

molecule to form the inactive meso form, so that $k_R = k_i$. However, with both *trans*-[Co(dien)₂]³⁺ (two reactive centers) and [Co(NH₃)₄(*N*-Meen)]³⁺ (one asymmetric center) only one center per two molecules need invert to form racemate, so that $k_R = 2k_i$. The inversion rates k_i are thus essentially similar for these latter ions of identical charge (allowing for the [Co] and μ differences), while that for *sym*-[Co(trenen)N₃]²⁺ ($k_R = 2k_i$) may be slightly higher (Table IV).

Statistical factors do not enter into the H-exchange rate measurements so that the deuteration rates for the two 3+ complexes differ threefold (Table IV) as do the retention ratios k_D/k_i , 2.5×10^5 for [Co(NH₃)₄(*N*-Meen)]³⁺ and 8×10^5 for *trans*-[Co(dien)₂]³⁺. These ratios for the 3+ complexes are considerably less than for *sym*-[Co(trenen)N₃]²⁺, $k_D/k_i = 4.6 \times 10^6$. This factor cannot be correlated with the charge difference and it is difficult to associate with some restriction on conformational interchange in the trenen complex since the k_i rates are similar, so that it is probably to be ascribed to the electronegative azido substituent. Although the two highly electronegative groups did not appear to increase the retention ratio in *trans,trans*-[Co(*N*-Meen)₂(NO₂)₂]⁺ ($k_D/k_i = 9 \times 10^4$), the nitro groups are *cis* to the asymmetric centers in this instance. It seems likely that the azido group is exerting a *trans* effect in *sym*-[Co(trenen)N₃]²⁺, enhancing k_D and k_D/k_i . This may not be a general effect however, since estimates of N-H exchange rates at both "angular" and "planar" secondary nitrogen donor sites in α -[Co(trien)NH₃Cl]²⁺¹⁸ and the various configurations of β -[Co(trien)gly]²⁺¹⁹ (trien = triethylenetetramine; gly = glycinate anion) indicate that both detailed ring geometry and position of elec-

tronegative substituent affect these rates, but so far few generalizations have emerged.

Other features found common with previous observations are an isotope effect for exchange similar to that in [Co(NH₃)₄(*N*-Meen)]³⁺ ($k_D/k_H \approx 3$)⁴ and a decrease of racemization rate in phosphate buffers (Table III) associated with ion pairing.

A feature not observed previously^{3,5} however is a small dependence of all rates on complex concentration, and the effect of ionic strength on all rates is larger than previously noted³ (Tables I and II). These features may be rationalized on the basis of ion pairing. Ion association of Cl⁻ (or NO₃⁻) may restrict access of the catalyzing base to the exchangeable proton or reduce the effective positive charge on the complex moiety, so that the ion pair would be less reactive toward exchange (on both mechanisms A and B) and the racemization rate would be consequently diminished also. Slower rates would thus result from increasing μ or by adding KCl to maintain μ constant when [complex] is reduced. Such interactions may be rather specific²⁰ so that the smaller effects noted by the previous workers need not be surprising, despite the larger specific effect of phosphate on the [Co(NH₃)₄sarc]²⁺ system.³

The parallel effects of varying [complex] and μ on both the exchange and racemization rates are more consistent with mechanism A, involving a common intermediate for both processes, than with mechanism B (Figure 2), so that we concur with the remarks of the previous authors. The conceptual difference between the alternative mechanisms is small however.

Acknowledgment.—We are grateful to Drs. D. A. Buckingham (Australian National University) and M. Dwyer (University of Adelaide) for helpful discussions on this work.

(20) S. F. Mason and B. J. Norman, *Proc. Chem. Soc., London*, 339 (1964); *Chem. Commun.*, 73 (1965); I. R. Lantzke and D. W. Watts, *Aust. J. Chem.*, **19**, 999 (1966); **20**, 2623 (1967).

(18) M. Dwyer, Ph.D. Thesis, Australian National University, Canberra, 1971.

(19) D. A. Buckingham, M. Dwyer, L. G. Marzilli, A. M. Sargeson, and K. R. Turnbull, unpublished results.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON, W.C.1, ENGLAND

Mechanism and Steric Course of Octahedral Aquation. XV.¹ The Acid-Catalyzed Hydrolysis of *trans*-Diacetatobis(ethylenediamine)cobalt(III) Ions

BY T. P. DASGUPTA AND M. L. TOBE*

Received August 16, 1971

The aquation of *cis*- and *trans*-[Co(en)₂(OAc)₂]⁺ (en = 1,2-diaminoethane, OAc = acetate) is acid catalyzed and in both cases obeys the rate law $-d \ln [\text{Co}(\text{en})_2(\text{OAc})_2]/dt = kK[\text{H}^+](1 + K[\text{H}^+])^{-1}$. The *cis* isomer is considerably more labile than the *trans* as a result of larger values of k and K . The acid dependence arises from a preequilibrium protonation which, in the case of the *trans* isomer, has been examined independently by spectrophotometry. The *trans*-diacetato cation yields both *cis*- and *trans*-[Co(en)₂OAc(H₂O)]²⁺ in the ratio found at equilibrium (75% *cis*, 25% *trans*) even when the aquation is faster than the subsequent isomerization. The *cis*-diacetato complex aquates with complete retention of configuration. The rates of approach to equilibrium of *cis*- and *trans*-[Co(en)₂(OAc)H₂O]²⁺ are independent of acid concentration; $k_{\text{isom}} = 2.5 \times 10^{-6} \text{ sec}^{-1}$ at 25° (0.01 *M* HClO₄), $\Delta H^\ddagger = 28.5 \pm 0.4 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = +15.6 \pm 1.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$. In strong acid, the [Co(en)₂(OAc)H₂O]²⁺ species aquate further to form *cis*-[Co(en)₂(H₂O)₂]³⁺.

Introduction

Many years ago it was shown that the rates and steric courses of solvolytic displacement of X from *trans*-[Co(en)₂AX]ⁿ⁺ were very sensitive to the nature of A.²

(1) Part XIV: V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, **9**, 1785 (1970).

(2) M. L. Tobe, *ibid.*, **7**, 1260 (1968), and references therein.

In general, configuration is retained in the act of solvolysis, but when A is a potential π donor, aquation is accompanied by stereochemical change. The number of ligands producing this effect is severely restricted, e.g., A = OH, Cl, Br, and -NCS (and -NHR presumably since base hydrolysis often leads to stereochemical

changes). Having recently demonstrated¹ that $A = N_3$ does not induce stereochemical change it seemed reasonable to search for others to take its place. The carboxylate ligand $R\text{COO}^-$ can be formulated as a potential π donor, although not a particularly good one, and we have embarked on a study of the acid- and the base-catalyzed solvolyses of complexes of the type $[\text{Co}(\text{en})_2(\text{O}_2\text{CR})\text{X}]^{n+}$. The complexes $[\text{Co}(\text{en})_2(\text{O}_2\text{CR})_2]^{n+}$ can also provide valuable information about the mechanism of the acid-catalyzed displacement of an RCO_2^- ligand. For example, C–O bond fission must, of necessity, lead to substitution with retention of configuration. While extensive studies have been made on $[\text{M}(\text{NH}_3)_5\text{O}_2\text{CR}]^{2+}$ systems^{3–6} where no means of signposting exist, little has been reported on the acid hydrolysis of complexes of the type $[\text{ML}_4\text{AO}_2\text{CR}]^{n+}$, where A can function as a signpost. Studies by Chester^{7,8} in glacial acetic acid indicate that solvolysis of acetate in $[\text{Co}(\text{en})_2(\text{O}_2\text{CCH}_3)_2]^{n+}$ might be accompanied by steric change.

Experimental Section

trans-Diacetatobis(ethylenediamine)cobalt(III) perchlorate was prepared by the method of Linhard and Stirn.⁹ The complex was recrystallized from methanol instead of ethanol. *Anal.* Calcd for $\text{C}_8\text{H}_{22}\text{N}_4\text{CoClO}_4$: C, 24.2; H, 5.55; N, 14.1. Found: C, 24.0; H, 5.78; N, 14.4. *cis*-Diacetatobis(ethylenediamine)cobalt(III) perchlorate was prepared from *cis*-diaquobis(ethylenediamine)cobalt(III) perchlorate by a method of Linhard and Stirn.⁹ *Anal.* Calcd for $\text{C}_8\text{H}_{22}\text{N}_4\text{CoClO}_4$: C, 24.2; H, 5.55; N, 14.1. Found: C, 23.9; H, 5.42; N, 14.3. *trans*-Aquoacetatobis(ethylenediamine)cobalt(III) perchlorate was prepared by a slight modification of the method of Illuminati.¹⁰ In our hands the original method gave a product that was contaminated with some *trans*-diacetato perchlorate and therefore more sodium perchlorate (0.8 g instead of 0.5 g) was added to the acidified solution which was then kept for 10–12 hr in a refrigerator to ensure precipitation of all the *trans*-diacetato impurity. The filtrate, on standing at 0° for a further 3 days, deposited the *trans*-aquoacetato perchlorate as well formed crystals which could be filtered off, washed with absolute ethanol, air-dried, and recrystallized by adding a small amount of sodium perchlorate to a saturated aqueous solution. Any remaining *trans*-diacetato salt precipitated first and the desired complex crystallized slowly from the cooled solution. After 24 hr the crystals were filtered off, washed with ethanol and ether, and air-dried. The purity was improved at the expense of the yield (10%). *Anal.* Calcd for $\text{C}_6\text{H}_{21}\text{CoN}_4\text{O}_{11}\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 15.2; H, 4.86; N, 11.8. Found: C, 15.1; H, 4.89; N, 12.0. The best criterion for the purity of this compound is the spectrum of the aqueous solution (pH 3) after the *trans* \rightleftharpoons *cis* isomerization is complete. *trans*- $[\text{Co}(\text{en})_2(\text{OAc})_2]^{2+}$ does not react under these conditions. *cis*-Aquoacetatobis(ethylenediamine)cobalt(III) perchlorate was prepared, *in situ*, by adding dilute perchloric acid to an aqueous solution of *cis*- $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$. The spectrum agrees closely with that reported in the literature.¹⁰

Kinetics.—The slower reactions were studied spectrophotometrically using a Unicam SP800 spectrophotometer. Solutions were prepared by dissolving weighed amounts of the solid complex in the minimum amount of water and then adding the required amount of sodium perchlorate–perchloric acid solution previously brought to the reaction temperature. The volume was made up to a known amount by prethermostated water and the solution was quickly transferred to the spectrophotometer cell. The re-

action was followed, either by repeatedly scanning the spectrum over the range 700–250 nm or else, especially in the faster reactions, by fixing the wavelength and allowing the recorder to move at a constant rate.

For reactions of half-life shorter than 30 sec, it was necessary to use a Durrum–Gibson stopped-flow apparatus. Solutions of the complex and of perchloric acid, each at the same ionic strength, were mixed and the change in transmission at 505 nm was recorded on a storage oscilloscope. For the relatively slower reactions it was convenient to couple the oscilloscope with a fast-moving pen recorder and in this way it was possible to use the stopped-flow apparatus for accurate kinetics with half-lives between 5 and 30 sec.

All reactions were carried out under pseudo-first-order conditions and the pseudo-first-order rate constants were determined from the absorbance changes by the appropriate standard graphical methods.

Equilibria.—The protonation equilibrium for *trans*- $[\text{Co}(\text{en})_2(\text{OAc})_2]^{2+}$ was measured spectrophotometrically using a Unicam SP500 spectrophotometer with a thermostated cell housing. Solutions were prepared by adding a known volume of a concentrated aqueous solution of the complex to a thermostated sample of dilute perchloric acid. The absorbance at 320 nm was measured as rapidly as possible. The whole operation was complete in less than 40 sec, during which time aequation was negligible.

Results

(A) **The *Trans* \rightleftharpoons *Cis* Isomerization of $[\text{Co}(\text{en})_2\text{CH}_3\text{COOH}_2\text{O}]^{2+}$.**—Carunchio and Ortaggi¹¹ have reported that *trans*- $[\text{Co}(\text{en})_2\text{CH}_3\text{COOH}_2\text{O}]^{2+}$ changes to the *cis* isomer in aqueous and methanolic solutions and have recorded the rate constants over a range of temperature, ionic strength, and pH. In view of the fact that they did not mention the presence of any *trans* isomer at equilibrium, we present our results for comparison.

The spectrum of a solution of *trans*- $[\text{Co}(\text{en})_2\text{CH}_3\text{COO}(\text{H}_2\text{O})](\text{ClO}_4)_2$ changes with time, with clean isosbestic points at 547, 440, and 403 nm. These correspond exactly to the common points in the spectra of *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{CH}_3\text{COOH}_2\text{O}]^{2+}$ and the process is identified as a *trans* \rightleftharpoons *cis* isomerization. The equilibrium mixture contains $75 \pm 2\%$ *cis* and $25 \pm 2\%$ *trans* isomer and this composition is essentially independent of temperature or pH. The same equilibrium is obtained from *cis*- $[\text{Co}(\text{en})_2\text{CH}_3\text{COOH}_2\text{O}]^{2+}$, generally formed, *in situ*, by the acid hydrolysis of *cis*- $[\text{Co}(\text{en})_2(\text{CH}_3\text{COO})_2]^{2+}$. The approach to equilibrium is first order with respect to complex, and the specific rate constants (obtained from the slope of the plot of $\log |D_t - D_\infty|$ against time, where D_t and D_∞ are the optical densities of the solutions at time t and after 8 half-lives, respectively) of approach to equilibrium are the same starting from the *cis* and *trans* substrates. These values are collected in Table I. Calculations were made using data at 490 nm where there is the maximum change in optical density, but the rate constants are independent of the wavelength chosen.

The agreement between these data and those of Carunchio and Ortaggi¹¹ is reasonably good. Their activation parameters are somewhat lower ($\Delta H^\ddagger = 26.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 11.1 \text{ cal deg}^{-1} \text{ mol}^{-1}$) but the Eyring plot in this paper covers a greater temperature range.

(B) **The Aequation of *trans*- $[\text{Co}(\text{en})_2(\text{CH}_3\text{COO})_2]^{2+}$.**—The spectra of *trans*- $[\text{Co}(\text{en})_2(\text{CH}_3\text{COO})_2]^{2+}$ and *trans*- $[\text{Co}(\text{en})_2(\text{CH}_3\text{COO})\text{H}_2\text{O}]^{2+}$ are very similar over the whole range of the visible and near-ultraviolet spectra,

(3) F. Basolo, J. G. Bergmann, and R. G. Pearson, *J. Chem. Phys.*, **66**, 22 (1952).

(4) C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

(5) F. Basolo, F. Monacelli, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

(6) R. Davies, G. B. Evans, and R. B. Jordan, *Inorg. Chem.*, **8**, 2035 (1969).

(7) A. W. Chester, *Inorg. Chem.*, **8**, 1584 (1969).

(8) A. W. Chester, *ibid.*, **9**, 1746 (1970).

(9) M. Linhard and G. Stirn, *Z. Anorg. Allg. Chem.*, **268**, 105 (1952).

(10) V. Carunchio, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **6**, 2168 (1968).

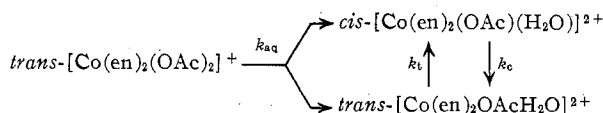
(11) V. Carunchio and G. Ortaggi, *Ric. Sci.*, **37**, 1121 (1967). We thank the referee who drew our attention to this paper.

TABLE I^a
SPECIFIC FIRST-ORDER RATE CONSTANTS FOR THE
APPROACH TO EQUILIBRIUM IN THE REACTION

<i>trans</i> -[Co(en) ₂ (CH ₃ COO)(H ₂ O)] ²⁺ ⇌			<i>cis</i> -[Co(en) ₂ (CH ₃ COO)(H ₂ O)] ²⁺		
Temp, °C	[H ⁺], M	10 ³ k _{obsd} , sec ⁻¹	Temp, °C	[H ⁺], M	10 ³ k _{obsd} , sec ⁻¹
30.0	0.01	0.057 ^b	39.0	1.0	0.25 ^c
34.0	0.01	0.096 ^b	39.0	2.0	0.33 ^b
39.0	0.01	0.24 ^b	49.0	0.01	1.02 ^b
39.0	0.5	0.27 ^c	56.0	0.01	2.3 ^b
39.0	1.0	0.28 ^b			

^a ΔH[‡] = 28.5 ± 0.4 kcal mol⁻¹; ΔS[‡] = 15.6 ± 1.6 cal deg⁻¹ mol⁻¹. ^b Starting from *trans*-[Co(en)₂(CH₃COO)H₂O](ClO₄)₂. ^c Starting from *cis*-[Co(en)₂(CH₃COO)₂]ClO₄.

whereas that of the *cis*-[Co(en)₂(CH₃COO)H₂O]²⁺ cation is completely different.¹⁰ Consequently a complete and accurate spectrophotometric analysis is impossible, although the fraction in the form of the *cis*-aquoacetato complex can be determined quite accurately. The general features of the changes consequent to acidifying a solution of *trans*-[Co(en)₂(CH₃COO)₂]ClO₄ with perchloric acid are nevertheless relatively simple. There is an immediate change, the extent of which depends on the concentration of acid, in the near-uv region. This is discussed separately below. A slow change then follows, with clean isosbestic points at 536, 435, and 413 nm at the lower acid concentrations but these shift to 538, 437, and 407 nm at the highest acid concentrations studied. The final spectrum corresponds fairly closely with that of the equilibrium *cis*- and *trans*-[Co(en)₂(CH₃COO)H₂O]²⁺ mixture. Except at the highest acid concentrations used, this reaction is very much faster than the subsequent loss of the second acetate. The change in optical density at any wavelength in the range 460–510 nm follows a first-order rate law using the equilibrium optical density as *D*_∞. The apparent rate constant *k*_{app} is independent of the wavelength chosen. At the lowest acid concentration *k*_{app} is sufficiently smaller than *k*_{isom}, determined independently, for the solvolytic process to be rate determining. Under these circumstances the overall spectrophotometric change will be unaffected by any subsequent isomerization of the aquoacetato product and *k*_{app} can be equated to *k*_{aq} for the *trans*-diacetato complex. As [H⁺] is increased, so *k*_{app} increases and, without any change in the form of the first-order kinetics or the isosbestic points in the course of reaction, approaches and then passes the value of *k*_{isom}. At 39.0° and 1.5 M perchloric acid, *k*_{app} = 5.8 × 10⁻⁴ sec⁻¹ and *k*_{isom} = 3.0 × 10⁻⁴ sec⁻¹. Under these circumstances, the solvolysis is no longer rate determining. In the absence of any direct measurement of the rate of release of CH₃COO⁻ we were unable to assign an independent value to *k*_{aq}. However, the data can be analyzed for a reaction of the type



by means of the expression

$$\frac{f - f_\infty}{f_0 - f_\infty} = \frac{k_{aq}}{k_{isom} - k_{aq}} \left[\frac{\exp(-k_{aq}t) - \exp(-k_{isom}t)}{1 - \exp(-k_{aq}t)} \right]$$

where *f* is the fraction of the aquo product in the form of the *cis* isomer at time *t*, *f*_∞ is the fraction of *cis* isomer

at equilibrium, *f*₀ is the fraction of *cis* isomer in the product when it is formed and before it has isomerized, and *k*_{isom} = *k*_i + *k*_o. Using *f*₀ and *k*_{aq} as independent variables it was possible to calculate sets of curves for *A*_{cis} as a function of time, where

$$A_{cis} = \frac{[\text{cis-aquoacetato}]}{[\text{complex}]_{total}} = f[1 - \exp(-k_{aq}t)]$$

It is possible to obtain a wide range of connected pairs of values for *k*₀ and *f* that will lead to an essentially linear plot of log (*D*_∞ - *D*) against *t*. In order to do this, as *f*₀ increases, *k*_{aq} must increase in compensation. The initial part of the experimental curve can be closely fitted by a wide range of such values but the only way to cover the later stages of the reaction as well is to make *f*₀ ≈ 0.70–0.80 *cis*. If the aquo product is produced in its equilibrium *cis*:*trans* ratio, there will be no subsequent isomerization and *A*_{cis} = [1 - exp(-*k*_{aq}*t*)]*f*_∞; *i.e.*, there will be a true exponential change in optical density and *k*_{aq} ≈ *k*_{app}. Thus the observed first-order behavior, through and past the acidity where *k*_{aq} and *k*_{isom} become comparable in magnitude, can be easily understood, and the departure from the first-order dependence on acid concentration can be related to a protonation equilibrium and not an error in the determination of *k*_{aq} as a result of ignoring the subsequent isomerization. The first-order rate constants determined in this way are collected in Table II.

TABLE II
FIRST-ORDER RATE CONSTANTS FOR THE AQUATION
OF *trans*-[Co(en)₂(CH₃COO)₂]ClO₄ AT
μ = 2.0 M AND [COMPLEX] = 5 × 10⁻³ M

39.0°		50.0°		60.0°	
[H ⁺], M	10 ⁴ k _{obsd} , sec ⁻¹	[H ⁺], M	10 ⁴ k _{obsd} , sec ⁻¹	[H ⁺], M	10 ⁴ k _{obsd} , sec ⁻¹
				0.00	0.03 ^a
0.10	0.92	0.10	4.5	0.10	12.7
0.15	1.3	0.125	5.8	0.15	19.2
0.18	1.6	0.15	6.4	0.20	23
0.20	1.85	0.20	9.2	0.30	33
0.40	2.8	0.25	8.8	0.40	39
0.50	3.4	0.40	14.6	0.50	46
0.80	4.3	0.50	15.3	0.70	59
1.00	5.5	0.70	19.8	0.80	51
1.50	5.8	0.70	25	1.00	57
2.00	7.0	0.80	26	2.00	70
		1.00	21		
		1.50	28		

^a No added acid, μ = 5 × 10⁻³ M.

A further confirmation of the steric course is shown in Figure 1 where a set of curves of ε vs. time have been calculated using the known values of *k*_{aq}, *k*_{isom}, and *f*_∞ and varying *f*₀. The experimental data lie close to the line for *f*₀ = 0.80.

(C) **The Aquation of *cis*-[Co(en)₂(CH₃COO)₂]⁺.**—The spectrophotometric study of this reaction presents none of the difficulties encountered with the *trans* isomer. The rate of reaction is so much greater that, except at the lowest acid concentrations, the reaction is complete before there is any interference from the subsequent isomerization. Spectrophotometric analysis indicates that the first product is pure *cis*-[Co(en)₂(OAc)H₂O]²⁺, and using calculated values for *D*_∞ based on this product or experimental values in the fast stopped-flow experiments, it was possible to calculate *k*_{aq} for this species. These values are collected in Table III.

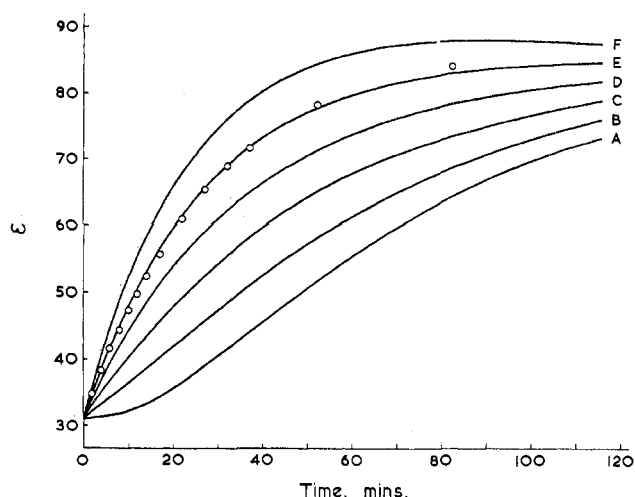


Figure 1.—Plots of ϵ (apparent extinction coefficient at 497 nm) against time: O, experimental points (39.0° , $2.00 M$ ionic strength); curves are calculated for $f_0 = 0$ (A), 0.20 (B), 0.40 (C), 0.60 (D), 0.80 (E), 1.00 (F), using $k_{aq} = 5.8 \times 10^{-4} \text{ sec}^{-1}$, $k_{isom} = 3.3 \times 10^{-4} \text{ sec}^{-1}$, $f_\infty = 0.75$, $\epsilon(\text{trans-Co(en)}_2(\text{OAc})_2^+) = 31.0$, $\epsilon(\text{trans-Co(en)}_2(\text{OAc})\text{H}_2\text{O}^{2+}) = 30.0$, and $\epsilon(\text{cis-Co(en)}_2(\text{OAc})\text{H}_2\text{O}^{2+}) = 103.5 M^{-1} \text{ cm}^{-1}$.

TABLE III
FIRST-ORDER RATE CONSTANTS FOR THE AQUATION
OF $\text{cis-Co(en)}_2(\text{CH}_3\text{COO})_2\text{ClO}_4$ AT $\mu = 2.0 M$
AND $[\text{COMPLEX}] = 10^{-3} M$

30.0°		39.0°		50.0°	
[H ⁺], M	10 ³ k _{obsd} , sec ⁻¹	[H ⁺], M	10 ³ k _{obsd} , sec ⁻¹	[H ⁺], M	10 ³ k _{obsd} , sec ⁻¹
0.020	1.66	0.01	2.1	0.01	4.4
0.025	1.88	0.02	4.0	0.002	9.9
0.04	3.1	0.03	5.3	0.03	13.9
0.05	3.5	0.04	6.5	0.04	18.0
0.08	4.9	0.05	7.9	0.05	19.1
0.10	5.4	0.075	9.2	0.10	34
0.15	7.4	0.10	12.8	0.20	44
0.20	8.3	0.20	19.3	0.30	52
0.30	9.5	0.30	21	0.40	63
0.40	9.8	0.40	23		
0.50	9.6	0.50	23		
0.70	9.6	0.60	23		
0.80	9.4	0.70	23		
1.00	9.4	0.80	23		
		1.00	23		
		0.01	0.3 ^a		
		0.01	3.6 ^b		
		0.01	4.7 ^c		

^a $\mu = 0.01 M$. ^b $\mu = 4.0 M$. ^c $\mu = 6.0 M$.

(D) Protonation Equilibrium of $\text{trans-Co(en)}_2(\text{CH}_3\text{COO})_2^+$.—Whereas the visible absorption spectrum of $\text{trans-Co(en)}_2(\text{CH}_3\text{COO})_2^+$ in aqueous acid is virtually independent of the hydrogen ion concentration, the absorbance at wavelengths below 340 nm markedly increases with acid concentration when this is greater than $0.3 M$. Addition of sodium or lithium perchlorate in similar concentration does not affect the spectrum indicating that the effect is due to the proton rather than to ion association with the perchlorate. The changes in optical density follow a relationship of the type

$$\frac{D - D_0}{cl} = \frac{a[\text{H}^+]}{1 + K[\text{H}^+]}$$

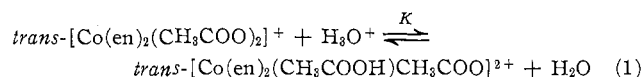
(where c is the total concentration of complex and l is the length of light path) and a plot of $cl/(D - D_0)$ against $1/[\text{H}^+]$ is linear with slope $1/a$ and intercept K/a . Values of K are collected in Table IV. If the

TABLE IV
EQUILIBRIUM AND RATE CONSTANTS DERIVED FROM
VARIATION OF SPECTRAL AND RATE DATA
WITH ACID CONCENTRATION ($\mu = 2.0 M$)

Temp, °C	Slope	Intercept	K, M^{-1}	$\epsilon_{\text{BH}^+} - \epsilon_{\text{B}}$	$10^3 k_1, \text{sec}^{-1}$	$10^3 k_2, M^{-1} \text{sec}^{-1}$
<i>trans-Co(en)₂(OAc)₂⁺</i>						
26.0	0.028 ^a	0.030 ^a	1.08	33
30.0	0.028 ^a	0.032 ^a	1.16	31
35.0	0.025 ^a	0.034 ^a	1.35	29
39.0	0.022 ^a	0.032 ^a	1.44	31
39.0	970 ^b	1020 ^b	1.05	...	0.98	1.03
50.0	217 ^b	270 ^b	1.22	...	3.7	4.6
60.0	65 ^b	97 ^b	1.48	...	10.3	15.3
<i>cis-Co(en)₂(OAc)₂⁺</i>						
30.0	1.07 ^b	7.0 ^b	6.5	...	142	930
39.0	0.47 ^b	3.5 ^b	7.4	...	290	2120
50.0	0.17 ^b	1.4 ^b	8.2	...	710	5900

^a From a plot of $cl/(D - D_0)$ vs. $1/[\text{H}^+]$. ^b From a plot of $1/k_{\text{obsd}}$ vs. $1/[\text{H}^+]$.

spectral changes arise from an equilibrium of the type



then it can easily be shown that K is the equilibrium constant for this process and $a = (\epsilon_{\text{BH}^+} - \epsilon_{\text{B}})K$, where ϵ_{BH^+} and ϵ_{B} are the molar extinction coefficients of the protonated and unprotonated complex at the wavelength studied.

Discussion

The aquation of both *cis*- and *trans*- $[\text{Co(en)}_2(\text{OAc})_2]^+$ is clearly acid dependent, the order in hydrogen ion changing from 1 at low acid concentrations to zero at higher acid, and the general dependence is consistent with a relationship of the form

$$-d \ln [\text{Co(en)}_2(\text{OAc})_2^+] / dt \equiv k_{\text{obsd}} = k[\text{H}^+](1 + K[\text{H}^+])^{-1}$$

Under these circumstances $1/k_{\text{obsd}} = (1/k[\text{H}^+]) + (K/k)$ so that a plot of $1/k_{\text{obsd}}$ vs. $1/[\text{H}^+]$ should be linear with slope $1/k$ and intercept K/k . These plots are shown in Figures 2 and 3 and the slopes and intercepts are collected in Table IV. The observed rate

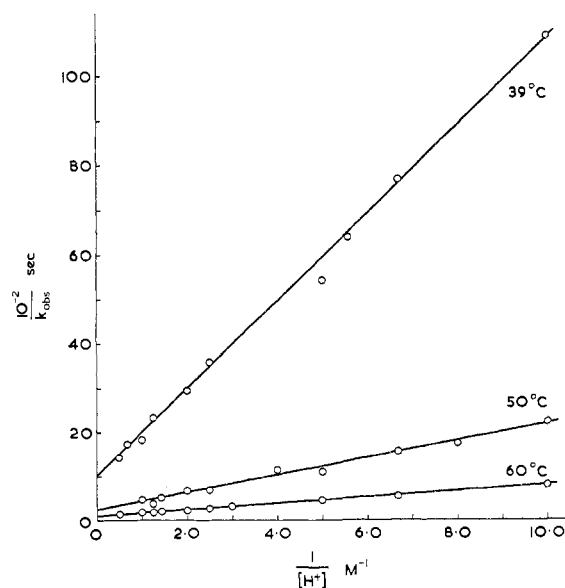


Figure 2.—Plots of $1/k_{\text{obsd}}$ vs. $1/[\text{H}^+]$ for the acid-catalyzed aquation of $\text{trans-Co(en)}_2(\text{CH}_3\text{COO})_2\text{ClO}_4$ ($\mu = 2.00 M$, NaClO_4).

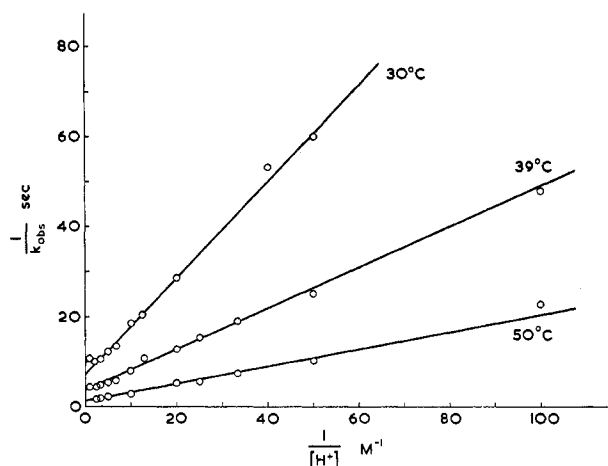
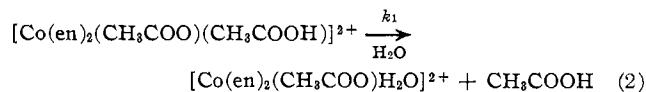
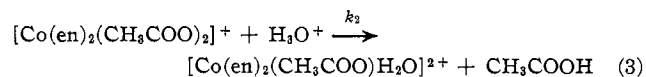


Figure 3.—Plots of $1/k_{\text{obs}}$ vs. $1/[\text{H}^+]$ for the acid-catalyzed aquation of $\text{cis-}[\text{Co}(\text{en})_2(\text{CH}_3\text{COO})_2]\text{ClO}_4$ ($\mu = 2.00 \text{ M}$, NaClO_4).

law can be accounted for by assuming the rapid and reversible protonation of the substrate, as in (1), followed by either a slow dissociation of the protonated species



or a slow bimolecular attack of H_3O^+ on the unprotonated species



Both sequences will lead to the observed rate law; (1) + (2) requires that $k = k_1K$ while (1) + (3) requires that $k = k_2$. Values of k_1 , k_2 , and K are also collected in Table IV. The agreement between the spectrophotometric and kinetically determined values for K , the protonation constant for the *trans*-diacetato complex, while not being particularly good, is as good as, if not better than, that obtained by Deutsch and Taube,¹² who have made a similar study of the acid hydrolysis of $[\text{Cr}(\text{H}_2\text{O})_5\text{OAc}]^{2+}$ and their explanations for the discrepancies apply equally well in this case. The differences are not large enough for us to invoke a second protonation as did Wakefield and Schaap¹³ in order to account for similar but much greater discrepancies observed in the aquation of *fac*- $[\text{Cr}(\text{H}_2\text{O})_3(\text{CN})_3]$ and *cis*- $[\text{Cr}(\text{H}_2\text{O})_4(\text{CN})_2]^+$. The enthalpy and entropy changes associated with protonation are collected in Table V. The spectrophotometric and kinetic data have been treated separately since when $\log K$ is plotted against $1/T$, the two sets of data produce two parallel lines. The best straight line through all points yields $\Delta H^\circ = 1.7 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = 6 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The *cis*-diacetato complex was too reactive to allow a nonkinetic investigation of the protonation equilibrium. This is unfortunate because there is a marked discrepancy between k_1 obtained from the plot of $1/k_{\text{obs}}$ vs. $1/[\text{H}^+]$ and the limiting rate constant at high acid concentration. This is especially noticeable at the lower temperatures studied. Indeed, at 30° , $k_1 = 0.142 \text{ sec}^{-1}$; yet the maximum value for k_{obs} , found at 0.40 M H^+ , is 0.098 sec^{-1} and at greater acidity

(12) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(13) D. K. Wakefield and W. B. Schaap, *ibid.*, **10**, 306 (1971).

TABLE V
ENTHALPY AND ENTROPY CHANGES OF PROTONATION
AND ACTIVATION FOR THE ACID HYDROLYSIS OF
cis- AND *trans*- $[\text{Co}(\text{en})_2(\text{OAc})_2]^+$ ($\mu = 2.0 \text{ M}$)

	<i>trans</i> -(OAc) ₂	<i>cis</i> -(OAc) ₂
ΔH° , kcal mol ⁻¹	3.7 (3.5) ^a	1.7
ΔS° , cal deg ⁻¹ mol ⁻¹	+11 (+12) ^a	+9
ΔH_1^\ddagger , kcal mol ⁻¹	23.0	15.4
ΔS_1^\ddagger , cal deg ⁻¹ mol ⁻¹	+1	-13
ΔH_2^\ddagger , kcal mol ⁻¹	26.7	16.0
ΔS_2^\ddagger , cal deg ⁻¹ mol ⁻¹	+12	-5

^a Values in parentheses are from the spectrophotometric study of protonation.

there is a noticeable decrease in reactivity. It is possible that this indicates a second protonation and a more stable species (or attack by H_3O^+ on the monoprotonated species) but it may very well arise from the replacement of Na^+ by H^+ in the medium of "constant" ionic strength when there is the possibility of "chelation" by the noncoordinated carbonyl oxygens of the *cis* acetato groups. Further work is indicated in this system. The activation parameters for the two independent paths are, of course, numerically related through the relationship in which k_1K is numerically equal to k_2 .

Although the kinetic form does not permit a distinction between the two possible mechanisms (paths 2 and 3), the assignment for the *trans*-diacetato complex presents little difficulty. The fact that the acid-catalyzed aquation goes with stereochemical change demonstrates unequivocally that the substitution *cannot* occur with carbon-oxygen fission. This being so, we would expect to find that the normal mode of dissociative activation, characteristic of substitution at Co(III), takes place. The role of an attacking H_3O^+ is by no means obvious in such a situation, whereas the weakening of the Co-O bond by protonation of the acetato ligand would obviously lead to a much more rapid bond dissociation. Even were it possible for attack by H_3O^+ on Co(III) to be the mechanism, it would be necessary to find why the protonated species is unreactive toward this mode of attack. It would be necessary to assume that the labilizing power of the nonleaving *trans* acetate was the dominant factor and that protonation drastically reduced its *trans* effect. Studies of the aquation of *trans*- $[\text{Co}(\text{en})_2(\text{OAc})\text{Cl}]^+$ ¹⁴ give no indication that the rate of chloride release is retarded by added acid. The steric course of acid-catalyzed aquation of the *trans*-diacetato complex and a 75% *cis*- + 25% *trans*-aquoacetato complex is identical with that of the Hg^{2+} -catalyzed aquation of *trans*- $[\text{Co}(\text{en})_2(\text{OAc})\text{Cl}]^+$.¹⁴ It is common to find that the steric course of aquation of a species of the type *trans*- $[\text{Co}(\text{en})_3\text{AX}]^{n+}$ is independent of X provided the Co-X bond is weak enough. The observation would therefore be consistent with a dissociative process in which either CH_3COOH or HgCl^+ is the leaving group.

The assignment of mechanism to the aquation of the *cis* complex is far less definite. The observed retention of configuration does not distinguish between C-O and Co-O bond fission because whereas the first demands it, aquation of complexes of the type *cis*- $[\text{Co}(\text{en})_2\text{AX}]$ almost invariably proceeds with complete retention of configuration. The activation parameters

(14) T. P. Dasgupta and M. L. Tobe, part XVI, *Inorg. Chem.*, in press.

also admit two possible explanations. Taube¹² has suggested that the similarity of the activation energies for the reactions $\text{H}_3\text{O}^+ + \text{Cr}(\text{H}_2\text{O})_5\text{OAc}^{2+} \rightarrow \text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{HOAc}$ (19 kcal mol⁻¹) and $\text{H}_3\text{O}^+ + \text{CH}_3\text{OAc} \rightarrow \text{CH}_3\text{OH} + \text{HOAc}$ (16.4 kcal mol⁻¹), which must involve C-O fission, indicates that the acetatochromium(III) complex aquates with carbon-oxygen fission. It is of interest to note that the activation energy for the *cis*-[Co(en)₂(OAc)₂]⁺ complex falls closely into this category. However, there are many examples in cobalt ammine chemistry where the entropy of activation for the aquation of a *cis*-diacidotetraamine is considerably less positive (or more negative) than that of its *trans* isomer and in most of these cases the activation energy is significantly lower as well.¹⁵⁻¹⁹ In all of these cases (Table VI) the *trans* isomer aquates with stereochemical change but there is no possibility of fission other than at the Co-X bond. Apart from its unusually low activation energy (not unknown in cobalt ammine chemistry), the *cis*-[Co(en)₂(OAc)HOAc]²⁺ complex fits this behavior reasonably well. At this stage, therefore, we consider the mechanism of the acid-catalyzed aquation of *cis*-[Co(en)₂(OAc)₂]⁺ to be still in some doubt, but, until the isotopic labeling or other convincing experiments cause us to believe the contrary, we can find no reason why the *cis*-diacetato complex should be mechanistically so different from its *trans* isomer and prefer to assign a dissociative mechanism with Co-O bond fission to them both.

- (15) J. P. Mathieu, *Bull. Soc. Chim. Fr.*, **3**, 2152 (1936); **4**, 687 (1937).
 (16) S. C. Chan, *Aust. J. Chem.*, **20**, 595 (1967).
 (17) M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 4275 (1960).
 (18) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *ibid.*, 1691 (1956).
 (19) A. M. Sargeson and G. M. Searle, *Inorg. Chem.*, **6**, 2172 (1967).

TABLE VI
ACTIVATION PARAMETERS FOR AQUATION OF SOME
CIS-TRANS ISOMERIC PAIRS IN WHICH THE
TRANS ISOMER AQUATES WITH STERIC CHANGE

Complex	ΔH^\ddagger , kcal mol ⁻¹		ΔS^\ddagger , cal deg ⁻¹ mol ⁻¹		Ref
	Cis	Trans	Cis	Trans	
[Co(en) ₂ (OAc)(HOAc)] ⁺	15.4	23.0	-13	+1	This work
[Co(en) ₂ Cl ₂] ⁺	21.5	26.2	-5	+14	14, 15
[Co(en) ₂ NCSCl] ⁺	20.1	30.2	-14	+9	16, 17
[Co(en) ₂ NCSBr] ⁺	23.1	30.1	-5	+11	16, 17
[Co(trien)Cl ₂] ⁺	21.0 ^a	25.5	-6 ^a	+16	18
	20.3 ^b		-3 ^b		

^a α -Cis. ^b β -Cis.

In his studies of the isomerization and acetate exchange of *cis*- and *trans*-[Co(en)₂(CH₃COO)₂]⁺ in glacial acetic acid, Chester⁸ has suggested that the *trans*-diacetato complex isomerizes intramolecularly to the *cis* which then undergoes a rapid exchange reaction with the solvent acetic acid. In view of the great difference in reactivity of the *cis*- and *trans*-[Co(en)₂(CH₃COO)₂]⁺ isomers, such a mechanism cannot be ruled out in aqueous solution on the basis of the kinetic data alone. However, it has been shown quite clearly that the aquation of the *trans* complex yields 75% *cis*-aquoacetato product. If aquation went by way of the labile *cis* isomer, this should have yielded 100% *cis* product. In any case, there are no precedents for an acid-catalyzed intramolecular isomerization in cobalt(III) complexes of this type, and since it does not seem reasonable that change in solvent from dilute perchloric acid to pure acetic acid should promote an intramolecular isomerization, we would view Chester's mechanism with some caution.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK,
STONY BROOK, NEW YORK 11790

Kinetics and Mechanism of the Reductions of *cis*- and *trans*-Diformatobis(ethylenediamine)cobalt(III) by Vanadium(II)¹

BY THEODORE J. PRZYSTAS AND ALBERT HAIM*

Received September 24, 1971

The reductions of *cis*- and *trans*-Co(en)₂(HCO₂)₂⁺ by V(II) obey the rate law $-d[\text{Co(III)}]/dt = k_2[\text{Co(III)}][\text{V(II)}]$ when $[\text{H}^+]$ is constant. The second-order rate coefficients k_2 have been measured as a function of $[\text{H}^+]$ in the range 0.11-0.91 M. For the *trans* complex k_2 is independent of $[\text{H}^+]$ and has the value $k_{\text{trans}} = 13.0 \pm 0.2 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°. For the *cis* complex k_2 decreases with increasing $[\text{H}^+]$ according to $k_2 = k_{\text{cis}}/(1 + Q[\text{H}^+])$. At 25° $k_{\text{cis}} = 14.8 \pm 0.2 \text{ M}^{-1} \text{ sec}^{-1}$ and $Q = 0.17 \pm 0.03 \text{ M}^{-1}$. The activation parameters associated with k_{cis} and k_{trans} are $\Delta H^\ddagger(\text{cis}) = 10.9 \pm 0.6 \text{ kcal mol}^{-1}$, $\Delta H^\ddagger(\text{trans}) = 11.0 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger(\text{cis}) = -16.7 \pm 1.9 \text{ eu}$, and $\Delta S^\ddagger(\text{trans}) = -20.2 \pm 0.6 \text{ eu}$. An inner-sphere, substitution-controlled mechanism is suggested to account for the results. Comparisons of the Cr(II) and V(II) reductions of *cis*- and *trans*-Co(en)₂(HCO₂)₂⁺ are made, and an indirect criterion for mechanistic assignments is tentatively proposed.

Introduction

The effect of nonbridging ligands on the rates of oxidation-reduction reactions of transition metal complexes has been the subject of several recent papers.² Most of the previous work involving inner-sphere mech-

anisms has been carried out with systems for which the rate of the electron-transfer step is slower than the rate of formation of the precursor binuclear complex.³ In the present work, we report the kinetics of the reductions of *cis*- and *trans*-diformatobis(ethylenediamine)cobalt(III) by vanadium(II). The choice of these particular reactants was dictated by two considera-

(1) This work was supported by Grant GP-9669 from the National Science Foundation.

(2) For a review, see J. O. Earley, *Advan. Inorg. Chem. Radiochem.*, **13**, 243 (1970).

(3) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).