e^{-kt} + A_\infty$. ($A_0$, A_t, and A_∞ are the absorbance readings at zero time, time *t*, and infinite time, respectively.) In some cases a steady absorbance was not observed at long reaction times because of instability of products, and rate constants were then obtained by the Guggenheim method.[6] Under Results are noted situations in which the log $(A_t - A_\infty)$ plots were resolvable into two linear portions.

In some kinetic runs the progress of the cleavage reaction was followed by measuring the rate of acid consumption, using a Sargent Recording pH-Stat. At the beginning of each such run the pH-Stat was calibrated against standard buffer solutions and then adjusted to add acid if the solution in contact with its pH electrode became more basic than the pH chosen for the run. An aliquot of 1 *M* $NaClO_4$ or 1 *M* $NaNO_3$ solution (usually 20–25 ml) was pipetted into the reaction vessel and brought to the temperature of the run. The instrument was allowed to add sufficient acid to bring the solution to the pH of the run. Reaction was then initiated by adding a weighed portion of the dimer perchlorate to the reaction vessel. The titrant used in these runs was standard 0.1 *M* $HClO_4$ or 0.05 *M* HNO_3 made up to unit ionic strength with $NaClO_4$ or $NaNO_3$.

Since all concentrations except that of the dimer remained constant in a given pH-Stat run, pseudo-first-order rate constants, *k*, could be calculated from the relationship $\ln (V_\infty - V_t) - \ln (V_\infty - V_0) = -kt$. where, V_∞, V_t, and V_0 are the volumes of the titrant which had been added at infinite time, time *t*, and zero time, respectively, in order to maintain the solution at the pH chosen for the run.

Ion-Exchange Separations.—Separation of the products of the acid-cleavage reaction was achieved with 20 cm × 10 mm columns of Dowex 50W-X8 cation-exchange resin (100–200 mesh, Na^+ form). Product solutions were forced through the column with complete adsorption of all Co species. The cationic complexes were selectively eluted with solutions of increasing $HClO_4$ concentration and the progress of the colored bands down the column was followed visually. Identification of the Co complex in each eluted fraction was made on the basis of the conditions for its elution and the ultraviolet spectrum, which was compared with data in the literature. To permit better comparisons small amounts of these species were synthesized by methods in the literature.

Results

Spectra.—The visible absorption spectrum of the dimer was found to be rather insensitive to ionic environment, being the same within experimental error in water and in 1 *M* solutions of Na_2SO_4, $NaNO_3$, $NaClO_4$, and NaCl. Beer's law was obeyed by the dimer in all these solutions. At the 525-mμ peak the molar extinction coefficient, ε, was found to be 298 ± 6 per mole of dimer in water and in 1 *M* $NaClO_4$ and 299 ± 5 per mole of dimer in 1 *M* $NaNO_3$. The spectra were remarkably insensitive to temperature changes, and the limits on the values above cover any differences between 25 and 40°. Rasmussen and Bjerrum[1] reported an absorption maximum at 520 mμ with ε 302.4 per mole of dimer for a solution 1 *M* in $NaNO_3$ at 25°.

Solutions of the dimer in water and in neutral salt solutions showed a slow change in spectra toward that of *cis*-$Co(en)_2(H_2O)OH^{2+}$, but evaluation of rate constants for the reaction in neutral solutions was precluded by the fact that a constant absorbance was never reached. At 30° the absorbance at 525 mμ decreased by 5.8, 6.0, and 7.8% in 1 *M* solutions of $NaClO_4$, $NaNO_3$, and NaCl, respectively, during a period of 50 min.

Kinetics in Perchlorate and Nitrate Media.—Figure 1 shows the typical changes with time in the spectrum of the dimer in perchloric acid solutions. The lowest curve of Figure 1 represents the stage of apparent complete reaction, and no further changes were noted over the next 3 days. At this final stage there was a maximum at 492 mμ, ε 78.0 ± 1.5 (calculated on the basis of the known dimer concentration), and the spectrum matched very closely that of freshly prepared solutions of *cis*-$[Co(en)_2(H_2O)_2](ClO_4)_3$. Bjerrum and Rasmussen[7] reported a maximum at 492 mμ (ε 80.0 in H_2O; 80.9 in 1 *M* $NaNO_3$) for *cis*-$Co(en)_2(H_2O)_2{}^{3+}$. The general behavior of the dimer in nitrate solutions was

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[4] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, **85**, 1215 (1963).

[5] A. Werner and J. Rapiport, *Justus Liebigs Ann. Chem.*, **375**, 84 (1910).

[6] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

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

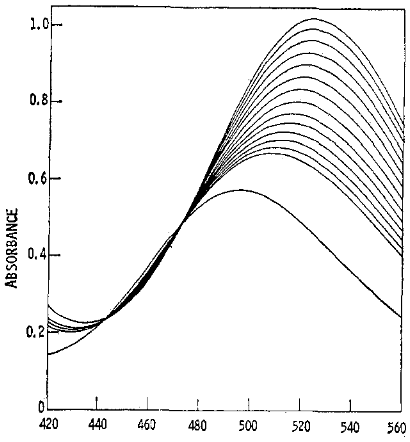

Figure 1.—Change in absorption spectrum with time during cleavage of $(en)_2Co(OH)_2Co(en)_2^{4+}$ in 0.01 *M* $HClO_4$ at 35°. The highest curve was recorded after 15 min and the lowest curve after 265 min. [Dimer] = 0.0037 *M*; μ = 1.00, adjusted with $NaClO_4$.

quite similar to its behavior in perchlorate solutions. Isosbetic points were the same for the two media, and in both media the *cis*-$Co(en)_2(H_2O)_2^{3+}$ ion was the only cobalt species found when reacted solutions were run through a Dowex 50 cation-exchange column. Further, in the pH-Stat runs 2.00 ± 0.05 mol of acid was consumed/mol of dimer, and the spectra of solutions at the end of such runs were identical with that of *cis*-$Co(en)_2(H_2O)_2^{3+}$. All these observations support the conclusion that the reaction of the dimer with perchloric or nitric acid obeys the stoichiometry

$$(en)_2Co(OH)_2Co(en)_2^{4+} + 2H_3O^+ \longrightarrow 2\textit{cis}\text{-}Co(en)_2(H_2O)_2^{3+} \quad (1)$$

Plots of log $(V_\infty - V_t)$ *vs.* time and of log $(A_t - A_\infty)$ at 525 mμ *vs.* time for $[H^+] < 0.5$ *M* were linear over the whole period of change. However, a slight curvature at the beginning of the rate plots, in the direction of slow initial rates, was observed for reactions in 1 *M* $HClO_4$, but these first-order rate plots also were linear over the last *ca.* 90% of the total absorbance change. The reason for the induction period at high acidity will be discussed later.

First-order rate constants for cleavage of the dimer in nitrate and perchlorate solutions of low acidity, from rate measurements using the pH-Stat, are given in Table I. First-order rate constants for solutions of higher acidity, based on absorbance measurements at 525 mμ, are given in Table II. Large numbers of rate measurements were made at 25 and 35° for nitrate media and at 35° for perchlorate media, and these data are shown plotted against $[H^+]$ in Figure 2.

Table I

First-Order Rate Constants for Cleavage of Dimer at Low Acidities[a]

Temp, °C	pH	10^4k, sec^{-1} 1 *M* NO_3^- soln	 1 *M* ClO_4^- soln
25.0	4.00	0.155	. . .
35.0	2.00	3.5 ± 0.4	1.42 ± 0.04
35.0	2.20	2.9	. . .
35.0	2.50	1.9 ± 0.2	. . .
35.0	3.00	1.3 ± 0.2	0.61 ± 0.02
35.0	3.50	0.8	0.55 ± 0.02
35.0	4.00	0.55 ± 0.01	0.51 ± 0.02
40.0	4.00	1.05 ± 0.04	1.00
45.0	4.00	2.0 ± 0.1	2.08
50.0	4.00	3.9	. . .

[a] From pH-Stat measurements.

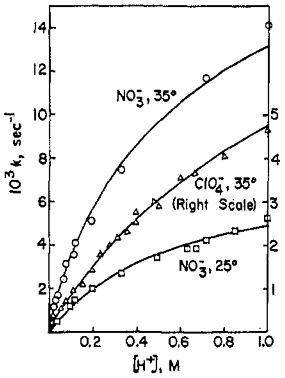

Figure 2.—Variation of pseudo-first-order rate constant with $[H^+]$ for cleavage of dimer in 1 *M* ClO_4^- and 1 *M* NO_3^- solutions. Points are experimental points. Curves are nonlinear least-squares fits of points to eq 2.

The curves of Figure 2 were generated assuming the rate law for the reaction to be

$$-\mathrm{d}\ln[\text{dimer}]/\mathrm{d}t = k = k_0 + \frac{a[H^+]}{1 + b[H^+]} \qquad (2)$$

Values of *a* and *b* used in generating the curves of Figure 2 are given in Table III. Values of k_0, obtained by extrapolating the data of Table I to $[H^+] = 0$ or correcting the data for pH 4 for the acid-dependent contribution, are also given in Table III. The values obtained for k_0 at a given temperature were the same within experimental error for 1 *M* NO_3^- and 1 *M* ClO_4^- solutions.

It is evident from Figure 2 that the hydrogen ion dependence of the first-order rate constant, *k*, in perchlorate solutions is described very well by the hyperbolic term of eq 2. The fit is not quite so good in nitrate solutions, but even in this case the worst disagreement between the observed rate constant and that calculated from Table III and eq 2 is about 9% for any experimental point over the range 0.05–1 *M* H^+.

It is seen also from Table II that the cleavage rate increases markedly with increasing ionic strength at a given temperature and $HClO_4$ concentration. From the entries for $[H^+] = 0.10$ *M* it is seen that the cleavage rate nearly doubled when the ionic strength was increased from 0.11 to 1.0 *M*. The cleavage rate in nitrate solutions was found to be even more sensitive to ionic strength (or perhaps to $[NO_3^-]$) than in perchlorate solutions. With $[H^+] = 0.04$ *M*, the first-order rate constant at 35° increased from 4.4×10^{-4} to 1.7×10^{-3} sec^{-1} when the ionic strength was increased from 0.11 to 1.0 *M*. Attempts to look separately at the effects of ionic strength and nitrate concentration were thwarted by the extremely low solubility of the dimer in mixed ClO_4^-–NO_3^- solutions.

Reaction of Dimer with HCl Solutions.—When the dimer underwent cleavage in mixed HCl–$HClO_4$ solutions, chloride complexes were among the monomeric species found upon ion-exchange separation of the reaction products. In reaction mixtures with $[Cl^-] \leq 0.1$ *M*, *cis*-$Co(en)_2(H_2O)_2^{3+}$ and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ were the only products found. A more complex mixture of products was found at higher chloride concentrations. For example, a solution of the dimer in 1 *M* HCl which

TABLE II

FIRST-ORDER RATE CONSTANTS FOR CLEAVAGE OF DIMER IN NITRATE AND PERCHLORATE SOLUTIONS[a]

ClO_4^- solutions					
[H⁺],	10^3k, sec⁻¹				
M	10°	25°	30°	35°	40°
0.016	...	...	...	0.22	...
0.022	...	...	...	0.35	...
0.028	...	...	...	0.37	...
0.040	...	...	...	0.41	...
0.060	...	...	...	0.55	...
0.080	...	...	...	0.70	...
0.10	0.037	0.27	0.44	0.84	1.2
0.10[b]	...	...	0.22	0.41	...
0.10[c]	...	...	0.38	0.68	...
0.16	...	...		1.1	...
0.20	0.075	0.49	0.82	1.4	2.4
0.24	...	...	...	1.8	...
0.28	...	...	...	2.0	...
0.30	...	...	1.2	2.1	3.3
0.32	...	...	...	2.2	...
0.36	...	...	...	2.3	...
0.40	0.14	0.95	1.4	2.60	4.1
0.48	...	...		3.0	...
0.50	...	...		2.91	...
0.60	...	1.5	2.3	3.57	...
0.67	0.22	...		3.67	...
0.80	...	1.7	2.8	4.07	...
1.00	0.28	...	1.97	4.66	...
1.00[d]	0.34	2.0		...	...
2.00[d]	0.52	...	...	...	...
4.0[e]	...	...	7.8	...	...

NO_3^- solutions				
[H⁺],	10^3k, sec⁻¹			
M	25°	30°	35°	40°
0.0065	...	...	0.40	...
0.008	...	0.26	0.48	0.64
0.016	...	0.56	0.87	1.2
0.024	0.41	0.70	1.2	1.6
0.032	0.50	0.85	1.5	2.1
0.040	0.67	0.95	1.7	...
0.040[f]	...	0.15	0.32	...
0.040[g]	...	0.60	0.86	...
0.070	1.02	...	...	...
0.080	1.27	1.9	3.1	4.9
0.091	1.20	...	...	...
0.120	1.57	2.7	3.90	...
0.200	1.99	4.3	5.1	...
0.333	2.69	...	7.4	...
0.50	3.45	...	...	...
0.67	3.97	...	...	...
0.72	4.25	...	11.8	...
0.84	4.70	...	...	...
1.00	5.30	...	14.1	...

[a] Measured spectrophotometrically; $\mu = 1$, except as noted. [b] $\mu = 0.11$. [c] $\mu = 0.51$. [d] $\mu = 2.0$. [e] In 4 *M* $HClO_4$. [f] $\mu = 0.04$. [g] $\mu = 0.44$.

TABLE III

CALCULATED VALUES OF k_0, a, AND b

		10^3a, M^{-1} sec⁻¹		b, M^{-1}	
Temp, °C	10^5k_0, sec⁻¹	In 1 *M* NO_3^-	In 1 *M* ClO_4^-	In 1 *M* NO_3^-	In 1 *M* ClO_4^-
25	1.4	14	...	1.9	...
35	5.0	38	8.38	1.9	0.77
40	9.8	...	...	...	...

had reacted for 4 min at 25° gave three major fractions when separated on an ice-cold column of Dowex 50W-X8 resin. The spectrum of the fraction which eluted with 1.5 *M* $HClO_4$ matched very well that of *cis*-$Co(en)_2Cl_2^+$ (λ_{max} 535 mμ), but a small shoulder at *ca.* 610 mμ suggested that some *trans*-$Co(en)_2Cl_2^+$ was also present. A fraction eluting with 2.5 *M* $HClO_4$ was identified as *cis*-$Co(en)_2(H_2O)Cl^{2+}$ (λ_{max} 517 mμ). The rest of the cobalt on the column was removed with 5 *M* $HClO_4$, and this fraction was identified as *cis*-$Co(en)_2(H_2O)_2^{3+}$ (λ_{max} 492 mμ). Based on the known extinction coefficients,[8] 70% of the cobalt was found as *cis*-$Co(en)_2(H_2O)_2^{3+}$, 18% as *cis*-$Co(en)_2(H_2O)Cl^{2+}$, and 11% as *cis*-$Co(en)_2Cl_2^+$. These three species accounted for 99% of the cobalt originally added as the dimer. The quantity of *cis*-$Co(en)_2Cl_2^+$ found undoubtedly represents the minimum quantity formed in the reaction, since about 45 min was required for removal of this ion from the column. The presence of a small quantity of *trans*-$Co(en)_2Cl_2^+$ in the *cis*-$Co(en)_2Cl_2^+$ fraction was confirmed by allowing this fraction to sit at *ca.* 25° for 5 hr and then passing it through a second short column of Dowex 50 to remove the *cis*-$Co(en)_2(H_2O)Cl^{2+}$. The effluent had an absorption maximum at 615 mμ, confirming the presence of *trans*-$Co(en)_2Cl_2^+$, which accounted for *ca.* 1% of the cobalt originally added as the dimer. The aquation of *trans*-$Co(en)_2Cl_2^+$ is about seven times slower than that of *cis*-$Co(en)_2Cl_2^+$.[9]

No isosbestic point was observed in the region 350–650 mμ during the reaction of the dimer with 1 *M* HCl. Plots of log $(A_t - A_\infty)$ at 525 mμ *vs.* time for chloride solutions had an initial linear portion covering 75–92% of the total absorbance decrease, depending on [Cl⁻]. Over the last 8–25% of the absorbance change the rate plot curved and then became linear with a shallow slope. A first-order rate plot for the reaction in 1 *M* HCl at 25° is shown in Figure 3, which also shows the change of absorbance with time at 525 and 635 mμ under the same conditions. A large change of absorbance at 525 mμ is expected to accompany the cleavage of the dimer regardless of which of the possible monomeric products are formed. The possible monomeric products which absorb most strongly at this wavelength are *cis*-$Co(en)_2Cl_2^+$ and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ for both of which ϵ is $\simeq$90 at 525 mμ, compared to ϵ 149 at 525 mμ for the dimer. Thus the large change in absorbance associated with the first linear portion of the rate plot in Figure 3 must correspond to the disappearance of the dimer and the second linear portion to the reaction of some product. It is seen in Figure 3 that the absorbance–time data for 525 mμ give a good fit to a first-order rate equation over about 75% of the total absorbance change. The half-time for the second linear portion of the rate plot of Figure 3 is *ca.* 3000 sec, which is nearly identical with that reported for the aquation of *cis*-$Co(en)_2Cl_2^+$. The conversion of *cis*-$Co(en)_2Cl_2^+$ to a mixture of *trans*- and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ would result in a decrease in absorbance at 525 mμ.

Values of the first-order rate constant, *k*, for mixed Cl^-–ClO_4^- solutions were evaluated either by fitting the

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[8] P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).

[9] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 171.

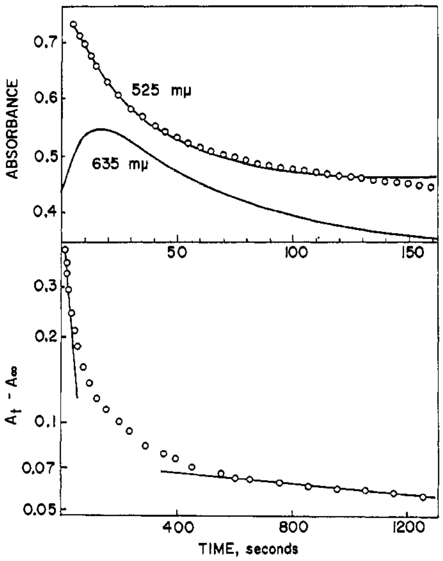

Figure 3.—Reaction of dimer with 1 *M* HCl at 25°. Top curve is a nonlinear least-squares fit of absorbance–time data for 525 mμ to a first-order rate equation using the data for the first 160 sec. Middle curve is the absorbance–time plot for 635 mμ. Bottom curve is a first-order rate plot based on absorbance–time data for 525 mμ, using the absorbance recorded after 6 hr as A_∞.

absorbance–time data to a scheme for consecutive first-order reactions or by means of a nonlinear least-squares fit of the data to a first-order rate equation, using about the first three half-times of the first reaction. The two methods gave nearly identical results. Values of *k* under various conditions are given in Table IV. The most extensive and most reliable data are those for 25°, and these have been used to construct Figure 4 in which *k* is

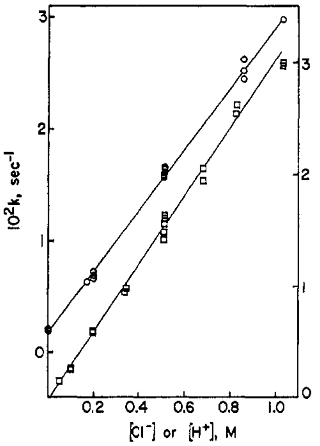

Figure 4.—Variation of pseudo-first-order rate constant with [Cl$^-$] in 1 *M* H$^+$ (top curve, left scale) and with [H$^+$] in 1 *M* Cl$^-$ (bottom curve, right scale) at μ = 1.0 and at 25°. Lines were obtained by linear least-squares fits of data. Mixed HCl–HClO$_4$ solutions were used to obtain the top curve, and NaCl–HCl solutions, to obtain the bottom curve.

shown plotted against [Cl$^-$] for solutions of constant [H$^+$] and against [H$^+$] for solutions of constant [Cl$^-$]. It is seen from Figure 4 that *k* increases linearly with [Cl$^-$]. Further, in contrast to the behavior in ClO$_4^-$ and NO$_3^-$ solutions (Figure 2), the plot of *k vs.* [H$^+$] for 1 *M* Cl$^-$ solutions shows no significant curvature but is clearly linear up to 1 *M* H$^+$. We conclude then that the additional rate term introduced when Cl$^-$ is present is of the form $k_{\text{Cl}}[\text{H}^+][\text{Cl}^-]$, where $k_{\text{Cl}} = 2.8 \times 10^{-2}\ M^{-2}$ sec^{-1} at 25° and $\mu = 1.0$. From a plot of *k vs.* [Cl$^-$], using the data of Table IV for 35° and [H$^+$] = 0.08 *M*,

Table IV

First-Order Rate Constants for Cleavage of Dimer in Mixed Chloride–Perchlorate Solutions[a]

[Cl$^-$], *M*	[H$^+$], *M*	10^3k, sec^{-1}	[Cl$^-$], *M*	[H$^+$], *M*	10^3k, sec^{-1}
	25°			35°	
1.00	0.020	0.51	1.0	0.016	1.5
1.00	0.040	1.00	1.0	0.024	1.7,[b] 2.0, 2.1[c]
1.00	0.051	1.42	1.0	0.032	2.5
1.00	0.080	1.76	1.0	0.040	3.1
1.00	0.100	2.54	1.0	0.080	5.9
1.00	0.120	2.63	0	0.080	0.66
1.00	0.20	5.92	0.008	0.080	0.70
1.00	0.34	9.6	0.024	0.080	0.84
1.01	0.51	15.3	0.040	0.080	0.94
1.01	0.68	19.9	0.056	0.080	1.0
1.02	0.82	25.8	0.12	0.080	1.4
1.03	1.03	29.8	0.20	0.080	1.7
0	1.03	1.98	0.28	0.080	2.2
0.17	1.03	6.26	0.36	0.080	2.6
0.20	1.03	7.0	0.44	0.080	2.9
0.34	1.03	10.7	0.60	0.080	3.4
0.51	1.03	16.2	0.92	0.080	4.5
0.86	1.03	25.4			
	30°			40°	
1.0	0.020	0.82	1.0	0.004	0.43
1.0	0.040	1.43	1.0	0.008	1.0
1.0	0.080	2.93	1.0	0.012	1.5
1.0	0.20	9.4	1.0	0.020	2.2
			1.0	0.040	4.1

[a] μ = 1.00–1.03, adjusted with NaClO$_4$ when necessary. Measured at 525 mμ. [b] Measured at 555 mμ. [c] Measured at 350 mμ.

we estimate that $k_{\text{Cl}} = (6.2 \pm 0.5) \times 10^{-2}\ M^{-2}$ sec^{-1} at 35°. From the stated values of k_{Cl} at 25 and 35° the Arrhenius activation energy is calculated to be 14.5 kcal/mol.

Reaction of the Dimer with Sulfate Solutions.—When the dimer was added to H$_2$SO$_4$–Na$_2$SO$_4$ solutions, a rapid color change was observed. Plots of log ($A_t - A_\infty$) at 525 mμ were curved almost from the beginning but could be resolved into two linear portions. Two cobalt-containing species were found upon ion-exchange separation of the product solutions: *cis*-Co(en)$_2$(H$_2$O)$_2^{3+}$ and a sulfate-containing complex identified by its spectrum[10] as *cis*-Co(en)$_2$(SO$_4$)H$_2$O$^+$. For a solution where [H$^+$] = 0.024 *M* and [SO$_4^{2-}$] = 0.55 *M*, which had reacted for 5 hr at 25°, *cis*-Co(en)$_2$(H$_2$O)$_2^{3+}$ accounted for 42% and *cis*-Co(en)$_2$(SO$_4$)H$_2$O$^+$ for 47% of the cobalt originally in the dimer. For this same solution, resolution of the rate plot into two linear portions gave a first-order rate constant of 7.5 × 10^{-3} sec^{-1} for the first portion and 2.7 × 10^{-4} sec^{-1} for the second portion. Detailed kinetics was not obtained for the reaction of the dimer in sulfate media because of the difficulty of varying the H$^+$ and SO$_4^{2-}$ concentrations independently.

Evidence for Reaction Intermediates.—The absorbance–time plot for 635 mμ shown in Figure 3 provides clear evidence for the involvement of an intermediate in the reaction of the dimer with 1 *M* HCl. It is seen that

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(10) C. G. Barraclough and R. S. Murray, *J. Chem. Soc.*, 7047 (1965); C. G. Barraclough and M. L. Tobe, *ibid.*, 1993 (1961).

the absorbance at 635 mμ first increases, reaching a maximum after about 15 sec, and then decreases rapidly. The increase and decrease in absorbance at 635 mμ occurs much too rapidly to correspond to the formation and subsequent disappearance of a monomeric product, for the most reactive of the possible monomeric products, *cis*-$Co(en)_2Cl_2^+$, has a half-time for aquation of *ca.* 3000 sec, whereas the decrease in absorbance after the maximum is attained has a half-time at least an order of magnitude shorter than this. Further, if the increase in absorbance at 635 mμ were associated with the formation of monomeric products, then it should continue monotonously until the dimer was essentially gone, since neither the acidity nor the chloride concentration changes appreciably during the reaction. The absorbance increase at 635 mμ must then be due to the formation of a binuclear intermediate. The fact that the maximum absorbance at 635 mμ is not attained until almost 1 half-time for the absorbance change at 525 mμ has transpired suggests that the intermediate has a much lower extinction coefficient than does the dimer at 525 mμ.

The presence of good isosbestic points for the reactions in nitrate and perchlorate solutions argues against the formation of intermediates in substantial concentration, as does the fact that no sudden uptake of acid was observed upon the addition of the dimer in the pH-Stat runs. The linearity of the first-order rate plots over almost the entire period of change for ClO_4^- and NO_3^- solutions also suggests that any intermediates involved are present only at low concentration. However, when reactions at high $HClO_4$ concentrations (*ca.* 1 *M*) were followed at 525 mμ, the rate plots were curved at the beginning, suggesting a short induction period. When solutions of the dimer were acidified rapidly to allow observations of the early part of the reaction, the absorbance at wavelengths longer than *ca.* 570 mμ was seen first to increase and then to decrease. Since a monotonous decrease would have been observed if the only reaction had been the conversion of the dimer to *cis*-$Co(en)_2(H_2O)_2^{3+}$, the increase in absorbance provides evidence for the formation of an intermediate in $HClO_4$ solutions also.

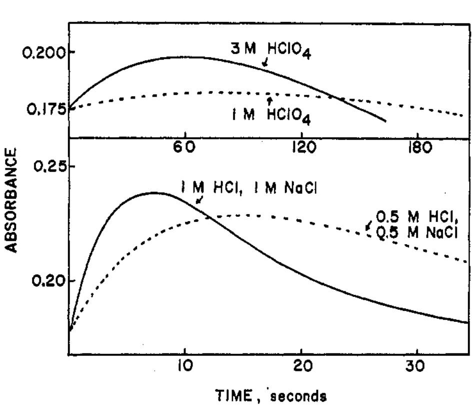

Figure 5.—Change of absorbance at 635 mμ with time during early part of reactions of dimer with $HClO_4$ and HCl solutions at 25°. Initial dimer concentration and path length were the same for all runs.

Figure 5 shows the early part of absorbance–time curves for the reactions of the dimer with HCl and $HClO_4$ solutions as recorded at 635 mμ. Several interesting points are to be noted from Figure 5. For solutions containing initially the same concentration of the dimer, the absorbance increase in ClO_4^- solution becomes more pronounced, and the maximum is achieved earlier, as the H^+ concentration increases. The absorbance increase is greater and the maximum is achieved much earlier for HCl solutions than for $HClO_4$ solutions of the same concentrations. Further, the maximum absorbance attained increases only slightly with increasing H^+ concentration at a given Cl^- concentration.[11]

Since the Hoffman–Taube mechanism requires that the formation of single-bridged intermediates be acid dependent, it is of interest to determine the dependence of the rate of the dimer-to-intermediate conversion on H^+ concentration. To minimize interference from decomposition of intermediates to products or back to reactants, initial rates, *i.e.*, the tangents to the absorbance–time curves at zero time are used in Figure 6 in an attempt to determine the reaction order with respect to H^+. It is seen from Figure 6 that the reactions in both Cl^- and ClO_4^- solutions appear to be first order in H^+. No absolute comparison of the rates in Cl^- and ClO_4^- solution can be made from Figure 6, since the intermediates involved are probably different for the two cases, so that the absorbance change per mole of reaction would also be different.

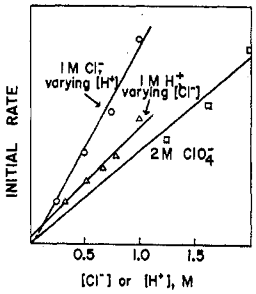

Figure 6.—Variation of initial rate (slope of tangent to absorbance–time plot at zero time) with increasing $[H^+]$ for 2 *M* ClO_4^- solutions (squares) and 1 *M* Cl^- solutions (circles) and with $[Cl^-]$ in mixed Cl^-–ClO_4^- solutions for which $[H^+]$ = 1 *M* (triangles). The initial [dimer] was the same for all points on a given line.

Discussion

As anticipated by Hoffman and Taube, the acid-dependent path for the cleavage of the dimer $(en)_2Co(OH)_2Co(en)_2^{4+}$ in $HClO_4$ and HNO_3 solutions follows the same rate law as that reported by them for the dimer $(NH_3)_4Co(OH)_2Co(NH_3)_4^{4+}$. At low acidities the rate law indicated by our data reduces to the same form as that reported by Rasmussen and Bjerrum for HNO_3 solutions.[12] In contrast to the behavior of the analogous chromium(III) dimer, the behavior of the cobalt(III) dimer is qualitatively the same in $HClO_4$ and HNO_3 so-

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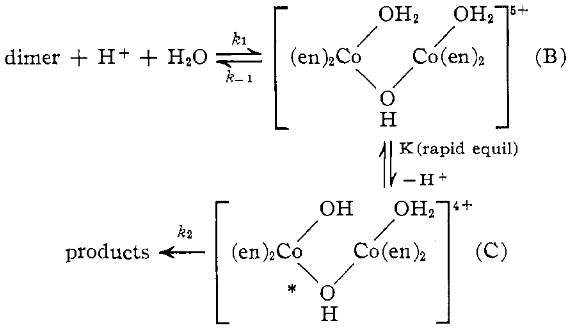
(11) It should be noted that the maximum in the absorbance–time curve does not correspond to the attainment of the maximum concentration of the intermediate. In the present case the products absorb less strongly at 635 mμ than the reactant, so that the maximum concentration of the intermediate is attained after the absorbance maximum, since the decomposition of the intermediate involves a greater absorbance change than does its formation.

(12) Our own kinetic data are consistent with the experimental data of Table V and Figure 1 of ref 1. However, we are unable to reconcile the rate constants quoted in ref 1 with either our own data or the experimental data of ref 1. For example, from the rate constants quoted in ref 1 we estimate that the half-time for the cleavage reaction in 0.004 *M* HNO_3 at 25° should be at least 2300 min, whereas the half-time for these conditions from Table V of ref 1 is *ca.* 120 min.

lutions, although the cleavage rate is substantially higher in NO_3^- solutions than in ClO_4^- solutions at a given H^+ concentration.

The acid-dependent term of the rate law for the cleavage reaction in HNO_3 and $HClO_4$ solution is explained quite adequately by the mechanism proposed by Hoffman and Taube for the ammine dimer



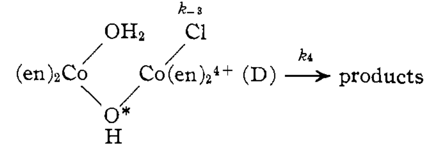
When intermediates B and C have attained steady state, the rate law corresponding to this mechanism is

$$\frac{-\mathrm{d}\ln[\text{dimer}]}{\mathrm{d}t} = \frac{k_1[H^+]}{1 + (k_{-1}/k_2K)[H^+]} \qquad (3)$$

which is of the same form as the rate law of eq 2, if $k_1 = a$ and $k_{-1}/k_2K = b$. In the proposed mechanism the Co–O bond of intermediate C which is expected to cleave in the decomposition of C is indicated by an asterisk. This bond is expected to cleave because it is made labile by the adjacent hydroxo ligand, which is also the feature of intermediate C which is expected to make it more labile than intermediate B.[13,14]

In addition to its consistency with the observed rate law, the proposed mechanism is consistent with other of our observations. The increase and subsequent decrease in absorbance at 635 mμ is evidence for the involvement of intermediates. At the higher $HClO_4$ concentrations at which the absorbance increase at 635 mμ was noted it is expected that intermediate B will be much more abundant than its conjugate base, intermediate C. Few stable complexes having structures similar to B are known, the most similar complex for which the pK is known being the ion *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2^{5+}$, for which the acid dissociation constant[15,16] is *ca.* 1.5×10^{-3}. If the dissociation constant of B is of similar magnitude, then the absorbance increase at 635 mμ in the early stages of the reaction would be due primarily to the conversion of the dimer to B. The proposed mechanism would predict that the initial rate of this absorbance increase would then be first order in H^+, as was observed. Further, the proposed mechanism predicts that the maximum concentration of B achieved will increase with increasing $[H^+]$, *i.e.*, $[B]_{max} = k_1[\text{dimer}]/(k_{-1} + k_2K/[H^+])$. This latter prediction is supported by the dramatically greater increase in absorbance at 635 mμ for 3 M $HClO_4$ than for 1 M $HClO_4$, as illustrated in Figure 5.

The chloride-dependent rate term found for HCl solutions is consistent with the mechanism



This mechanism leads to the steady-state rate law

$$\frac{-\mathrm{d}\ln[\text{dimer}]}{\mathrm{d}t} = \frac{k_3k_4[H^+][Cl^-]}{k_{-3} + k_4} \qquad (4)$$

Equation 4 has the same form as the observed chloride-dependent rate term if $k_{Cl} = k_3k_4/(k_{-3} + k_4)$. That Co–O bond of intermediate D which is indicated by the asterisk is expected to break in the decomposition of D to products, since Cl^- has a considerably greater labilizing effect on other ligands in a complex than does H_2O.[9]

In addition to its consistency with the observed rate law, the proposed mechanism is supported by other evidence. If the absorbance increase at 635 mμ observed during the cleavage of the dimer in HCl solutions is attributed to the conversion of the dimer to intermediate D, then the initial rate of absorbance increase is expected to be directly proportional to both $[H^+]$ and $[Cl^-]$. This expectation is borne out by Figure 6. The above mechanism also requires that, even under conditions such that the chloride-dependent term is dominant, at least half the cobalt originally in the dimer be found in the *cis*-$Co(en)_2(H_2O)_2^{3+}$ product. This was true in all cases, and the distribution of products found at low HCl concentrations agreed fairly well with the quantities predicted using the measured rate constants. For example, in an experiment at 25° and with $[H^+] = 0.08$ M and $[Cl^-] = 0.12$ M which was quenched after *ca.* 3 half-lives, 21% of the cobalt from the dimer was found as *cis*-$Co(en)_2(H_2O)Cl^{2+}$ and 62% as *cis*-$Co(en)_2(H_2O)_2^{3+}$. The cleavage rate under such conditions is about twice that for a ClO_4^- solution of the same acidity so that the ratio *cis*-$Co(en)_2(H_2O)_2^{3+}$:*cis*-$Co(en)_2(H_2O)Cl^{2+}$ expected is about 3:1, as observed. However, substantially larger amounts of *cis*-$Co(en)_2(H_2O)_2^{3+}$ than predicted were formed in the reaction with 1 M HCl. As noted earlier, *cis*-$Co(en)_2(H_2O)_2^{3+}$ accounted for about 70% and chloro complexes for only 30% of the cobalt in 1 M HCl, whereas chloro complexes would be expected to comprise 45% of the products, since the chloride-dependent path accounts for >90% of the reaction in 1 M HCl. A possible explanation for this discrepancy is that part of the original dimer is converted to a new chloride-bridged dimer, such as $(en)_2Co(Cl,OH)Co(en)_2^{4+}$, which could be formed from intermediate D by the elimination of the aquo ligand. A chloride-bridged dimer of similar structure, $(NH_3)_4Co(NH_2,Cl)Co(NH_3)_4^{4+}$, is formed from $(NH_3)_4Co(NH_2,OH)Co(NH_3)_4^{4+}$ in concentrated HCl solutions.[17] To explain the low quantities of chloride complexes found, the proposed new dimer would have to decompose on the ion-exchange column with the loss of chloride.

Another observation which suggests that part of the original dimer is converted to a new dimer is that the

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[13] As examples of the dramatic labilizing effect of OH^- compared to H_2O, *cis*-$Co(en)_2(OH)H_2O^{2+}$ exchanges water 280 times as rapidly[14] as does *cis*-$Co(en)_2(H_2O)_2^{3+}$, and *cis*-$Co(en)_2(OH)Cl^+$ loses Cl^- *ca.* 10^4 times as rapidly[9] as does *cis*-$Co(en)_2Cl(H_2O)^{2+}$.

[14] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961).

[15] G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, **45**, 1425 (1962).

[16] The abundance of C is expected to be even smaller if we take as a model of B the ion $(NH_3)_4(H_2O)Co(NH_2)Co(NH_3)_4(H_2O)^{5+}$, for which p$K$ = 6.2: M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc. A*, 937 (1969).

[17] A. G. Sykes and R. S. Taylor, *ibid.*, *A*, 1424 (1970).

absorbance change associated with the second linear portion of Figure 3 is substantially larger than expected for any reaction of the monomeric products. The main reactions expected for the monomeric products in 1 *M* HCl is the conversion of *cis*-$Co(en)_2Cl_2^+$ and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ to an equilibrium mixture of *cis*- and *trans*-$Co(en)_2(H_2O)Cl^{2+}$. From the known extinction coefficients and equilibrium constants[18] we estimate that these reactions of the monomers should account for only about 8% of the absorbance change at 525 mμ, whereas nearly 30% of the total absorbance change occurs after the first-order reaction of Figure 3 is complete. It must be admitted, however, that no direct evidence for the hypothetical chloride-bridged dimer has been obtained.

The formation of intermediate D has been written as a reversible reaction. If this reaction is irreversible, then it should be possible to use the increase and subsequent decrease in absorbance at 635 mμ to calculate the pseudo-first-order rate constants for the reaction scheme

$$\text{dimer} \xrightarrow{k_5} \text{D} \xrightarrow{k_6} \text{products}$$

where $k_5 = k_3[H^+][Cl^-]$. A reiterative computer fit[19] of the absorbance–time data at 635 mμ to such a scheme for consecutive first-order reactions gave $k_5 = 5.6 \times 10^{-2}$ sec^{-1} and $k_6 = 4.0 \times 10^{-2}$ sec^{-1} in 1 *M* HCl at 25°. From these values we calculate that the half-time for the production of products after the intermediate reaches steady state would be 23 sec, whereas a half-time of 21 sec for disappearance of the dimer is calculated from the data of Table IV. However, such a scheme also predicts a substantial induction period unless the reaction is followed at a wavelength such that the intermediate has an extinction coefficient similar to that of the product mixture. The rate of absorbance change at such a wavelength would of course yield the rate constant for the conversion of the dimer to the intermediate. The value of *k*, the first-order rate constant obtained from the absorbance change at 525 mμ where there is no induction period, is 2.98×10^{-2} sec^{-1} in 1 *M* HCl at 25° (see Table IV), which is substantially lower than the value $k_5 = 5.6 \times 10^{-2}$ sec^{-1}. This difference between *k* and k_5 may simply mean that the conversion of the dimer to the intermediate is after all a reversible reaction.

It cannot be claimed that the reaction of the dimer with HCl solutions is completely understood. However, it is at least clear from our observations that the dimer disappears in HCl solutions by a path involving the addition of one hydrogen ion and one chloride ion and that an intermediate which most likely is also dimeric and contains chloride is the immediate product of the diappearance of the dimer.

Since nitrato complexes were not found among the reaction products and since the behavior of the dimer in nitrate solutions was qualitatively similar to that in perchlorate solutions, there is no basis for ascribing a role to nitrate similar to that ascribed to chloride. The effect of nitrate on the parameter *a* (k_1 of the proposed mechanism) is not unreasonably large for a salt effect when the 4+ charge of the dimer and the 4+ and 5+ charges of the proposed intermediates are considered.

There is a drastic difference between the behavior of $(en)_2Co(OH)_2Co(en)_2^{4+}$ and that of $(en)_2Cr(OH)_2Cr(en)_2^{4+}$ in cleavage reactions. The chromium(III) complex cleaves at a rate independent of $[H^+]$ in perchlorate solutions but is subject to very effective nitrate-catalyzed cleavage, the cleavage rate in 1 *M* HNO_3 being *ca.* 100 times that in 1 *M* $HClO_4$.[20]

Acknowledgment.—The authors are grateful to the National Science Foundation for support of this research through Grants GP-5425 and GP-9115.

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[18] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *ibid.*, 4637 (1961).

[19] K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York, N. Y., 1965, p 181.

[20] NOTE ADDED IN PROOF.—Results of an independent kinetic study of the reaction of the dimer in $HClO_4$ solutions have been reported recently: A. A. El-Awady and Z Z. Hugus, Jr., *Inorg. Chem.* **10**, 1415 (1971).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN 48202

Metal Chelates Containing Bicyclic Rings. II. Preparation and Characterization of Hydroxymethylenenorcamphor and Its Metal Chelates

BY LONDA L. BORER AND RICHARD L. LINTVEDT*

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A new ligand, hydroxymethylenenorcamphor (HMNC), has been synthesized and characterized. Several new $HMNC^-$ chelates have been prepared from the first transition series metals. These compounds are the simplest members of a class of chelates in which a bicyclic-ring system is fused to an unsaturated, six-membered chelate ring. The infrared spectra indicate a significant chelate ring asymmetry due to the presence of the strained five-membered ring fused to it. Magnetic, molecular weight, and analytical data indicate that several of the bis chelates exist as oligomeric molecules containing bridging oxygens from chelated $HMNC^-$.

Introduction

Chelates in which an anionic, bidentate ligand contains a bicyclic-ring system are not well known. The only compounds of this type previously reported contain the camphor group. Certain features have prompted us to investigate a number of chelates containing bicyclic groups, including the camphor group. These features are as follows: (1) optically pure ligands are obtainable in many cases, (2) there are readily variable structural features in the bicyclic-ring system, and (3) the electronic structure of the chelate ring can be significantly modified by changing the size of the bicyclic ring system fused to it.