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

# The Base Hydrolysis of *trans*-Chlorohydroxobis(ethylenediamine)-cobalt(III) Cations

BY M. E. FARAGO, B. PAGE, AND M. L. TOBE

*Received September 27, 1968*

In a recent paper,[1] Dittmar and Archer have reexamined the kinetics and steric course of the base hydrolysis of *trans*-$Co(en)_2OHCl^+$ (en = ethylenediamine) and claimed to have shown that there is a fast and reversible stereoretentive loss of chloride that is accompanied by a slow, irreversible formation of the *cis*-dihydroxo product, *i.e.*

$$\begin{tikzcd} trans\text{-}Co(en)_2OHCl^+ + OH^- \arrow[r, shift left, "fast"] \arrow[d, "slow"', "+OH^-"] & trans\text{-}Co(en)_2(OH)_2^+ + Cl^- \arrow[l, shift left] \\ cis\text{-}Co(en)_2(OH)_2^+ + Cl^- & \end{tikzcd}$$

They reach this conclusion because a computer-controlled spectrophotometric analysis indicates that, almost immediately after adding alkali to a solution of [*trans*-$Co(en)_2OHCl$]Cl, approximately 9% of the complex is present as *trans*-$Co(en)_2(OH)_2^+$ and that the concentration of this species *decreases* as the reaction proceeds.

They therefore suggest that the work of Chan and Tobe,[2] who appear to have reported only the rate of formation of the *cis*-$Co(en)_2(OH)_2^+$ product, is in error and that, far from reacting relatively slowly and with considerable steric change, *trans*-$Co(en)_2OHCl^+$ is very labile and undergoes base hydrolysis mainly with retention of configuration. In view of this startling result and the implications that it raises in connection with the general consideration of the mechanism of base hydrolysis of these cobalt(III) complexes, we have applied two very simple tests which these authors failed to report. Our observations are given in this note.

## Experimental Section

*trans*-Chlorohydroxobis(ethylenediamine)cobalt(III) chloride monohydrate was prepared from [*trans*-$Co(en)_2Cl_2$]Cl by a previously published method.[3] The spectrum of an acidified aqueous solution was completely identical with that of a fully characterized sample over the whole wavelength range studied (300–800 mμ).

*trans*-Hydroxoaquobis(ethylenediamine)cobalt(III) perchlorate was prepared by a modification of the method of Baldwin, Chan, and Tobe.[3] The *trans*-dichloro complex was provided as the chloride, which is much more soluble than the nitrate so that the use of a much more concentrated solution (10 g/25 ml of water) removed the need to concentrate the acidified effluent by freeze-drying. In fact, when the alkaline effluent, containing [*cis*- and *trans*-$Co(en)_2(OH)_2$]OH, was neutralized to pH 7 with 72% perchloric acid, the *trans*-hydroxoaquo perchlorate crystallized out on cooling in an ice bath. The purity of this sample was also established by comparing the spectrum of an acidified aqueous solution with that of a fully characterized, authentic specimen.

**Isomerization Kinetics.**—Two standard spectrophotometric methods were used to follow the reaction. In the first, a known amount of solid complex was added to the solution containing the other reagents previously brought to the reaction temperature and the reaction followed *in situ* with a thermostated spectrophotometric cell housing. The reaction was started in the same way in the second method but aliquot portions were withdrawn from time to time and the reaction stopped in acid. The spectra of these solutions were then measured at leisure.

**Tracer Studies.**—A weighed amount of the complex [*trans*-$Co(en)_2OHCl$]$Cl\cdot H_2O$ was added to a solution of 0.04 *M* $Na^{36}Cl$ (obtained from $H^{36}Cl$ from the Radiochemical Center, Amersham, England) and 0.16 *M* NaOH, previously brought to 0° in an ice–water bath. Samples of 5.00 ml were withdrawn at known times and pipetted into 5 ml of 1.44 *M* perchloric acid. The volume of the solution was made up to 25.00 ml and the absorption spectrum was measured in order to assess the extent of the reaction. A concentrated solution of sodium tetraphenylborate (*ca.* 1–2 ml) was then added dropwise and, with sufficient care, green [*trans*-$Co(en)_2H_2OCl$][$B(C_6H_5)_4$]$_2$ could be precipitated in a pure form. If too much precipitant was used or if the mixture was allowed to stand too long, the precipitate was contaminated. This is especially true at the later stages of the reaction. The complex was filtered off and washed with water until no significant activity could be detected in the washings. The dried tetraphenylborate was dissolved in 10.0 ml of acetone and the spectrum was measured immediately in order to confirm the purity and establish the concentration. The solution was then transferred to a liquid counter and the activity was measured with a Dynatron Radio Ltd. SC 200 scaling unit. A 0.2-ml quantity of the original chloride–hydroxide reaction solution was diluted to 10.0 ml with acetone and its activity was determined in the same way. Spectra were measured with a Unicam SP 800 recording spectrophotometer.

## Results and Discussion

If the Dittmar–Archer mechanism is correct, one would expect to find that, when chloride is added to an alkaline solution of *trans*-$Co(en)_2(OH)_2^+$, 91% of the complex should be converted very rapidly to *trans*-$Co(en)_2OHCl^+$. This should then change to the *cis*-$Co(en)_2(OH)_2^+$ cation at a rate that is equal to the apparent rate of base hydrolysis of an authentic sample of the *trans*-chlorohydroxo complex. Thus, the mechanism predicts a chloride-catalyzed isomerization of the dihydroxo species. However, since the *cis*-dihydroxo complex does not appear to react with chloride and since the equilibrium mixture has been shown to contain 56% *trans* and 44% *cis* complex (independent of [OH]),[4] it is difficult to reconcile this mechanism with the laws of thermodynamics.

We find that, on adding sodium chloride (0.35 *M*) to a solution of *trans*-$Co(en)_2(OH)_2^+$ (0.01 *M*, provided as the hydroxoaquo perchlorate) in sodium hydroxide solution (0.07 *M*), there is no change in the spectrum over a period of at least 25 min at 0°, nor is there any change in the spectrum of portions of the reaction mixture that have been acidified after various periods of

---

[1] E. A. Dittmar and R. D. Archer, *J. Am. Chem. Soc.*, **90**, 1468 (1968).

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

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

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

time up to 25 min at 0°. The spectrum remains identical with that of *trans*-$Co(en)_2(H_2O)_2{}^{3+}$ and is quite different from that of the *trans*-$Co(en)_2H_2OCl^{2+}$ cation. Under these reaction conditions the proposed anation of the *trans*-dihydroxo complex to the *trans*-chlorohydroxo intermediate should have been complete in a few seconds and the chlorohydroxo intermediate should have been 80–90% converted to the *cis*-dihydroxo complex in this time. However, in order to induce any change in the spectrum within a reasonable time, it was necessary to raise the temperature. At 50.8°, samples withdrawn from time to time, cooled, and acidified gave a set of spectra with isosbiestic points at 551, 446, 385, and 348 mμ which were fully consistent with those of mixtures of *cis*- and *trans*-$Co(en)_2(H_2O)_2{}^{3+}$[4] and were essentially identical with spectra obtained under the same conditions but in the absence of chloride. The spectrophotometric change followed a first-order rate law and the rate constant was independent of the wavelength and independent of the concentration of hydroxide and chloride. The value obtained, $4.4 \times 10^{-4}$ sec$^{-1}$, is identical with that reported in the absence of chloride.[4–7]

The second test of the Dittmar–Archer mechanism arises from the reversibility of the fast stereoretentive base hydrolysis. This would require that the *trans*-$Co(en)_2OHCl^+$ cation exchanges its chloride rapidly with free chloride ions in solution. We therefore took a solution of [*trans*-$Co(en)_2OHCl]Cl$ in alkali, under similar conditions to those reported by Dittmar and Archer, except for the presence of $Na^{36}Cl$, and, after stopping the reaction at various stages, isolated the unreacted complex as [*trans*-$Co(en)_2H_2OCl][B(C_6H_5)_4]_2$. The data reported in Table I indicate that, even after there has been considerable base hydrolysis, there is no significant exchange of the chloride in the unreacted complex.

TABLE I

UPTAKE OF $^{36}Cl$ IN UNREACTED *trans*-$Co(en)_2OHCl^+$ AT 0°[a]

| Time, sec | % reaction | $10^{-2} \times$ specific activity of [*trans*-$Co(en)_2H_2OCl][B(C_6H_5)_4]_2$, counts/mmol min | % exchange |
|---|---|---|---|
| 40 | 13 | 7.8 | 0.26 |
| 60 | 18 | 6.9 | 0.23 |
| 90 | 29 | 9.5 | 0.32 |
| 180 | 38 | 10.9 | 0.36 |

[a] Initial [complex] = 0.050 *M;* [NaCl] = 0.04 *M;* initial $[OH^-]$ = 0.16 *M;* specific activity of $Cl^{*-} = 1.08 \times 10^6$ counts/mmol min.

Thus we have been unable to find any evidence that supports the mechanism of Dittmar and Archer and can only assume that their observation of the rapid formation of *trans*-$Co(en)_2(OH)_2{}^+$ is the consequence of the overrefinement of their data by means of a computer. Therefore, there is no reason to change significantly the original data for the rates and steric course of the base hydrolysis of *trans*-$Co(en)_2OHCl^+$.[2]

---

(5) J. Y-P. Tong and P. E. Yankwich, *J. Am. Chem. Soc.*, **80,** 2664 (1958).

(6) W. Kruse and H. Taube, *ibid.*, **83,** 1280 (1961).

(7) M. E. Farago and B. Page, to be submitted for publication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MANKATO STATE COLLEGE, MANKATO, MINNESOTA 56001

## The *cis–trans* Equilibrium of Diaquobis(ethylenediamine)cobalt(III) Ion in Nitrate and Perchlorate Media

BY ROBERT C. HENNEY

*Received July 22, 1968*

Since the diaquobis(ethylenediamine)cobalt(III) ion is the product in acid hydrolysis of the acido-substituted parent compounds, the *cis–trans* and acid–base equilibria of the system are important in kinetic and mechanistic studies of aquation. Bjerrum and Rasmussen,[1] in a careful study of the system in 1 *M* sodium nitrate, reported the *cis*:*trans* equilibrium ratio to be 58, a figure subsequently used by other investigators working in different ionic media.[2–5] Investigation in this laboratory confirmed the findings of Bjerrum and Rasmussen; however, pmr spectra[6] suggested a greater amount of *trans* ion in perchlorate medium. The validity of comparing studies in the two media had already been questioned;[7] accordingly a determination of the effects of the two ions on the *cis*:*trans* equilibrium ratio was undertaken.

### Experimental Section

The *cis*:*trans* ratios of diaquobis(ethylenediamine)cobalt(III) ion in perchlorate and nitrate media were determined by potentiometry, by spectrophotometry, and by pmr measurements.

**Preparation of Compounds.**—The aquohydroxobis(ethylenediamine)cobalt(III) compounds were prepared in preference to the diaquo compounds used by Bjerrum and Rasmussen, which are difficult to prepare and purify because of their great solubility. The aquohydroxo ions are converted to the diaquo ions on dissolution in acidic media.

*trans*-**$[Co(en)_2(H_2O)(OH)](ClO_4)_2$.**—*trans*-Aquohydroxobis(ethylenediamine)cobalt(III) perchlorate was prepared as described previously.[6] *Anal.* Calcd for $[Co(en)_2(H_2O)(OH)](ClO_4)_2$: Co, 14.3. Found: Co, 13.9.

*cis*- **and** *trans*-**$[Co(en)_2(H_2O)(OH)]Br_2$.**—The *cis* salt was prepared by the method of Werner[8] and recrystallized from 2 *M* hydrobromic acid. When the pH was raised to 4–5 by addition of potassium hydroxide pellets, some *trans* salt precipitated and was filtered off. The pH of the filtrate was then immediately raised to 7–8, causing precipitation of the *cis* salt.

*Anal.* Calcd for *trans*-$[Co(en)_2(H_2O)(OH)]Br_2$: Br, 42.7; Co, 15.8; N, 15.0. Found: Br, 43.1; Co, 15.5; N, 14.7. Calcd for *cis*-$[Co(en)_2(H_2O)(OH)]Br_2 \cdot H_2O$: Br, 40.8; Co, 15.0. Found: Br, 41.0; Co, 14.7.

**Spectrophotometric Solutions.**—The nitrate and perchlorate solutions were both prepared by dissolving weighed amounts of the *cis*- and *trans*-aquohydroxobis(ethylenediamine)cobalt(III) bromides in enough 0.2 *M* nitric or perchloric acid to make the

---

(1) J. Bjerrum and S. Rasmussen, *Acta Chem. Scand.*, **6,** 1265 (1952).

(2) P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7,** 1872 (1968).

(3) C. G. Barraclough and R. S. Murray, *J. Chem. Soc.*, 7047 (1965).

(4) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83,** 1280 (1961).

(5) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5,** 1376 (1966).

(6) R. C. Henney, H. F. Holtzclaw, Jr., and R. C. Larson, *ibid.*, **5,** 940 (1966).

(7) J. B. Hunt and D. Wolcott, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 380.

(8) A. Werner, *Ber.*, **40,** 281 (1907).