configurations of diastereomers of tris(*N*-(*R*)-5-nitrosalicylaldiminato)cobalt(III) and those diastereomers of tris(*N*-(*R*)-5-nitrosalicylaldiminato)chromium(III) having the same relative rates of elution from tlc plates.[20] A somewhat related phenomenon was recently reported by Palamareva, *et al.*,[21] who compared the tlc behavior of 37 pairs of diastereomers of the type

(20) (a) J. E. Gray and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 2087 (1971); (b) K. S. Finney and G. W. Everett, Jr., unpublished observations.

(21) M. Palamareva, M. Haimova, J. Stefanovsky, L. Viteva, and B. Kurtev, *J. Chromatogr.*, **54**, 383 (1971).

Ar–CH(X)–CH(Y)–Ar. In all cases the erythro isomers had higher R_f values on silica gel than the corresponding threo isomers, regardless of the polarity of the developing solvents.

Mechanism and Steric Course of Octahedral Aquation. XVI.[1] The Acid-, Base-, and Mercury(II)-Catalyzed Hydrolysis of *trans*-Chloroacetato- and *trans*-Chlorobenzoatobis(ethylenediamine)cobalt(III) Perchlorates

By T. P. DASGUPTA, W. FITZGERALD, and M. L. TOBE*

The preparation and properties of *trans*-[Co(en)$_2$RCOOCl]ClO$_4$ (R = CH$_3$, C$_6$H$_5$) are reported. The kinetics and steric course of the replacement of Cl by H$_2$O have been examined; $k_{25°}$ = 3.1 × 10^{-6} sec^{-1}, $\Delta H^{\pm}$ = 26.8 ± 0.3 kcal mol^{-1}, $\Delta S^{\pm}$ = 6.7 ± 0.8 cal deg mol^{-1} for R = CH$_3$ and 1.2 × 10^{-6} sec^{-1}, 29.3 ± 0.7 kcal mol^{-1}, and 13.2 ± 2.2 cal deg^{-1} mol^{-1} for R = C$_6$H$_5$. The rate is independent of acid concentration and the immediate product of aquation (R = CH$_3$) is 80 ± 10% *cis*- and 20 ± 10% *trans*-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$ and the steric course of aquation of the benzoato complex is probably similar. The Hg^{2+}-catalyzed aquation (k_{Hg} = 0.40 M^{-1} sec^{-1} at 39.0°, μ = 0.10) produces 75 ± 2% *cis*- and 25 ± 2% *trans*-aquoacetato product. Base hydrolysis of the chloroacetato complex (k_{OH} = 10.8 M^{-1} sec^{-1} at 25.0°, μ = 0.1, $\Delta H^{\pm}$ = 22.6 ± 0.5 kcal mol^{-1}, $\Delta S^{\pm}$ = +22 ± 2 cal deg^{-1} mol^{-1}) yields 20% *cis*- and 80% *trans*-[Co(en)$_2$CH$_3$COOOH]$^{2+}$.

Introduction

In part XV,[1] the kinetics and steric course of the acid-catalyzed hydrolysis of *cis*- and *trans*-[Co(en)$_2$(OAc)$_2$]$^+$ were reported, and it was shown clearly that, in the trans complex, acetate served as a ligand that promotes substitution with stereochemical change. In order to separate the role played by acetate as "nonparticipating ligand" from that as leaving group, we have prepared and examined the *trans*-[Co(en)$_2$(CH$_3$COO)Cl]$^+$ complex, where the relatively labile chloride serves as leaving group. Although we have long been interested in assessing the role of –OCOR as a nonparticipating ligand in the acid and base hydrolysis of complexes of the type [CoL$_4$AX]$^{n+}$ (L$_4$ is a ligand or combination of ligands that provide four amine nitrogen donors; X is the leaving group) our attempts to prepare complexes with A = RCOO and X = Cl or Br were, until recently, without success. The method of Jackman, Scott, and Portman,[2] which involves the acetylation of the coordinated hydroxide, has been applied successfully to the preparation of *trans*-[Co(en)$_2$RCOOCl]$^+$ClO$_4^-$ (R = CH$_3$, C$_6$H$_5$), and the kinetics and steric course of acid and base hydrolyses of these complexes are reported in this paper.

(1) Part XV: T. P. Dasgupta and M. L. Tobe, *Inorg. Chem.*, **11**, 1011 (1972).

(2) L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968).

Experimental Section

trans-Chlorohydroxobis(ethylenediamine)cobalt(III) chloride was prepared and purified by the method of Baldwin, *et al.*,[3] and converted to the perchlorate by adding a saturated aqueous solution of sodium perchlorate to a cold saturated aqueous solution of the chloride. The spectrum of a freshly prepared aqueous acid solution was identical with that in the literature.

trans-Chloroacetatobis(ethylenediamine)cobalt(III) Perchlorate.—*trans*-[Co(en)$_2$OHCl]ClO$_4$ (1.4 g) was added to a solution of acetic anhydride (0.22 ml) and *N*,*N*-dimethylbenzylamine (1.2 ml) in dimethylformamide (15 ml). The mixture was heated on a water bath at 60–70° for 20–25 min and then cooled. (If the starting material is pure, no precipitate should form at this stage.) Ethanol (30 ml) was then added, followed by diethyl ether (200 ml) which was added slowly, with constant stirring. The mixture was allowed to stand for 30 min and the supernatant liquid was decanted from the oil which was dissolved in water (3 ml) and filtered from the green insoluble *trans*-[Co(en)$_2$Cl$_2$]ClO$_4$. The filtrate was saturated with solid sodium perchlorate and cooled in ice. The red-purple crystals were filtered off and recrystallized from water; yield 0.29 g. *Anal.* Calcd for C$_6$H$_{19}$O$_6$N$_4$Cl$_2$Co: C, 19.3; H, 5.1; N, 15.0; Cl, 19.1. Found: C, 19.3; H, 4.9; N, 15.1; Cl, 19.3.

trans-Chlorobenzoatobis(ethylenediamine)cobalt(III) Perchlorate.—*trans*-[Co(en)$_2$OHCl]ClO$_4$ (1.96 g) was added to a solution of benzoic anhydride (0.665 g) and *N*,*N'*-dimethylbenzylamine (1.7 ml) in dimethylformamide (15 ml) and the mixture heated at 50–60° for 5 min and then cooled. An orange precipitate was filtered off and discarded. The filtrate was worked up and the complex recrystallized in the same way as was reported for the chloroacetato complex. *Anal.* Calcd for C$_{11}$H$_{21}$O$_6$N$_4$Cl$_2$Co:

(3) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

TABLE I

CHARACTERISTIC ABSORPTION PEAKS IN THE VISIBLE AND NEAR-ULTRAVIOLET ABSORPTION

SPECTRA OF SOME *trans*-[Co(en)$_2$XY]$^{n+}$ COMPLEXES

| | | $^1A_{2g} \rightarrow {}^1A_{1g}$ | | $^1B_{2g} \rightarrow {}^1A_{1g}$ | | $^1E_g \rightarrow {}^1A_{1g}$ | | |
| | | | ϵ, cm^{-1} | | ϵ, cm^{-1} | | ϵ, cm^{-1} | |
X	Y	ν, cm^{-1}	M^{-1}	ν, cm^{-1}	M^{-1}	ν, cm^{-1}	M^{-1}	Ref
F$^-$	F$^-$	17,200	21	22,600	29	27,600	43	4
F$^-$	H$_2$O	17,500	27.5	22,400	32	28,300	55	5
Cl$^-$	Cl$^-$	16,150	36	~21,900 sh	27	~25,800 sh	36	6
Cl$^-$	H$_2$O	17,100	31	22,300	30	~28,500 sh	58	3
Cl$^-$	Br$^-$	15,500	41	~22,200 sh	40			7
Br$^-$	Br$^-$	15,400	45					6
Br$^-$	H$_2$O	16,200	34	~22,700 sh	45			7
H$_2$O	H$_2$O	18,400	33	22,600	37	28,600	54	8
CH$_3$COO$^-$	CH$_3$COO$^-$	18,500	55	22,200	30	27,700	69	9^a
CH$_3$COO$^-$	Cl$^-$	17,300	42.5	22,400	21	27,300	49.5	This work
CH$_3$COO$^-$	H$_2$O	18,400	49	21,900	28.5	28,000	65.5	This work
C$_6$H$_5$COO$^-$	Cl$^-$	17,300	52	22,200	21	27,300	5.7	This work

^{a} The middle peak is not reported in this reference.

C, 30.3; H, 4.8; N, 12.9; Cl, 16.3. Found: C, 30.9; H, 4.7; N, 13.0; Cl, 16.0.

Kinetics.—The spontaneous and mercury-catalyzed solvolyses were followed spectrophotometrically. Solutions were prepared by dissolving a weighed amount of complex in a known volume of dilute acid, previously brought to the reaction temperature and then transferred to the thermostated cell holder of a Unicam SP 800 recording spectrophotometer. In the Hg^{2+}-catalyzed reactions the appropriate amount of mercuric perchlorate, prepared by dissolving a weighed amount of AR mercuric oxide in dilute perchloric acid, was added after the complex dissolved and the solution was then transferred to the spectrophotometer cell. Spectra, over the range 700–320 nm, were scanned from time to time. The spontaneous aquation was also followed by chloride release. Solutions, made up as above, were stored in the thermostat and aliquots were pipetted out at noted times and frozen at −70°. These were then individually warmed to room temperature, diluted with acetone, and titrated potentiometrically with standard silver nitrate using a Radiometer PHM26, TTT11, ABU11, TTA31, SBR2 automatic micro titration assembly. The base hydrolysis was followed (a) at low pH in borate buffers using the above spectrophotometric technique and (b) at higher pH's, by a Durrum–Gibson stopped-flow apparatus. All wavelengths recorded are corrected for instrument calibration errors.

Results

(i) Characterization of Complexes.—The two chlorocarboxylato complexes have been characterized as such by elemental analysis and the nature of the products of their substitution reaction. The trans configuration is expected from the stereoretentive nature of their preparation since, as has been pointed out by Jackman, *et al.*,[2] the process is formally an acylation of oxygen and the Co–O bond is undisturbed. The visible and near-ultraviolet spectra are fully consistent with a trans configuration. A characteristic feature of the spectra of *trans*-[Co(en)$_2$X$_2$]$^{n+}$ and *trans*-[Co(en)$_2$XY]$^{n+}$ cations, where X and Y are relatively weak-field ligands such as F$^-$, Cl$^-$, Br$^-$, H$_2$O, and RCOO$^-$, is the resolution of the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ transitions and the observation of three peaks in the trans isomer as compared to two in the cis. (When X = Br, a strong absorbing transition in the near-ultraviolet region obscures the shorter wavelength bands.) A characteristic feature of the coordinated carboxylate is the relatively low extinction coefficient of the second band (Table I[8–9]) which is also observed in the *trans*-

(4) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **271**, 101 (1952).

(5) S. C. Chan and C. K. Poon, *J. Chem. Soc. A*, 146 (1966).

(6) J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

(7) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

(8) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).
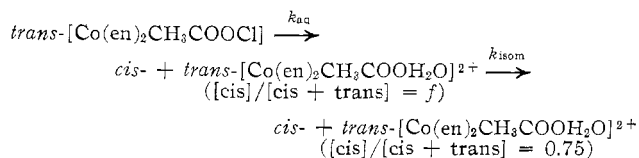
(9) V. Carunchio, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **6**, 2168 (1967).

dicarboxylato and *trans*-aquocarboxylato species. Attempts to prepare cis complexes by an equivalent method have so far been unsuccessful. The preparation of *cis*-[Co(en)$_2$OHCl]$^+$ salts by Werner's method yielded only the less soluble hydroxoaquo species in our hands, and the use of the easily prepared *cis*-[Co(en)$_2$ClH$_2$O]$^{2+}$ salts, which should have immediately formed the required hydroxo complex on encountering the base, did not lead to the desired products.

(ii) Kinetics of the Spontaneous Aquation.—The spectral changes of a solution of *trans*-[Co(en)$_2$CH$_3$COO-Cl]ClO$_4$ in 0.01 M perchloric acid are characterized by four well-defined isosbestic points at 553, 432, 379, and 337 nm which are maintained throughout the reaction. The final spectrum corresponds exactly to that of the 75% cis- + 25% *trans*-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$ equilibrium mixture[1] and the isosbestic points occur where this crosses the spectrum of *trans*-[Co(en)$_2$CH$_3$-COOCl]$^+$. Plots of log $(D_\infty - D_t)$ (D_t and D_∞ are the optical densities at time t and after 10 half-lives) against time are linear for at least 3 half-lives and the first-order rate constant, determined from the slope, is independent of the wavelength chosen. The spectral changes associated with the aquation of the benzoato complex are very similar although here we do not know the spectra of the aquo products. The first-order rate constants are collected in Table II. Each entry is the

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION

OF *trans*-[Co(en)$_2$RCOOCl]$^+$ IN 0.01 M HClO$_4$;

[COMPLEX] $\approx 2 \times 10^{-3}$ M

R	Temp, °C	10^4k, sec^{-1}	R	Temp, °C	10^4k, sec^{-1}
CH$_3$	39.5	0.35^a	C$_6$H$_5$	39.0	0.18^a
CH$_3$	50.0	1.45^a	C$_6$H$_5$	50.0	0.80^a
CH$_3$	50.0	1.50^b	C$_6$H$_5$	50.0	0.82^b
CH$_3$	50.0	1.48^c			
		1.50^d			
		1.40^e			
		1.70^f			
CH$_3$	60.0	5.30^a	C$_6$H$_5$	60.0	3.50^a

$\Delta H^{\ddagger} = 26.8 \pm 0.3$ kcal mol^{-1} $\Delta H^{\ddagger} = 29.3 \pm 0.7$ kcal mol^{-1}

$\Delta S^{\ddagger} = +6.7 \pm 0.8$ cal deg^{-1} mol^{-1} $\Delta S^{\ddagger} = +13.3 \pm 2.1$ cal deg mol^{-1}

^{a} Spectrophotometric data. ^{b} Titrimetric data. ^{c} 0.02 M HClO$_4$. ^{d} 0.05 M HClO$_4$. ^{e} 0.08 M HClO$_4$. ^{f} 0.10 M HClO$_4$.

average of at least three separate runs. Independent experiments have shown that the spectral changes are

associated with the release of chloride ions. Plotting log $(V_\infty - V)$ against time (V being the titer of silver nitrate at time t and V_∞ the titer after 10 half-lives and equal to that calculated for the release of one chloride) also gives a straight line, and the rate constants, derived from the slope, are also collected in Table II. The agreement between the titrimetric and spectrophotometric data is good.

The effect of acid concentration upon the nature of this reaction is of some interest. The form of the spectral changes is independent of the concentration of acid within the range 0.01 M < [H$^+$] < 0.1 M and the spectrophotometrically determined rate constants are also independent of the acidity in this region (Table II). In stronger acid it is clear that the reaction changes. The isosbestic point at 583 nm vanishes and the others become less well defined and shift. Above 1 M [H$^+$] the new behavior is well established and it is clear that at least two stages are involved, the first of which is acid catalyzed. In 3 M perchloric acid the first stage is complete within 10 min at 40° and isosbestic points develop at 574 nm (ϵ 25), 455 nm (ϵ 20), 407 nm (ϵ 24), and 360 nm (ϵ 46). The final spectrum has peaks at 515 nm (ϵ 49) and 372 nm (ϵ 49). Preliminary results indicate that the acid-catalyzed displacement of the acetate has become faster than the loss of chloride, and the system, which requires an independent and detailed study, will be reported elsewhere.

(iii) **The Steric Course of Spontaneous Aquation in 0.01 M Perchloric Acid.**—The occurrence of four well-defined isosbestic points throughout the reaction indicates that the second reaction step, namely, the isomerization of the aquocarboxylato product either is very much faster than the aquation of the chloro species or else does not occur at all. This latter possibility would only be relevant if the aquo species were actually produced at, or close to, their equilibrium cis–trans composition. The isomerization of cis- and trans-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$ is not so much faster than the aquation to permit the first explanation. At 50.0° k_isom (the specific rate constant for approach to equilibrium) is 1.12 × 10^{-3} sec^{-1},[1] which is between 6 and 7 times that of the aquation of this temperature. The activation energies of the two reactions differ only by about 1 kcal mol^{-1} and so it is not possible to seek a more favorable temperature for the study, as was possible with the aquation of trans-[Co(en)$_2$N$_3$Cl]$^+$.[10]

The steric course was determined by the method adopted in the study of the aquation of trans-[Co(en)$_2$(CH$_3$COO)$_2$]$^+$. Using the extinction coefficients (cm^{-1} M^{-1}) at 494 nm for trans-[Co(en)$_2$CH$_3$COOCl]$^+$ (10), trans-[Cl(en)$_2$CH$_3$COOH$_2$O]$^{2+}$ (30), and cis-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$ (103.5) and the rate constants k_aq = 1.45 × 10^{-4} sec^{-1} and k_isom (= $k_c + k_t$) = 1.12 × 10^{-3} sec^{-1} at 50.0° a set of curves was calculated for ϵ, the apparent extinction coefficient, as a function of time assuming a reaction sequence

$$\text{trans-[Co(en)}_2\text{CH}_3\text{COOCl]} \xrightarrow{k_\text{aq}}$$

$$\begin{array}{c}\text{cis- + trans-[Co(en)}_2\text{CH}_3\text{COOH}_2\text{O]}^{2+} \xrightarrow{k_\text{isom}} \\ (\text{[cis]/[cis + trans]} = f)\end{array}$$

$$\begin{array}{c}\text{cis- + trans-[Co(en)}_2\text{CH}_3\text{COOH}_2\text{O]}^{2+} \\ (\text{[cis]/[cis + trans]} = 0.75)\end{array}$$
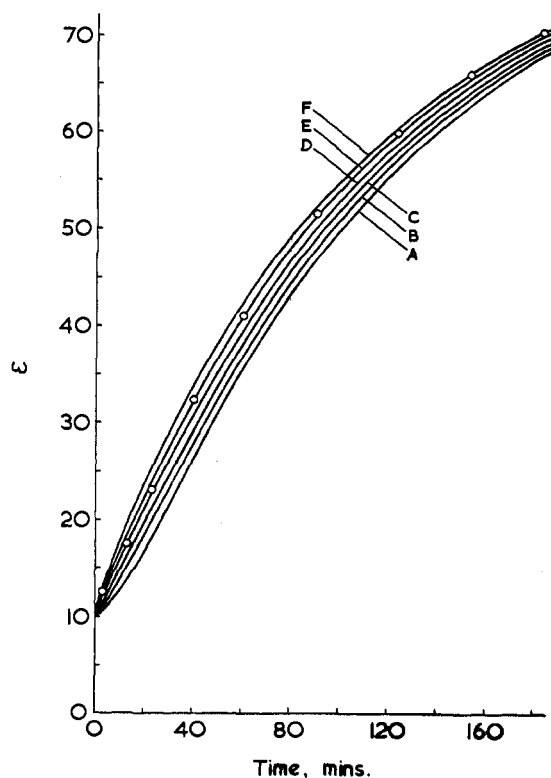

Figure 1.—Plots of ϵ (apparent extinction coefficient at 494 nm) against time. Circles are experimental points (50.0°, 0.01 M HClO$_4$, 0.012 M ionic strength). Curves are calculated for f = 0 (A), 0.2 (B), 0.4 (C), 0.6 (D), 0.8 (E), and 1.0 (F), using data given in text.

These are shown in Figure 1 for f = 0, 0.2, 0.4, 0.6, 0.8, and 1.0, together with the experimentally determined values. It is clear that the second stage is slow enough to allow a distinction between different values of f and that the initial composition of product corresponds to $f = 0.8 \pm 0.1$.

(iv) **Hg^{2+}-Catalyzed Aquation of trans-[Co(en)$_2$-CH$_3$COOCl]$^+$.**—The addition of mercuric perchlorate to a solution of trans-[Co(en)$_2$CH$_3$COOCl]$^+$ does not in any way alter the form of the changing spectra. Isosbestic points are still observed at the same wavelengths and the final spectrum is precisely that of the equilibrium mixture containing 75% cis- and 25% trans-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$. However, the rate of reaction is considerably enhanced and preliminary studies indicate that the rate law becomes k_obsd = k_aq + k_Hg[Hg(II)], where k_aq is equal to the rate constant for the spontaneous aquation. At 39.0° and [H$^+$] = 0.01 M the observed first-order rate constants are for [Hg^{2+}] = 0.001 M, k_obsd = 4.6 × 10^{-4} sec^{-1}, for [Hg^{2+}] = 0.002 M, k_obsd = 9.6 × 10^{-4} sec^{-1}, and for [Hg^{2+}] = 0.01 M, k_obsd = 40.0 × 10^{-4} sec^{-1}. It is of interest to note that, even in the first case, when [Hg^{2+}] is less than the concentration of complex (held at 2.0 × 10^{-3} M) a first-order rate law is obeyed. This suggests that HgCl$^+$ is as effective a catalyst as Hg^{2+}. This is in agreement with the experience of others.[11–14] The rate constant for the overall catalyzed process is k_Hg = 0.40 M^{-1} sec^{-1}. The maintenance of the same

(10) V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, **9**, 1785 (1970).

(11) J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965).
(12) J. H. Espenson and S. R. Hubbard, *ibid.*, **5**, 686 (1966).
(13) C. Bifano and R. G. Linck, *ibid.*, **7**, 908 (1968).
(14) R. Niththyananthan, Ph.D. Thesis, London, 1968.

isosbestic points as the rate of the solvolysis increases from being only one-sixth of that of isomerization (in the uncatalyzed aquation) until it is 20 times faster than the isomerization indicates clearly that the direct product of the Hg^{2+}-catalyzed aquation has the composition 75 ± 2% cis- and 25 ± 2% trans-[Co(en)$_2$-CH$_3$COOH$_2$O]$^{2+}$.

(v) Base Hydrolysis of *trans*-[Co(en)$_2$RCOOCl]$^+$.— The reaction was followed spectrophotometrically by the stopped-flow technique. The hydroxide concentration was at least 10 times greater than that of the complex (5×10^{-4} M) and the reaction was studied under pseudo-first-order conditions. The plots of the pseudo-first-order rate constant against [OH$^-$] are linear, passing through the origin, and the second-order rate constants, determined from the slopes of these plots, are collected in Table III. By taking a known amount of complex

TABLE III
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE
BASE-CATALYZED HYDROLYSIS OF *trans*-[Co(en)$_2$RCOOCl]ClO$_4$;
[COMPLEX] = 5×10^{-4} M, μ = 0.10 (NaClO$_4$)

(a) R = CH$_3$

24.5°		30.2°		35.2°		40.0°	
[OH$^-$], M	k_{obsd}, sec^{-1}	[OH$^-$], M	k_{obsd}, sec^{-1}	[OH$^-$], M	k_{obsd}, sec^{-1}	[OH$^-$], M	k_{obsd}, sec^{-1}
0.005	0.053	0.01	0.21	0.01	0.42	0.01	0.72
0.010	0.107	0.02	0.42	0.02	0.81	0.02	1.38
0.020	0.21	0.03	0.62	0.03	1.21	0.03	2.16
0.030	0.33	0.04	0.84	0.04	1.60	0.04	2.9
0.040	0.37	0.05	1.04	0.05	1.95	0.05	3.6
0.050	0.535						

k_2 = 10.8 M^{-1} sec^{-1}, k_2 = 20.8 M^{-1} sec^{-1}, k_2 = 40.6 M^{-1} sec^{-1}, k_2 = 72.6 M^{-1} sec^{-1}
$\Delta H^{\ddagger}$ = 22.6 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 22 ± 2 cal deg^{-1} mol^{-1}

(b) R = C$_6$H$_5$

26.0°		34.0°		39.5°	
[OH$^-$], M	k_{obsd}, sec^{-1}	[OH$^-$], M	k_{obsd}, sec^{-1}	[OH$^-$], M	k_{obsd}, sec^{-1}
0.01	0.093	0.01	0.22	0.01	0.58
0.02	0.20	0.02	0.46	0.02	1.14
0.03	0.28	0.03	0.69	0.03	1.74
0.04	0.38	0.04	0.91	0.04	2.3
0.05	0.47	0.05	1.10	0.05	2.9

k_2 = 9.3 M^{-1} sec^{-1}, k_2 = 22.6 M^{-1} sec^{-1}, k_2 = 58.0 M^{-1} sec^{-1}
$\Delta H^{\ddagger}$ = 24.8 ± 3.0 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 28 ± 10 cal deg^{-1} mol^{-1}

and allowing it to react with excess base for 10 half-lives it was possible to show that the spectrophotometric change corresponded to the release of one chloride. The subsequent base hydrolysis of the hydroxoacetato species is very much slower and does not interfere with this study, nor does it prevent a direct estimation of the product composition. In the case of the chloroacetato complex, this final spectrum after acidification is identical with that of a mixture of 80 ± 3% trans- and 20 ± 3% cis-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$.

Discussion

The kinetic and stereochemical studies indicate that the carboxylate ligand in *trans*-[Co(en)$_2$RCOOX]$^{2+}$ promotes the replacement of X with stereochemical change. In all three cases now studied, where R = CH$_3$ and X = Cl, HgCl$^+$, and CH$_3$COOH,[1] the kinetically determined isomeric composition of the product (75% cis–25% trans) is independent of the nature of the leaving group. This is not unexpected for a mechanism that is essentially dissociative, the only example

so far published where this is definitely not so being the spontaneous and Hg^{2+}-catalyzed aquation of *trans*-[Co(trien)Cl$_2$]$^+$ [15] and the spontaneous and Hg^{2+}-catalyzed aquation of *cis*-[Co(en)$_2$Cl$_2$]$^+$.[16] It is of interest to observe that the aquoacetato products have been formed virtually at their equilibrium composition. This is not a normal feature of aquation with steric change (Table IV[3,7,17]) but since the final amount of

TABLE IV
A COMPARISON OF THE KINETICALLY AND THERMODYNAMICALLY
CONTROLLED ISOMERIC COMPOSITION OF AQUO SPECIES
WHEN THE ORIGINAL AQUATION INVOLVES STERIC CHANGE

	% cis		
	Kinet	Equil	
Halogeno complex	prod.	prod.	Ref
trans-[Co(en)$_2$OHCl]$^{+a}$	75	59	3
trans-[Co(en)$_2$ClCl]$^+$	35	74	3
trans-[Co(en)$_2$BrBr]$^+$	30	76	7
trans-[Co(en)$_2$SCNBr]$^+$	45	86	17
trans-[Co(en)$_2$CH$_3$COOCl]$^+$	75	75	This work

^{a} The leaving group is boldface. It has been assumed that the initial product composition is independent of the nature of the leaving group and the most reliable literature examples have been chosen.

cis product can be less than or greater than the amount originally formed, depending on the nature of A, there seems to be no purpose to be served in seeking an explanation more significant than one of coincidence at this stage. If more was known about the relationship between the water-exchange rates and the isomerization rates in the *cis*-[Co(en)$_2$AH$_2$O]$^{n+}$ series, it might be possible to consider the problem in more detail. The observation of direct stereochemical change, coupled with the relatively high entropy of activation (+6.7 kcal mol^{-1}) for the *trans*-[Co(en)$_2$CH$_3$COOCl]$^+$ aquation, is in full agreement with the correlation made by one of us[18] some time ago which indicated that aquation reactions that were accompanied by stereochemical change were characterized by a considerably higher entropy of activation than those which took place with complete retention of configuration, provided, of course, that a constant leaving group was maintained in the comparison. Although the isomerization of the aquobenzoato species has not yet been studied in detail, there is nothing in the spectrophotometric evidence to suggest that the steric course of aquation of the *trans*-[Co(en)$_2$C$_6$H$_5$COOCl]$^+$ cation is vastly different from that of the acetato analog. Here, too, the entropy of activation (+13.3 cal deg^{-1} mol^{-1}) is consistent with an aquation involving stereochemical change.

A comparison of the rates of aquation of these chloro-carboxylato complexes indicates a reactivity sequence for the stereochemical change aquation of *trans*-[Co(en)$_2$ACl]$^+$ as A is varied as follows: OH (160^3) > Br (4.5^7) > Cl (3.5^{19}) > CH$_3$COO (0.31) > C$_6$H$_5$COO (0.12) > NCS (0.005^{17}) (values in parentheses are 10$^5 k$ at 25°). On the basis of two data points only, a comparison of the effect of the nature of R upon the labilizing power of RCOO would be rash indeed. The effect at least goes in the right direction for the idea that the labilizing effect is one of charge donation to

(15) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).
(16) A. Sargeson, *Aust. J. Chem.*, **17**, 384 (1964).
(17) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956).
(18) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).
(19) J. P. Mathieu, *Bull. Soc. Chim. Fr.*, **3**, 2121 (1926).

the reaction center; benzoic acid (pK_a = 4.22[20]) providing a less basic ligand than acetic acid (pK_a = 4.74[20]) also has a weaker labilizing effect. However, the pK_a values represent the σ-donor abilities of the oxygen rather than the π-donor properties that have been invoked to explain the labilizing properties of ligands of this sort.[1,21] We are extending the study to a much wider range of carboxylate ligands to see whether the labilizing effect is significantly dependent upon substituents or whether it is markedly insensitive as in the case of amine donors.

The Hg^{2+}-catalyzed aquation of trans-[Co(en)$_2$CH$_3$-COOCl]$^+$ conforms to the usual pattern of behavior now fully documented in the literature. Furthermore, if the data for this complex are plotted on the graph of log k_{aq} vs. log k_{Hg} constructed by Bifano and Linck,[18] the point sits very close to their line (a rate constant of 3.1 $\times$ 10^{-6} sec^{-1} at 25° for the spontaneous aquation would require a rate constant of 0.2 M^{-1} sec^{-1} at 25° for the Hg^{2+}-catalyzed aquation (μ = 1.0 M)). The form of the base-hydrolysis reaction is also reasonably typical of these trans-[Co(en)$_2$ACl]$^{n+}$ species. The complex is neither excessively labile like the dichloro species nor unduly inert as the hydroxochloro species but in both its rate constant and activation parameters resembles the other members of the series (A = N_3, NCS, CN, NO$_2$, NH$_3$, etc.).[22] Illuminati, et al.,[9,23,24] have examined the kinetics of the base hydrolysis of a variety of cis- and trans-dicarboxylatobis(ethylenediamine)cobalt(III) complexes and showed that the rate of reaction is very sensitive to the nature of the substituents in the carboxylate ligand. Obviously a

(20) C. K. Rule and V. K. La Mer, *J. Amer. Chem. Soc.*, **60**, 1974 (1938).
(21) F. Basolo and R. G. Pearson, *ibid.*, **78** (1956).
(22) M. L. Tobe, *Accounts Chem. Res.*, **3**, 377 (1970).
(23) F. Aprile, V. Caglioti, and G. Illuminati, *J. Inorg. Nucl. Chem.*, **21**, 325 (1961).
(24) V. Carunchio, G. Illuminati, and F. Maspero, *ibid.*, **28**, 2693 (1966).

major part of the effect is due to the relationship between the basicity and lability of the carboxylato leaving group but it is hoped that the data for the rates of replacement of the chloride from a series of trans-chlorocarboxylatobis(ethylenediamine)cobalt(III) complexes will help separate the leaving-group effect from the trans (and cis) effect. On the basis of our observations on the acetato complex and the bis-ethylenediamine complexes in general, we would be surprised if the rate of base hydrolysis was particularly sensitive to the nature of the nonparticipating ligand. This seems to be true when the trans-chloroacetato complex is compared with the chlorobenzoato analog. However, the rate constants for the base hydrolysis of the trans-diacetato- and trans-dibenzoatobis(ethylenediamine)cobalt(III) cations (5.1 $\times$ 10^{-2} M^{-1} sec^{-1} [24] and 3.20 $\times$ 10^{-2} M^{-1} sec^{-1} [23] at 25.0°, $\mu \approx$ 0.027) do not differ greatly either, in spite of the trends noted in the rest of the series.

It has been reported that the base hydrolysis of trans-[Co(en)$_2$(CH$_3$COO)$_2$]$^+$ [9] gives 100% trans-[Co(en)$_2$OHCH$_3$COO]$^+$ but if the dissociative mechanism, now accepted for these base hydrolyses (dissociation of the conjugate base), was operating one would expect to find that the steric course was independent of the nature of the leaving group.[25] Thinking that the observations of retention in the base hydrolysis of trans-[Co(en)$_2$-(CH$_3$COO)$_2$]$^+$ might indicate C–O bond fission, we have reexamined this reaction with our own techniques. We find that, having made correction for the second stage of base hydrolysis (which really cannot be ignored in this case) and the unreacted starting material, the spectrum of the product, after acidification, is identical with that found after base hydrolysis of trans[Co(en)$_2$-CH$_3$COOCl]$^+$ and indicates that here, too, contrary to the previous report,[9] the initial product contains 20% of the cis isomer.

(25) R. B. Jordan and A. M. Sargeson, *Inorg. Chem.*, **4**, 433 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND 21218

Cobalt(II)-Catalyzed Ligand Exchange Reactions of *trans*-Chloro(triphenylphosphine)bis(dimethylglyoximato)cobalt(III)

By LUIGI G. MARZILLI,* JAMES G. SALERNO, AND LEON A. EPPS

The reaction of cobaloximes, LCo(DH)$_2$X (where L = a neutral monodentate ligand, DH = monoanion of dimethylglyoxime, and X = an acido ligand), with neutral monodentate nitrogen or phosphorus donor ligands (L') has been found to yield L'Co(DH)$_2$X rather than [L'Co(DH)$_2$L]X. When L = (C$_6$H$_5$)$_3$P and L' = pyridine or substituted pyridines, the equilibrium constant for the exchange reaction (C$_6$H$_5$)$_3$PCo(DH)$_2$Cl + X-py $\rightleftharpoons$ (X-py)Co(DH)$_2$Cl + (C$_6$H$_5$)$_3$P could be determined. The values of K were found to be markedly dependent on the nature of the substituted pyridine. Qualitative evidence suggested the exchange was catalyzed by Co(II) species. The exchange reaction when L = (C$_6$H$_5$)$_3$P and L' = pyridine was too rapid to measure by conventional techniques in 10^{-5} M (C$_3$H$_5$)$_3$PCo(DH)$_2$ solution. However, the analogous reaction with X = NO$_2$ was slower and the rate expression was found to be $-d[\text{Co(III)}]/dt$ = 1.5 $\times$ 10^4[Co(III)][Co(II)]. A mechanism was proposed to account for the exchange reaction which involves an inner-sphere electron transfer *via* the acido bridge as the rate-limiting step.

Introduction

Cobaloximes, LCo^{III}(DH)$_2$X (where DH = monoanion of dimethylglyoxime, L = a number of neutral ligands, and X = a number of uninegative ligands),

have been studied extensively, particularly by Schrauzer,[1] as vitamin B$_{12}$ models and are usually formulated as having the geometry I (X = Cl). Costa has

(1) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).