

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

## Exchange and Isomerization Rates of Complex Ions of the Aquo-bis-(ethylenediamine)-cobalt(III) Series

BY W. KRUSE AND H. TAUBE

RECEIVED SEPTEMBER 30, 1960

The rates at which oxygen exchanges between water and the ions  $\text{Coen}_2(\text{H}_2\text{O})_2^{+++}$ ,  $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})^{++}$ ,  $\text{Coen}_2(\text{OH})_2^+$  (both *cis* and *trans* forms) have been measured, and existing information on the rates of isomerization has been augmented. The exchange accompanying isomerization was also studied. It was found that in the isomerization of *t*- $\text{Coen}_2(\text{H}_2\text{O})_2^{+++}$ , one molecule of water is brought into exchange with the solvent. In the isomerization of  $\text{Coen}_2(\text{OH})_2^+$  only a fraction of one oxygen per ion exchanges for each act of isomerization. This observation and the fact that  $\Delta H^*$  for the isomerization processes varies with temperature indicates that more than one mechanism operates in the isomerization of  $\text{Coen}_2(\text{OH})_2^+$ . The data for the diaquo ions cannot be explained by a single intermediate (such as an ion of formula  $\text{Coen}_2(\text{H}_2\text{O})^{+++}$  having a trigonal bipyramidal structure). The kinetic, exchange, isomerization and related data are discussed in terms of a plausible but still unproven mechanism involving two intermediates.

In this paper we report the results we have obtained in a study of the rates of exchange of oxygen between ions of formula  $\text{Coen}_2(\text{H}_2\text{O})_2^{+++}$ ,  $\text{Coen}(\text{OH})(\text{H}_2\text{O})^{++}$ ,  $\text{Coen}_2(\text{OH})_2^+$  and water as solvent. These rates are compared with the rates of isomerization, in part as they have been reported in the literature<sup>1-3</sup> and in part as measured in the present work. The study in the course of which the present data were obtained was undertaken in the hope of establishing the mechanisms of the reactions in question. While our measurements are an essential contribution to the description of the processes, they do not appear to lead to an unambiguous conclusion even with respect to a feature of mechanism as fundamental as this: do the reactions involve intermediates of reduced coordination number (as compared to the reactant complexes or to intermediates and/or activated complexes in which the coordination number has been increased?

### Experimental

**Syntheses of Complex Ions.**—*trans* [ $\text{Coen}_2\text{Cl}_2$ ]Cl was prepared as described elsewhere.<sup>4</sup> To prepare *trans*- $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_2$ , 12.5 g. of *trans*-[ $\text{Coen}_2\text{Cl}_2$ ]Cl was dissolved in 10 cc. of  $\text{H}_2\text{O}$  (for the  $\text{O}^{18}$  enriched salt,  $\text{O}^{18}$  enriched solvent was used), and an equivalent amount of  $\text{AgClO}_4$  was added. The  $\text{AgCl}$  was filtered off, and *trans*-[ $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_2$ ] was precipitated by adding  $\text{NaOH}$  to bring the solution into the pH range of 3-4. The precipitation of the *trans* salt rather than the *cis* takes place in spite of the fact that the latter predominates in the original solution of the aquo ions, for the *trans* diaquo form is more acidic than the *cis*, and the *trans*-monohydroxy perchlorate is less soluble than the corresponding *cis* form. Equilibrium between *cis* and *trans* forms is established rapidly in the half-neutralized solutions. The product salt was purified by recrystallization and obtained in about 55% yield in the purified form. A similar procedure was employed in the attempted preparation of *trans*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2(\text{ClO}_4)_3$  but this attempt met with no success; instead the ammino salt was largely decomposed to a black oxide.

*trans*-[ $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_2$ ] can be dissolved in cold aqueous  $\text{HClO}_4$  to form the corresponding aquo salt and without much isomerization. If concentrated  $\text{HClO}_4$  is added to a cold concentrated solution of the diaquo salt, the solid phase *trans*-[ $\text{Coen}_2(\text{H}_2\text{O})_2(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ] separates.

To prepare *cis*-[ $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_2$ ], a solution of the *trans* diaquo salt was left to isomerize to the *cis* form,

then under intensive cooling,  $\text{NaOH}$  was added to form ( $\text{Coen}_2(\text{OH})_2$ )<sup>+</sup>; by slowly adding  $\text{HClO}_4$ , *cis*-[ $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_2$ ] was precipitated at a pH of ca. 7.

*cis*-[ $\text{Coen}_2(\text{H}_2\text{O})_2(\text{ClO}_4)_3$ ] was prepared by heating the *trans* salt at 100° for an hour. It should be noted that neither the *cis* nor *trans* forms of [ $\text{Coen}_2(\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_2$ ] undergoes isomerization on being heated at 100° for 2 hr. in the solid.

The solution containing the chloro complex of  $\text{Tl(III)}^5$  was prepared by dissolving 25 g. of  $\text{Tl}_2\text{O}_3$  in 100 cc. of  $\text{HCl}$ .  $\text{NaClO}_3$  being added to ensure that  $\text{Tl}^+$  is oxidized to the +3 state.

The solution containing the  $\text{Bi(III)-Br}^-$  complex<sup>6</sup> was made up by dissolving  $\text{Bi}_2\text{O}_3$  in a concentrated solution of  $\text{HBr}$  and  $\text{NaBr}$ .

**Method.**—Because the solvent water is so much more abundant than is water in the coordination sphere of the solute, a method of isotopic analysis based on sampling the solute is more sensitive and therefore to be preferred. Many of the salts of  $\text{Coen}_2(\text{H}_2\text{O})_2^{+++}$  are very soluble, and we had some difficulty in finding anions which would bring about formation of a solid phase and a solid phase that is otherwise suitable for isotopic analysis. The precipitants we used are far from ideal, but with care, the procedure based on their use is reasonably precise.

The *trans* diaquo ion is precipitated as the brown solid [ $\text{Coen}_2(\text{H}_2\text{O})_2$ ] [ $\text{TlCl}_6$ ]· $2\text{H}_2\text{O}$ , and a solution containing also the *cis* form can be freed of the *trans* component using the  $\text{Tl(III)-Cl}^-$  complex (at room temperature when *cis* < 0.20 *M*). The precipitate of the *trans* form was washed with cold water and dried for 0.5 hr. over  $\text{P}_2\text{O}_5$ . The crystal water is not removed in a vacuum desiccator at room temperature.

The *cis* diaquo ion is precipitated as the  $\text{BiBr}_6^{3-}$  salt. This anion will also bring down the *trans* salt, so when analysis of mixtures is necessary, the *trans* salt must first be removed as described above. The *cis* salt of the bromobismuthate(III) anion comes down with variable amounts of water, the water content depending on the conditions of precipitation such as the temperature. The crystal water is lost in a vacuum at room temperature.

We found to our surprise that exchange between crystal and complex-bound water takes place quite readily in the hydrated solids. In spite of this, good data on the rate of exchange in solution can be found by handling successive samples of a series in the same way. Alternatively, all the water can be collected, its isotopic composition determined, and from the stoichiometry, knowing the isotopic composition of the solvent water, that of the complex bound water can be computed. This method is not optional but is mandatory when comparisons of the isotopic composition of the *cis* form growing from the *trans* are made and was employed in getting the data of Table IV. The hydroxy forms were converted to the aquo forms by acidifying and the isotopic analyses then was carried out as for the diaquo forms.

To remove the water from the solid salts, they were heated at 140° for 30 minutes. The water was collected and the isotopic composition determined as usual with  $\text{CO}_2$  as the indicator gas. The solids left as products are green

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

(2) J. Y. Long and P. E. Yankwich, *J. Am. Chem. Soc.*, **80**, 2664 (1958).

(3) Racemization rate of *cis* diaquo: J. P. Mathieu, *Bull. soc. chim.*, [5] **4**, 687 (1937).

(4) J. C. Bailar, Jr., and C. W. Rollinson, *Inorg. Syntheses*, **11**, 222 (1946).

(5) G. Spacu and A. Pap, *Z. Anal. Chem.*, **120**, 323 (1940).

(6) C. Mähr, *ibid.*, **93**, 433 (1933).

and are presumably in the *trans* form for both the Bi(III) and Tl(III) complex salts.

Isomerization rates were followed spectrophotometrically at 492 m $\mu$  for the diaquo forms and at 520 m $\mu$  for the dihydroxo forms. The cell compartment was thermostated. Optical densities were measured for one to two half-lives and the final optical density measured after ten half-lives.

The exchange experiments were done with the Co(III) salt at 0.20 *M* level. Early, orienting experiments showed that the exchange half-life is independent of the Co(III) concentration. The experiments on isomerization were done with solutions 0.010 *M* in Co(III).

In the following, T represents the group Coen<sub>2</sub>.

### Results

The results of the exchange experiments are summarized in Table I.

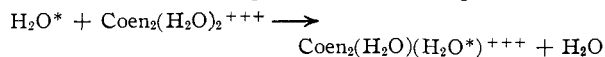
TABLE I  
RATES OF EXCHANGE

Complex	Temp., °C.	Other	$k \times 10^4$ , min. <sup>-1</sup>
<i>cis</i> -T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>	14.4	0.8 <i>M</i> HClO <sub>4</sub>	0.66
<i>cis</i> -T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>	24.95	.8 <i>M</i> HClO <sub>4</sub>	4.4
<i>cis</i> -T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>	24.95	{ .3 <i>M</i> HClO <sub>4</sub>	4.6
		{ .5 <i>M</i> NaClO <sub>4</sub>	
<i>cis</i> -T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>	39.85	.8 <i>M</i> HClO <sub>4</sub>	46
50% <i>cis</i> T(OH)(H <sub>2</sub> O) <sup>++</sup>	24.95	.....	280
50% <i>cis</i> T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>			
<i>cis</i> -T(OH) <sub>2</sub> <sup>+</sup>	14.4	0.8 <i>M</i> NaOH	3.4
	24.95	.8 <i>M</i> NaOH	18
	24.95	{ .3 <i>M</i> NaOH	18
		{ .5 <i>M</i> NaClO <sub>4</sub>	
	39.85	.8 <i>M</i> NaOH	173
<i>trans</i> -T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>	14.4	.8 <i>M</i> HClO <sub>4</sub>	1.10
	24.95	.8 <i>M</i> HClO <sub>4</sub>	6.8
	24.95	{ .3 <i>M</i> HClO <sub>4</sub>	6.8
		{ .5 <i>M</i> NaClO <sub>4</sub>	
	24.95	.5 <i>M</i> HClO <sub>4</sub>	15
	39.85	0.8 <i>M</i> HClO <sub>4</sub>	87
20% <i>trans</i> -T(OH)(H <sub>2</sub> O) <sup>++</sup>	24.95	.....	150
80% <i>trans</i> -T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>			
<i>trans</i> -T(OH) <sub>2</sub> <sup>+</sup>	14.4	0.8 <i>M</i> NaOH	0.20
	24.95	.8 <i>M</i> NaOH	1.4
	24.95	{ .3 <i>M</i> NaOH	1.4
		{ .5 <i>M</i> NaClO <sub>4</sub>	
	39.85	.8 <i>M</i> NaOH	17.7

The specific rates quoted in column 4 of Table I are those obtained from the McKay plots which represent the exchange data. These specific rates are related to an exchange specific rate  $k_e$  by the equations

$$R = k \frac{2(\text{Co(III)})(\text{H}_2\text{O})}{(2(\text{Co(III)}) + (\text{H}_2\text{O}))} = k_e(\text{Co(III)})$$

where  $R$  is the rate of water turnover in  $M^{-1} \text{ min.}^{-1}$  and  $k_e$  refers to the specific rate of the process



which leads to exchange. The values of  $k_e$  are to a sufficient degree of approximation the values of  $k$  multiplied by 2. It should be noted that the values of  $k_e$  at 25° are greater than those for the exchange of  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$  with water<sup>7,8</sup> by a factor of 2.5 to 3, but it must be remembered that a factor of 2 is present as a purely statistical factor in the way the value  $k_e$  has been defined.

The exchange reaction is markedly catalyzed by charcoal; it was found to be complete within 1.5 hr. at 25° for the *cis* form in acid solution.

The data which were obtained in our measurements of the rates of isomerization are shown in Table II.

TABLE II  
RATES OF ISOMERIZATION

Reaction	Medium	Temp., °C.	$k' \times 10^4$ , min. <sup>-1</sup>	$k_c$ or $k_t$ , $\times 10^4$ , min. <sup>-1</sup>
1. <i>trans</i> $\rightarrow$ <i>cis</i>	10 <i>M</i> HClO <sub>4</sub>	24.95	$7 \times 10^2$	$7 \times 10^2$
2. <i>trans</i> $\rightarrow$ <i>cis</i>	5 <i>M</i> HClO <sub>4</sub>	24.95	13	13
3. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> HClO <sub>4</sub>	24.95	6.5	6.4
4. <i>trans</i> $\rightarrow$ <i>cis</i>	4 <i>M</i> NaClO <sub>4</sub>			
4. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> HClO <sub>4</sub>	24.95	4.1	4.0
	1 <i>M</i> HClO <sub>4</sub>	24.95	4.1	4.0
5. <i>trans</i> $\rightarrow$ <i>cis</i>	95% D <sub>2</sub> O			
6. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> HClO <sub>4</sub>	14.4	0.85	0.84
7. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> HClO <sub>4</sub>	37.5	24	24
8. <i>trans</i> $\rightarrow$ <i>cis</i>	Adjusted to 20% T(OH)H <sub>2</sub> O <sup>++</sup> , 80% T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup>	24.9	$5 \times 10^2$	...
9. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> NaOH	14.4	0.70	0.32
10. <i>cis</i> $\rightarrow$ <i>trans</i>	1 <i>M</i> NaOH	14.4	0.70	0.38
11. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> NaOH	24.95	4.3	1.9
12. <i>cis</i> $\rightarrow$ <i>trans</i>	1 <i>M</i> NaOH	24.95	4.0	2.2
13. <i>cis</i> $\rightarrow$ <i>trans</i>	1 <i>M</i> NaOH	24.95	3.9	2.1
	99% D <sub>2</sub> O	37.5	34	17
14. <i>trans</i> $\rightarrow$ <i>cis</i>	1 <i>M</i> NaOH			
15. <i>cis</i> $\rightarrow$ <i>trans</i>	1 <i>M</i> NaOH	37.5	36	19
16. <i>trans</i> $\rightarrow$ <i>cis</i>	10 <i>M</i> NaOH	24.95	Somewhat less than 4 <sup>a</sup>	

<sup>a</sup> Decomposition sets in and precipitate forms after 72 hr.

The values of  $k'$  recorded are those obtained in a plot of  $\log(OD_t - OD_\infty)$  against time, where  $OD$  represents the optical density. These specific rates are equal to  $k_c + k_t$ , where  $k_c$  governs the change of *cis* to *trans*, and  $k_t$  governs the change of *trans* to *cis*. For acidic solutions, in which the ratio of *cis/trans* at equilibrium is high,<sup>9</sup>  $k'$  is very nearly equal to  $k_t$ . Bjerrum and Rasmussen<sup>1</sup> also report a value of the equilibrium ratio *cis/trans* for the dihydroxo form. This value (0.80) agrees quite well with the value of 0.85 which we have measured. We find furthermore that there is no detectable change in the equilibrium ratio over the temperature interval from 14.4° to 37.5°. By using the relation that the ratio  $k_c/k_t$  is given by the equilibrium constant, in addition to the relation  $k' = k_c + k_t$ , the values of  $k_c$  and  $k_t$  can be calculated separately and are recorded in column 5.

Tong and Yankwich<sup>2</sup> report values of ( $k_c + k_t$ ) for the diaquo ions under conditions identical to ours except for a slight difference in temperature (24.84° whereas ours are run at 24.95°). Our value of  $k_c + k_t$  as  $4.1 \times 10^{-4} \text{ min.}^{-1}$  agrees well with their value,  $4.1 \times 10^{-4} \text{ min.}^{-1}$ . The specific rates reported by Bjerrum and Rasmussen<sup>1</sup> were determined for solutions much less acidic than ours,

TABLE III  
ACTIVATION PARAMETERS

	$k \times 10^4$ at 25°, min. <sup>-1</sup>	$\Delta H^*$	$\Delta S^*$
<i>cis</i> T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup> Exchange	4.5	28.8	15
<i>cis</i> T(OH) <sub>2</sub> <sup>+</sup> Exchange	18	27.4	13
<i>trans</i> T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup> Exchange	6.8	30.6	21
<i>trans</i> T(OH) <sub>2</sub> <sup>+</sup> Exchange	1.4	30.4	20
<i>trans</i> T(H <sub>2</sub> O) <sub>2</sub> <sup>+++</sup> $\rightarrow$ <i>cis</i>	4.1	25.6	4
<i>trans</i> T(OH) <sub>2</sub> <sup>+</sup> $\rightarrow$ <i>cis</i>	1.9	28.0, 30.9	..
<i>cis</i> T(OH) <sub>2</sub> <sup>+</sup> $\rightarrow$ <i>trans</i>	2.2	28.0, 30.9	..

(9) Given as 58 at 25° by Bjerrum and Rasmussen. We have observed that the ratio is strongly affected by illumination. Using the full light of a 1000 watt bulb close to the solution, ca. 30% is maintained in the *trans* form at the steady state.

(7) A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

(8) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

TABLE IV  
 RESULTS OF MILKING EXPERIMENTS

( $E$ , the enrichment ratio, is the  $O^{18}$  content compared to that of the solvent of normal isotopic composition.  $E_0$  refers to starting material,  $E_t$  to product formed,  $E_t'$  as calculated for no exchange on isomerization,  $E_t''$  as calculated for one  $H_2O$  being exchanged on isomerization.)

Medium	Temp., °C.	Reactant	Time $\times 10^{-3}$ min.	$E_0$	$E_t$	$E_t'$	$E_t''$
		80% <i>trans</i> -diaquo					
...	25	20% <i>trans</i> -hydroxoquo	0.21	3.14	1.94	$2.7 \pm 0.2$	$1.9 \pm 0.1$
0.8 M H <sup>+</sup>	25	<i>trans</i> -diaquo	8.4	2.14	1.37	1.69	1.37
.8 M H <sup>+</sup>	25	<i>trans</i> -diaquo	7.8	1.97	1.28	1.62	1.33
.3 M OH <sup>-</sup>	25	<i>cis</i> dihydroxo	7.8	2.61	1.87	1.93 <sup>a</sup>	1.47 <sup>a</sup>
.5 M NaClO <sub>4</sub>							
.3 M OH <sup>-</sup>	14.4	<i>cis</i> dihydroxo	14.4	2.03	1.65	1.78	1.39
.5 M NaClO <sub>4</sub>	14.4	<i>cis</i> dihydroxo	27.0	2.03	1.56	1.62	1.30

<sup>a</sup> Calcd. using  $14 \times 10^{-4}$  min.<sup>-1</sup> as specific rate at which *cis* exchanges rather than  $18 \times 10^{-4}$  as recorded in Table I. The specific rate of  $14 \times 10^{-4}$  was calculated from the isotopic composition of a sample of the *cis* salt withdrawn at the same time as the *trans*. Similar blanks were done in the other experiments and except in this one case agreed with the values in Table I within 5%.

and the reason for the higher specific rates (by a factor of almost 2) which they observed is that there was probably a contribution to the reaction by the more labile hydroxoquo complex, particularly when the acid concentration was as low as 0.05 M. Our value of ( $k_c + k_t$ ) ( $4.2 \times 10^{-4}$  min.<sup>-1</sup>) for the dihydroxo ion in alkaline solution agrees fairly well with that reported by Bjerrum and Rasmussen as  $4.6 \times 10^{-4}$  min.<sup>-1</sup> at 25° in a medium 0.5 M in NaOH and 0.5 M in NaNO<sub>3</sub>. These values and our values measured at 37.5° are in accord with those reported by Tong and Yankwich<sup>2</sup> at 35.0°.

The specific rates reported for solutions in which a substantial fraction of the complex is present in the monohydroxy form are only approximate, and to get good values considerable time and trouble needs to be invested. In addition to the obvious difficulty of measuring rates for the more labile species is that of defining the initial composition (that is the distribution between the monohydroxy and diaquo forms). Furthermore since isomerization inevitably takes place and since the *cis* and *trans* forms differ considerably in acidity, the distribution of the complex between the hydroxy and diaquo forms changes with time.

In Table III are recorded values of the activation parameters for the various rate processes which have been studied.

A number of experiments (see Table IV) were done to learn whether exchange of water takes place as a result of the isomerization process. In these experiments, one form of the ion, for example the *trans* form in acid solution, is dissolved in water of different isotopic composition, and after sufficient of the *cis* form has collected to make its isolation possible, the product ion is collected and its isotopic composition determined. These experiments are not feasible under all circumstances; a condition necessary for their success is that the rate of exchange be not too large compared to the rate of isomerization.

Calculations were made for each of the experiments of the isotopic composition to be expected for the product ion if no exchange takes place as a result of isomerization and if exactly one molecule of oxygen exchanges for each act of isomerization. The calculations were made by an approximate method, following the history of the product

ion formed during successive small intervals. The intervals were short compared to the half-life (at most 1/4 of a half-life) and the values calculated are therefore not in error by more than 2 or 3%.

NOTE ADDED IN PROOF.—The case in which the isomerization is substantially unidirectional, as it is in acid solution, also was treated analytically, and the corresponding entries in the table are actually those found by the more exact treatment (the results do not differ by as much as 2% from those obtained by the approximate method). The analytic treatment of the kinetic problem is outlined herewith. Let  $A$  and  $B$  represent the concentrations of the enriched *trans* and *cis* forms, and  $k_t$ ,  $k_A$ ,  $k_B$  the specific rates for isomerization of the *trans*, exchange of *trans* and exchange of *cis*, respectively. Then if there is no exchange in the act of isomerization

$$\begin{aligned} dB/dt &= k_t A - k_B B \\ dA/dt &= -(k_t + k_A)A \end{aligned}$$

These equations can be solved to give  $B$  at time  $t$

$$B = \frac{A_0 k_t}{k_t + k_A - k_B} [e^{-k_B t} - e^{-(k+k_A)t}] \quad (1)$$

where  $A_0$  is the initial concentration of the *trans* salt and  $B$  is taken as 0 at  $t = 0$ . Now the total amount of *cis* at time  $t$  is given by  $A_0(1 - e^{-k t})$  (2) so that the residual enrichment of the *cis* salt can be calculated by comparing the concentration of  $B$  at time  $t$  (regarded as that concentration of *cis* salt which corresponds to the initial degree of enrichment of the *trans*) to the total amount of *cis*. In calculating the residual enrichment to be expected if exactly one molecule of water exchanges for each act of isomerization, the calculation is repeated with  $k_t$  in equation (1) but not in (2) replaced by  $k_t/2$ .

### Discussion

The data of Table I show that the rates of exchange for both *cis* and *trans* diaquo complexes are independent of acid concentrations at moderate levels. In alkali, the complexes are converted to the dihydroxo ions, and in this form, the rate of exchange is independent of the hydroxide concentration over a considerable range. In the intermediate range of acidity, in which the monohydroxy ions predominate, the rates reach a maximum. Thus there are three paths for the exchange corresponding to activated complexes of the composition  $T(H_2O)_2^{+++}$ ,  $T(OH)H_2O^{++}$  and  $T(OH)_2^+$  (these formulas do not take into account additional molecules of solvent which may be involved). The isomerization reactions proceed by activated complexes of the same composition, but the rates by the several paths are different from the ex-

change rates. For the isomerization reactions also the monohydroxy complexes are the most labile.

The most significant observation made in the course of this study appears to be that extensive exchange takes place in the isomerization of the diaquo and the hydroxo-aquo complex ions. The extent of the exchange corresponds closely to one of the two water molecules reaching isotopic equilibrium with the solvent for each exchange act. These observations can be understood on the basis that an intermediate of coordination number 5 is formed, which then rearranges and reassumes the coordination number 6. However, the observations by no means prove that an intermediate of reduced coordination number is formed. The exchange on isomerization can also be understood by assuming an edge displacement mechanism<sup>10,11</sup>—by assuming for example that a molecule of the solvent disrupts a Co(III)-amino bond and the displaced group in turn displaces a molecule of water from the coordination sphere. The observation that in addition to those reported earlier, favors somewhat the mechanism involving an intermediate of coordination number 5 is that the hydroxo-aquo complex is more labile than the diaquo. This relation is explained naturally by assuming that the electrons freed by the loss of a proton stabilize an intermediate of lower coordination number.<sup>12</sup> But the observation is not completely incompatible with the assumption that the reaction proceeds *via* an activated complex of coordination number 7, because it bears more directly on the issue of the extent of bond-breaking compared to bond-making in the activated complex than it does on its geometry. The fact that the lability of the dihydroxy complex is less than that of the hydroxo-aquo is qualitatively equally in accord with the two mechanisms.

The isomerization in alkaline solution may involve two different paths. This is indicated by the fact that although exchange takes place on isomerization, it is less in extent than corresponds to one molecule of water for each act of isomerization. It is also indicated by the fact that  $\Delta H^*$  is not constant even over the short temperature range covered in the experiments. One of the paths may correspond to breaking a Co(III)-OH<sup>-</sup> bond and the other a Co(III)-NH<sub>2</sub> bond in the activated complex. It seems reasonable that the two processes should be able to compete, the lability of the Co-O bond being decreased by the loss of a proton from the water to bring it into the range of lability of Co-NH<sub>2</sub>R bond.

We have been unable to base any particularly definitive or searching conclusions on the comparison of the rates of exchange and isomerization for a given ion. A special point of interest to consider is whether a single intermediate (such as a pentagonal bipyramidal structure) can account for isomerization and exchange. This is clearly not the case; a profile such as is shown in Fig. 1a can account for the isomerization of *cis* to *trans*

(10) D. O. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2673 (1953).

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 222.

(12) Ref. 11, pp. 124 *et seq.*

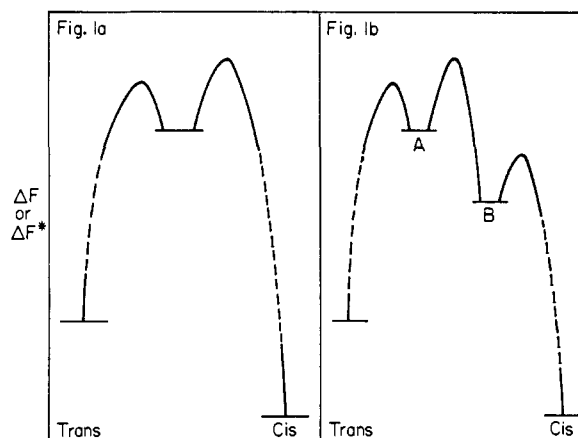


Fig. 1.—Free energy profiles for one assumed intermediate (1a) and for two assumed intermediates (1b): 1a expresses the fact that the rate at which *trans* exchanges is somewhat greater than that at which it changes to *cis* and also accounts for the rate at which *cis* changes to *trans*, but not for the rate at which *cis* exchanges water; in 1b the heights of the three barriers can be adjusted to account for all four rates.

in acid, *trans* to *cis*, and the exchange of the *trans*, but it cannot account for the exchange of the *cis*, which would be given a half-life of the same order as that for the change of *cis* to *trans*. In Fig. 1b the profile is amended to account also for the exchange of the *cis* form. On the basis of this formulation the intermediates A and B can be regarded as being derived from octahedra by the loss of water from one of the coordination positions. The further distortion required to bring about isomerization can be considered to be the change through a trigonal bipyramidal arrangement. This structure can in fact be formulated as an intermediate but this is not demanded by the data.

It is perhaps worth mentioning that a formulation of the type adopted in Fig. 1b does not require that the rate of water exchange for the *trans* diaquo ion, for example, must exceed the rate at which it isomerizes. These relative rates are governed by independent processes for the intermediate A, one requiring it to return to reactants and the other requiring it to rearrange further. It does require that the rate of total exchange, that accompanying isomerization and that peculiar to the *trans* ion exceed the rate of isomerization, and this condition is fulfilled by the system in acid, and in fact also in alkaline solution.

The comparison of the rate of isomerization of the *cis* diaquo form to the *trans* with the rate of racemization of the *cis* suggests that a principal path for the latter change is through the *cis-trans* equilibrium. Combining the known specific rate for the change of *trans* to *cis* with the value of the equilibrium quotient (*cis/trans* = 58 in acid solution),<sup>1</sup> the specific rate for the change of *cis* to *trans* is calculated as  $7.0 \times 10^{-6}$  min.<sup>-1</sup>. The half-life for the decay of optical rotatory power in a solution of the *cis* diaquo ion can be calculated from the data of Mathieu<sup>3</sup> as 50 days at 25°. Thus the specific rate for the change of the *l* form to the *d* (or the reverse) is given by

$$\frac{0.693}{2 \times 50 \times 24 \times 60} = 4.8 \times 10^{-6} \text{ min.}^{-1}$$

If the *cis-trans* equilibrium is to account entirely for the racemization reaction, the specific rate for the change of *cis* to *trans* would need to be  $2 \times 4.8$  (or  $9.6$ )  $\times 10^{-6} \text{ min.}^{-1}$  (the factor of two enters because the *trans* has an equal probability of giving the *l* form and the *d* form). The agreement with the value  $7.0 \times 10^{-6} \text{ min.}^{-1}$  probably is within the combined experimental error of the determinations entering the comparison. In particular the value of half-life calculated from the data for the racemization is only approximate.

It is implicit in the diagram of Fig. 1b that the activated complex for isomerization is arrived at through the intermediates A and B. This is clearly not a requirement of the data which were reported, even if the reactions are taken to proceed by mechanisms involving species of reduced coordination number as intermediates. Thus the activated complex for isomerization and that for exchange can be at equilibrium with respect to the reactants but as completely independent processes. The implication of the diagram is that the activated complex for isomerization is most economically arrived at by routes that involve intermediates A and B. It requires that any means of reducing the concentration of the intermediate as by reaction with another substance will reduce the rates of isomerization and exchange in the same proportion, replacing these reactions in part by the new one which results from consumption of the intermediate. We have only done some preliminary experiments on this essential part of the total study. On the basis of these experiments it seems likely that some success can be had investigating the point at issue by having  $\text{Cl}^-$  or  $\text{NCS}^-$  present in the solution at high concentration. But the analysis of the results of such experiments is very complex, so that the experiments constitute a major undertaking in themselves. We also tried an approach which is rather more novel, using the oxidation-reduction reagent  $\text{Fe}^{++}$ , in the hope that it would react much more rapidly with the postulated intermediate than with the reactant ions. We only carried these experiments far enough to learn that this approach, while it may be useful, also will require a detailed and careful study. Unfortunately,  $\text{Fe}^{++}$  reacts quite rapidly with the *trans* form, and if the effect sought for exists, it is only a small contribution to the total reaction. There is hope however that a reducing agent can be found which reacts rapidly with the intermediates but not with the starting complexes.

The activation parameters entered in Table III call for some comment. The water exchange reactions of the diaquo ions of the present series have entropies of activation considerably more positive than that measured for the pentammine  $\text{Co(III)}$

complex.<sup>8</sup> On the basis of an activated complex in which the principal change is stretching the  $\text{Co(III)-OH}_2$  bond, without at the same time making a new bond, part of this larger entropy can be attributed to internal degrees of freedom for the chelate which becomes available as a coordination position is opened. The higher values of  $\Delta H^*$  for the bisethylenediamine series compared to that of the pentammine may arise from the greater restrictions on the readjustment possible for the  $\text{Co-NH}_2\text{-R}$  bonds when chelating functions are present. The less favorable entropy for the isomerization compared to exchange fits with the view that isomerization involves a distortion of the intermediates A or B—a severe selection needs to be made among the various motions possible to bring about isomerization. But the lower value of  $\Delta H^*$  for isomerization compared to exchange is surprising—crystal field effects would appear to favor a lower value of  $\Delta H^*$  when a square pyramid is formed than when a trigonal bipyramid is formed.<sup>13</sup>

The "electrolyte" effects observed on the rate of isomerization, though not without precedent, still seem to us to be remarkable, particularly in view of the large magnitude on acceleration in rate by a factor of 170 by changing from 1 *M*  $\text{HClO}_4$  to 10 *M*  $\text{HClO}_4$  as solvent medium with an anion as neutral as is  $\text{ClO}_4^-$ . Part of the effect may be caused by  $\text{H}^+$ . Thus Ahmed and Wilkins<sup>14</sup> report an influence of  $\text{H}^+$  on the rate of dissociation of  $\text{Nien}^{++}$  suggesting that it assists in the opening of the chelate. It is possible that as the acid concentration becomes very large, the relation between isomerization and exchange is altered and isomerization may proceed in large part by opening the chelate. It should also be noted that the absorption spectra of *cis* diaquo complexes are different in 10 *M*  $\text{HClO}_4$  compared to dilute  $\text{HClO}_4$ ; the peak is shifted from 492 to 497  $\text{m}\mu$ .

Experiment 13 of Table II was done to test the hypothesis that rupture of a  $\text{Co}^{\text{III}}\text{-OH}^-$  bond would require the ion to be put into the form  $\text{R}_\text{N}^{\text{H}}\text{-Co}^{\text{III}}\text{-OH}_2$  (*i.e.* require moving a proton from N to O). Even if this change be viewed as an equilibrium that is established prior to the rate determining step, a somewhat slower rate in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  would be expected. No difference in rate is observed, but this does not prove that the process as outlined does not occur. The difference in rate expected, if the only influence were an equilibrium one, is small and some other compensating effect may also contribute to the total isotope effect.

**Acknowledgment.**—This work was supported by the National Science Foundation under Grant G-5411.

(13) Ref. 11, p. 109.

(14) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).