

$$\frac{\partial}{\partial \nu} \sum_{j=2}^{\infty} j^n N_j = k_3 C \left( \frac{\partial}{\partial q} q \right)^n \left[ \frac{q}{1-q} (e^p - e^{p^2}) \right] \quad (8^*)$$

Substituting the values of  $p$  and  $C$  in (8\*) and integrating with respect to  $\nu$ , one obtains

$$\sum_{j=2}^{\infty} j^n N_j = \frac{k_3 k_1}{k_2} (\text{XH})_0 \left( \frac{\partial}{\partial q} q \right)^n \left[ \frac{q}{1-q} \left( \frac{1 - e^{-(k_1 + k_4)\nu}}{k_1 + k_4} - \frac{1 - e^{-(k_2 + k_3 + aq)\nu}}{k_2 + k_3 + aq} \right) \right] \quad (9^*)$$

For the special case  $n = 0$ , (9\*) gives

$$\sum_{j=2}^{\infty} N_j = \frac{k_3 k_1}{a + k_2} (\text{XH})_0 \left[ \frac{e^{-(k_1 + k_4)\nu} - 1}{k_1 + k_4} - \frac{e^{-k_2\nu} - 1}{k_2} \right] \quad (10^*)$$

**Acknowledgment.**—This investigation was supported by a research grant (PHS-G-3677) from the U. S. A. National Institutes of Health, Public Health Service.

REHOVOT, ISRAEL

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF MELBOURNE AND THE UNIVERSITY OF BUFFALO]

## The Kinetics of the Carbonate Exchange and Racemization Reactions of Carbonato-bis-(ethylenediamine)-cobalt(III) Ion<sup>1</sup>

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RECEIVED OCTOBER 28, 1954

Carbon-14 was used to trace the exchange of ligand carbonate with uncomplexed carbonate ion in aqueous solution. The en salt exchanges a little more slowly than does the previously studied tetrammine analog. The isotope fractionation effect at exchange equilibrium is very small in the case of the en compound, in contrast to the tetrammine. In spite of these differences, the exchange behavior of the en complex can be reasonably explained on the basis of a mechanism not greatly modified from that proposed for the tetrammine. Optically active en complex exchanges at the same rate as does the racemate. However, the rate of racemization is very much slower than that of ligand exchange, and has very different kinetic characteristics. It is concluded that racemization is an intramolecular process, largely independent of ligand substitution reactions. Nevertheless it involves some of the same intermediates postulated in explanation of the exchange kinetics.

The exchange reaction in aqueous solution between free uncomplexed carbonate ion and the corresponding ligand group in carbonatotetrammine-cobalt(III) ion has been recently investigated. A tracer technique utilizing radiocarbon was applied, and studies were made of the exchange kinetics,<sup>4</sup> the effect of ionic strength variation,<sup>5</sup> and the equilibrium isotope effect.<sup>6</sup> The present paper reports the results of a similar carbonate-exchange study of the ethylenediamine analog of the tetrammine complex. This aspect of the work was designed to provide evidence concerning the influence of type and structure of neutral ligand on the chemical reactivity of the complexed carbonate group. An additional approach is afforded by the occurrence of optically active forms of carbonato-bis-(ethylenediamine)-cobalt(III) salts. Comparison of exchange and racemization rate data enables conclusions as to the mechanism of the latter process, extending a technique suggested by early radioactive tracer studies of cobalt complexes.<sup>7,8</sup>

### Experimental

**A. Preparation of Compounds.**—*trans*-Dichloro-bis-(ethylenediamine)-cobalt(III) chloride was prepared by the

(1) Presented at the New York Meeting of the American Chemical Society, September, 1954.

(2) Taken in part from a thesis submitted by John S. Holden in partial fulfillment of the requirements for the M.Sc. degree of the University of Melbourne, 1953.

(3) Correspondence concerning this paper should be addressed to the senior author at the University of Buffalo, Buffalo 14, New York.

(4) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952).

(5) D. R. Stranks, *ibid.*, **48**, 911 (1952).

(6) D. R. Stranks and G. M. Harris, *J. Phys. Chem.*, **56**, 906 (1952).

(7) G. W. Ertle and C. H. Johnston, *J. Chem. Soc.*, 1490 (1939).

(8) F. A. Long, *J. Appl. Phys.*, **12**, 349 (1941); *THIS JOURNAL*, **63**, 1353 (1941).

standard procedure.<sup>9</sup> It was converted to racemic carbonato-bis-(ethylenediamine)-cobalt(III) chloride by boiling for one hour with the calculated quantity of sodium carbonate in aqueous solution. The product was purified by fractional crystallization. Complete analysis yielded results in agreement with the formula  $(\text{Coen}_2\text{CO}_3)\text{Cl}$ . Werner<sup>10</sup> has reported the existence of a monohydrate of this salt, but the water content of our product was negligible, nor did it show any deliquescent tendency.

Optically active *d*-( $\text{Coen}_2\text{CO}_3$ )Cl was obtained by treating aqueous solution of *d*-( $\text{Coen}_2\text{CO}_3$ )<sub>2</sub>CO<sub>3</sub>, prepared by the method of Bailar and Peppard,<sup>11</sup> with slight excess of BaCl<sub>2</sub>. After standing overnight, the BaCO<sub>3</sub> was filtered off and the *d*-( $\text{Coen}_2\text{CO}_3$ )Cl precipitated by addition of alcohol and ether. The specific rotation, measured on a 0.1% solution at room temperature, was 740° in sodium-D light.

**B. Exchange Experiments.**—The experimental technique was only slightly modified from that previously described.<sup>4</sup> It was found that aqueous solutions of the en complex, with or without added carbonate, underwent small changes in pH and conductance on standing. These were complete within two or three hours at 50°, but required about 12 hours at room temperature. For example, at 50° a solution 0.01 M in complex and 0.0033 M in Na<sub>2</sub>CO<sub>3</sub> decreased in pH from 10.76 to 9.96 in three hours and changed only very slightly more on long standing. The conductance decreased by about 7% during the same three-hour interval to a constant value. Solutions of complex without added carbonate showed a similar pH behavior, but for these the conductance increased by about 10% to attain a constant value. The absorption spectrum of the solutions was determined over the range 3000–7000 Å. on a Hilger "Uvispek" photoelectric spectrophotometer. It exhibited only slight alteration during the pH and conductance adjustments. No doubt aequation equilibrations are involved in these processes (see Discussion). Consequently, in all the exchange work the solutions were allowed to stand overnight at reaction temperature before adding the final small portion of highly radioactive carbonate and commencing the exchange rate measurements.

(9) W. C. Fernelius, Editor, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, 1946, Vol. II, p. 223.

(10) A. Werner, *Ann.*, **386**, 72 (1912).

(11) J. C. Bailar, Jr., and D. F. Peppard, *THIS JOURNAL*, **62**, 820 (1940).

In the series of runs at constant  $pH$ , the solutions were buffered by 0.05  $M$  sodium borate. Precipitation of  $BaCO_3$  from these for radioassay was achieved as follows. The  $pH$  of each 1-ml. aliquot was first raised by addition of 0.25 ml. of 1  $N$   $NH_4OH$ , then aqueous  $BaCl_2-NH_4Cl-NH_4OH$  mixture in the ratio  $N/2:N/4:N/4$  was added to slight excess. This procedure gave only 95% complete precipitation, but the precipitate weights were very reproducible. Isotopic fractionation effects are very small in this exchange<sup>12</sup> so the method was deemed satisfactory for the desired relative radioactivity measurements.

**C. Racemization Experiments.**—An "Officine Galileo" polarimeter, scaled to 0.01° unit, was employed. The intense red color of solutions of the complex made it impossible to use a sodium lamp for all but the most dilute. A 500-watt projection lamp served as the light source in measurements on the more concentrated solutions. The band of visible transmitted wave lengths is not wide, and no difficulty was experienced in making rotation readings to the limit of the instrument's precision. The glass-jacketed polarimeter tube was kept at constant temperature in some experiments by flow of thermostated water, but in most of the work condensing vapor provided constant temperature control. Boiling acetone maintained a temperature of  $56.1 \pm 0.1^\circ$  and ether,  $34.6 \pm 0.1^\circ$ . Samples were allowed to come to temperature equilibrium for at least 15 minutes before commencing measurements. Runs made after allowing the solution to stand 90 minutes at  $50^\circ$  gave results identical with others in which the waiting period was only 15 minutes, other conditions being held constant. Apparently, the initial  $pH$  and conductance variations mentioned above influence the over-all racemization rate only negligibly.

Initial rotations averaged about  $2^\circ$ , and readings were taken at intervals corresponding to about  $0.1^\circ$  loss of optical activity.  $pH$  measurements were made at room temperature on the cooled solutions subsequent to the runs. Corrections were then approximated for the higher temperature by use of published data for  $pH$  variations with temperature of carbonate<sup>13</sup> and borate<sup>14</sup> solutions.

## Results

Rates of exchange are recorded in terms of reciprocal half-times,  $\theta_e$ , following the conventional treatment of isotopic exchange in absence of isotope effect. For the present system, we have

$$\theta_e = \frac{1}{t_{1/2}} = \frac{R}{0.693} \left[ \frac{a+b}{ab} \right]$$

where  $R$  is the rate law governing the exchange, a function of the reactants involved, and  $a$  and  $b$  are the concentrations of the two exchanging species.<sup>15</sup> Data of the pertinent exchange runs are shown in Figs. 1 and 2. All runs shown were carried out using racemic en salt since it was found in separate experiments that no significant difference resulted from the use of the optically active form.

Rates of racemization are expressed in similar fashion, the reciprocal half-times,  $\theta_r$ , being determined in the customary way from  $\log$  (angle of rotation) vs. time plots. Thus  $\theta_r = 1/t_{1/2} = k/0.693$ , with  $k$  the experimental rate constant of racemization as defined by Basolo.<sup>16</sup> Tables I and II and Figs. 3 and 4 present the significant results of the racemization rate study.

(12) P. E. Yankwich and J. E. McNamara (*J. Chem. Phys.*, **20**, 1325 (1952)), reported a value of  $0.990 \pm 0.01g$  for the carbon-14 exchange equilibrium constant of this system. D. R. Stranks (private communication) has confirmed the small effect, finding a value of  $0.981 \pm 0.005$  for the constant.

(13) L. E. Kuentzel, J. W. Hensley and L. R. Bacon, *Ind. Eng. Chem.*, **35**, 1289 (1943).

(14) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I, p. 81.

(15) G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

(16) F. Basolo, *Chem. Revs.*, **52**, 459 (1953).

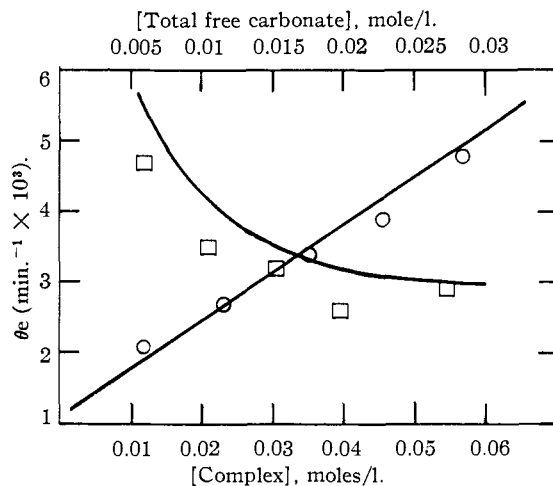


Fig. 1.—Variation of carbonate exchange rate in presence of 0.05  $M$  borate buffer at  $25^\circ$ : O, with change in (complex); (carbonate) = 0.0158  $M$ ,  $pH$  9.15; □, with change in (carbonate); (complex) = 0.0351  $M$ ,  $pH$  9.15.

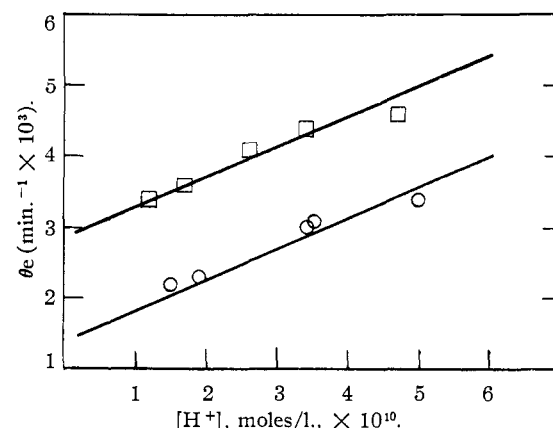


Fig. 2.—Variation of carbonate exchange rate with change in hydrogen ion concentration, no borate buffer added, concentrations of complex and carbonate, 0.0351 and 0.0158  $M$ , respectively: O, at  $25^\circ$ ; □, at  $30^\circ$ .

TABLE I

RATE OF RACEMIZATION REACTION AT  $56.1^\circ$  IN UNBUFFERED SOLUTION WITH ADDED "NEUTRAL" SALT  
(Complex concn. = 0.01  $M$ ,  $pH$  6.5.)

Added salt (0.01 $M$ )	..	..	..	KCl	CsCl	SrCl <sub>2</sub>	NaCl	NaNO <sub>3</sub>	MgCl <sub>2</sub>
$\theta_r$ (min. <sup>-1</sup> × 10 <sup>3</sup> )	1.3 <sup>a</sup>	7.3 <sup>b</sup>	14.5	31.3	22.2	23.3	21.7	21.7	21.7

<sup>a</sup> Run at  $34.6^\circ$ . <sup>b</sup> Run at  $50^\circ$ .

TABLE II

RATE OF RACEMIZATION REACTION AT  $50^\circ$  IN CARBONATE BUFFERED SOLUTION WITH ADDED "NEUTRAL" SALT  
(Concn. of complex, 0.01  $M$ ; of carbonate, 0.0033  $M$ ;  $pH$  9.15.)

Concn. of NaCl (moles/l.)	..	0.0053	0.0233	0.1570	..
$\theta_r$ (min. <sup>-1</sup> × 10 <sup>3</sup> )	2.4	2.4	2.5	2.8	4.7 <sup>a</sup>

<sup>a</sup> Run at  $56.1^\circ$ .

## Discussion

In the case of the tetrammine complex, it has been shown<sup>6</sup> that at exchange equilibrium carbon-

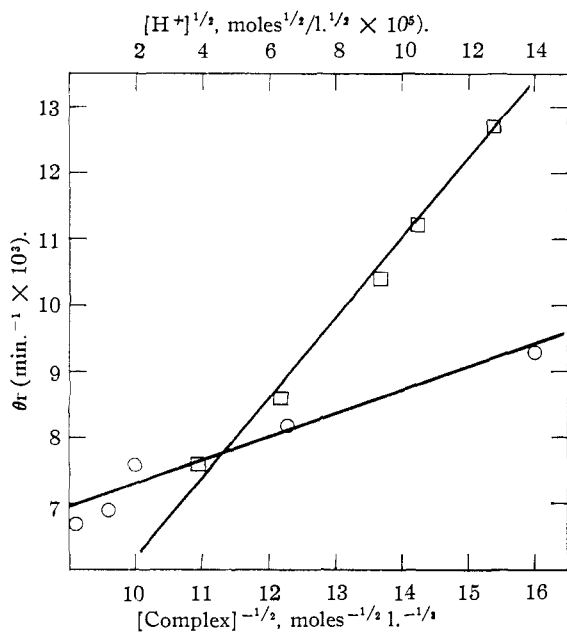


Fig. 3.—Variation of racemization rate in absence of carbonate; borate buffer, 0.0066 *M*: O, with change in (complex); (hydrogen ion) =  $1.3 \times 10^{-9}$  *M*; □, with change in (hydrogen ion); (complex) = 0.0100 *M*.

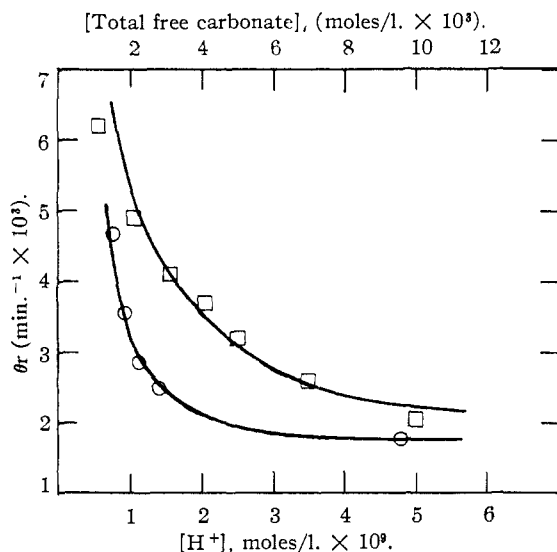


Fig. 4.—Variation of racemization rate in presence of carbonate, concentration of complex, 0.0100 *M*: O, with change in (hydrogen ion); (carbonate) = 0.0033 *M*; no borate; □, with change in (carbonate); (hydrogen ion) =  $1.2 \times 10^{-9}$  *M*; (borate) = 0.05 *M*.

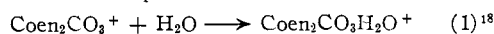
14 concentrates in the free carbonate such that

$$K = \frac{[\text{Co}(\text{NH}_3)_4\text{C}^{14}\text{O}_3^+]}{[\text{Co}(\text{NH}_3)_4\text{CO}_3^+]} \times \frac{[\text{HCO}_3^- + \text{CO}_3^{2-}]}{[\text{HC}^{14}\text{O}_3^- + 2^{14}\text{O}_3^{2-}]} = 0.89$$

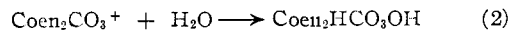
This deviation of *K* from the ideal value of unity was convincingly justified by presuming a modification of the vibrational frequencies of the chelated carbonate group as compared to free carbonate or bi-carbonate ion. It was noted above that, in contrast, the ethylenediamine complex exhibits only a slight isotope effect.<sup>12</sup> Apparently, the car-

bonate group of the latter complex is, in aqueous solution at least, nearly identical in structural properties to free carbonate ion.

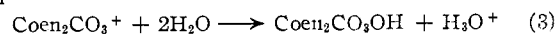
Recent measurements by Stranks<sup>17</sup> have demonstrated that for the pentammine complex ion,  $\text{Co}(\text{NH}_3)_5\text{CO}_3^+$ , there is a zero or negligible isotopic differentiation effect at carbonate exchange equilibrium. It would appear that a non-chelated carbonate group is almost identical structurally to free carbonate. A possible explanation of the behavior of the en complex could, therefore, be the occurrence of a *complete* reaction



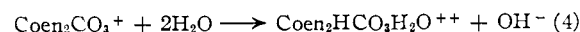
An alternative possibility is the reaction



but the product here differs from that of (1) only in the location of the proton. Since  $\text{OH}^-$  is far more basic than  $\text{CO}_3^{2-}$ , reaction (1) would seem to be the most likely of the two. In either event, the non-chelated carbonate group of the product could be expected to resemble more closely in properties that of  $\text{Co}(\text{NH}_3)_5\text{CO}_3^+$  than the bidentate group in  $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ .<sup>19</sup> Other reactions which the en complex might undergo on being dissolved in water which would produce monodentate carbonate species are

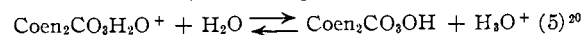


and



These probably do occur to a slight extent but may be excluded from consideration as *complete* reactions since the observed *pH* change when the salt is dissolved is quite small.

A logical explanation of the initial small changes in *pH* and conductance of the en complex solutions can now be given. The proposed carbonate-aquo ion of reaction (1) would probably equilibrate as



In absence of added free carbonate, establishment of this equilibrium would lead to a *pH* decrease and conductance *increase*; in presence of free carbonate, *pH* would still decrease slightly, but conductance would now *decrease* as the mobile hydrogen ions would be largely removed by reaction with  $\text{CO}_3^{2-}$  ions. The fact that the absorption spectrum remains practically unaltered during the *pH* and conductance adjustments no doubt means that the unidirectional aquation reaction (1) takes place very rapidly. Only the spectrum of the mono-aquo product is observed in aqueous medium. The slower subsequent establishment of equilibrium (5) or others of like nature would affect the spectrum but slightly since only a small fractional conversion of the parent ion need occur.

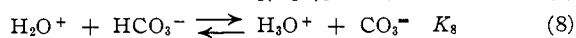
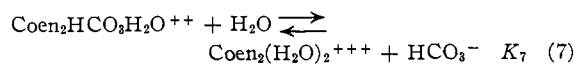
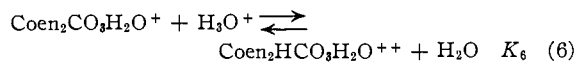
(17) D. R. Stranks, private communication.

(18) An incomplete aquation, leaving some bi-dentate carbonate complex in equilibrium with the mono-aquo species, would not of course offer a satisfactory explanation since isotope effect would be expected for the over-all exchange equilibrium.

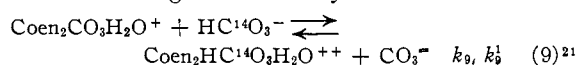
(19) It is not unreasonable that the carbonate group of  $\text{Coen}_2\text{CO}_3^+$  should become monodentate more easily than that of  $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ , since in the former the very stable double chelation by the en groups may introduce a strain into the chelated  $\text{CO}_3$  not present in the tetrammine.

(20) N. F. Hall, *Chem. Revs.*, **19**, 89 (1936).

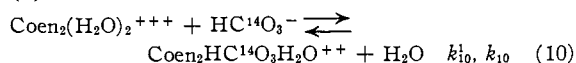
Plots of the carbonate-exchange data (see Figs. 1 and 2) show how the rate of exchange varies with reactant concentration. The variations are similar to those previously reported for the carbonato-tetrammine complex.<sup>4</sup> It therefore appears reasonable to devise a mechanism involving the same two types of reaction as before; (a) direct interchange of free carbonate with complexed carbonate and (b) exchange by means of a di-aquo intermediate. The following *pH*-dependent equilibria are assumed to be continuously maintained



Direct exchange will occur by the reaction



Exchange also results when the aquation product of (7) reacts thus



Isotope effects being negligible, the exchange rate law is

$$R = k_3ab \left( \frac{h}{h + K_8} \right) + k_{10}K_8ah \quad (11) \\ \cong k_3ab + k_{10}K_8ah$$

where *a*, *b* and *h* are molar concentrations of complex, total free carbonate and hydrogen ion, respectively. It follows that<sup>15</sup>

$$\frac{0.693}{t_{1/2}} = 0.693\theta_e = R \left( \frac{a+b}{ab} \right) = \\ k_3(a+b) + k_{10}K_8h \left( \frac{a+b}{b} \right) \quad (12)$$

The solid curves of Fig. 1 were calculated by assigning "best-fit" values of  $1.5 \times 10^{-2}$  and  $7.5 \times 10^5$  l. mole<sup>-1</sup> min.<sup>-1</sup> to *k*<sub>3</sub> and *k*<sub>10</sub>*K*<sub>8</sub>, respectively, and substituting in equation 12. The hydrogen ion concentration variation experiments were done in absence of borate buffer, so are not strictly comparable to the others. A short extrapolation of the experimental data of Fig. 2 shows that, at 25° and the *pH* of the complex and carbonate variation experiments,  $\theta_e = 4.3 \times 10^{-3}$  min.<sup>-1</sup>. The comparable rate in 0.05 *M* borate is  $3.4 \times 10^{-3}$  min.<sup>-1</sup> (see Fig. 1). Presence of borate of this concentration thus appears to reduce the rate by a factor of about 0.8.<sup>22</sup> Assuming this factor as a constant correction over the *pH* range of the experiments, curve A of Fig. 2 was obtained for the data at 25°. Curve B (experiments at 30°) was calculated by

(21) Direct exchange with the bicarbonato-aquo ion formed in (6) or with the hydroxycarbonato ion of (5) need not be considered, since these are minor species, with the  $\text{Coen}_2\text{CO}_3\text{H}_2\text{O}^+$  ion in very large excess. Reactions similar to (9) or (10) involving  $\text{C}^{14}\text{O}_3^{--}$  are also neglected since in the *pH* range of this work  $[\text{H}^+] \gg K_8$ , so  $[\text{HCO}_3^-] \gg [\text{CO}_3^{--}]$  ( $K_8 = 4.4 \times 10^{-11}$ ).

(22) Stranks<sup>5</sup> has studied salt effects on the tetrammine exchange reaction, and observed no retardations and only slight accelerations. However, only "neutral" salts were employed, so specific inhibition by the basic borate ion remains a definite possibility. Non-specific salt effects have not been investigated in the present work, but the ionic strength was always low and only varied slightly from the run to run.

assuming a zero temperature coefficient for the *pH*-dependent part of the exchange, and a coefficient of about 2.0 for the direct exchange. This is consistent with an activation energy  $E_9 = 25$  kcal./mole, while  $E_{10}$  must be approximately equal to but opposite in sign to the heat of reaction 6.

Because of the differences in mechanism, it is difficult to make close comparisons of the rates of exchange of tetrammine and ethylenediamine complexes. The over-all rate under one set of conditions common to both studies showed that the en salt exchanges about 0.8 as rapidly as the tetrammine.<sup>23</sup> The constant  $k_{10}K_8$  of the present work may be directly compared with  $k''$  for the tetrammine.<sup>4</sup> The latter was  $8.5 \times 10^5$  l. mole<sup>-1</sup> min.<sup>-1</sup>, making  $k_{10}K_8/k'' = 0.9$ . Apparently the rate of direct exchange defined by  $k_3$  above is also somewhat slower than the corresponding process with the tetrammine, though  $E_9$  is about the same as the similar constant in the previous work. However, not too much confidence can be placed in the  $E_9$  value due to the narrow range of the temperature variation study in the present research.

It is obvious that the racemization reaction bears little kinetic relationship to the exchange. The latter proceeds at a rate convenient for study at room temperature, while the racemization is very slow. It has been seen that borate slightly inhibits the exchange, while the racemization is accelerated by the same substance in presence of carbonate (see Fig. 4) though not in its absence under otherwise similar conditions.<sup>24</sup> There are other sharp contrasts between the kinetics of racemization in absence and presence of free carbonate as is obvious by comparison of Figs. 3 and 4, and Tables I and II. The addition of carbonate greatly decelerates the process, changes the dependence on  $[\text{H}^+]$ , and eliminates the neutral salt effect.

A reasonable explanation of the facts enumerated can proceed from the following assumptions: that each species of complex ion present at equilibrium in the aqueous solution of the carbonato-bis-(ethylenediamine)-cobalt(III) salt (see reactions 1, 5, 6 and 7 above) racemizes independently of the others; that the concentrations of the product ions in equilibria (5), (6) and (7) is small as compared to that of the parent  $\text{Coen}_2\text{CO}_3\text{H}_2\text{O}^+$  ion; and that the diaquo ion  $\text{Coen}_2(\text{H}_2\text{O})_2^{+++}$  racemizes much more rapidly than any of the others. The total rate of racemization will then be

$$\text{Rate} = k_1 [\text{Coen}_2\text{CO}_3\text{H}_2\text{O}^+] + k_2 [\text{Coen}_2\text{CO}_3\text{OH}] \\ + k_3 [\text{Coen}_2\text{HCO}_3\text{H}_2\text{O}^{++}] + k_4 [\text{Coen}_2(\text{H}_2\text{O})_2^{+++}] \quad (13)$$

where the *k*'s are first-order rate constants of racemization. In the *absence* of added carbonate, the concentration of diaquo ion will be at a maximum, and nearly all racemization will proceed through this species. The rate law thus becomes

$$\theta_r = \frac{1}{t_{1/2}} = 1.61k_4 \left( \frac{K_6K_7h}{a} \right)^{1/2} \quad (14)$$

(23) At 25°, with concentrations of complex, carbonate, and  $\text{H}^+$  given by 0.0575, 0.0147 and  $3.4 \times 10^{-10}$  *M*, respectively,  $\theta_e$  in the present work was  $4.0 \times 10^{-3}$  min.<sup>-1</sup>. A run with the tetrammine under identical conditions<sup>4</sup> gave  $\theta_e = 5.0 \times 10^{-3}$  min.<sup>-1</sup>.

(24) At 56.1°, with  $[\text{complex}] = 0.01$  *M*,  $[\text{H}^+] = 1.4 \times 10^{-9}$  *M*, and no carbonate, the value of  $\theta_r$  was constant at  $7.6 \times 10^{-3}$  min.<sup>-1</sup> with borate concentrations of 0.0017, 0.0033 and 0.0066 *M*, respectively.

The curves of Fig. 3 show how well the requirements of equation 14 are fitted by the experimental data. In the presence of added carbonate, all terms of equation 13 contribute due to the suppression of the diaquo intermediate, and the rate law is

$$\theta_r = \frac{1}{t_{1/2}} = 1.44(k_1 + k_2K_5/h + k_3K_6h + k_4K_6K_7h/b)$$

The lack of dependence of the rate on complex concentration in presence of carbonate was confirmed by experiment.<sup>25</sup> Figure 4 demonstrates the inverse proportionality to free carbonate, the empirically fitted heavy curve being of the form  $\theta_r = 7.9 \times 10^{-3}/b + 1.5 \times 10^{-3}$ . The variation of  $\theta_r$  with  $(H^+)$  is complex, but the curve drawn in Fig. 4 to fit the experimental data indicates that at low  $(H^+)$  the species  $Coen_2CO_3OH$  must contribute considerably to the racemization, since this is the only one which varies inversely as  $(H^+)$ .

The temperature dependence of the racemization was not adequately studied in this work. However, the data of Table I indicate an activation energy of about 23 kcal./mole in absence of carbonate, with

(25) At 56.1°, with [carbonate] = 0.004 M,  $[H^+] = 1.2 \times 10^{-9}$  M and [borate] = 0.05 M,  $\theta_r$  was 3.8, 3.7, 3.7 and  $3.6 \times 10^{-3}$  min.<sup>-1</sup> for [complex] 0.0036, 0.0067, 0.0100 and 0.0127 M, respectively.

a similar value in presence of carbonate suggested by the data of Table II. Due to the complexity of the racemization kinetics it is impossible to relate these activation energies to any specific rate constants with the data as they stand.

The exact mechanism of racemization cannot be stated unequivocally, but it clearly does not parallel the ligand exchange process. An intramolecular rearrangement must be involved, along the lines of proposals often made in this regard.<sup>16</sup> It is of interest that it is only at low pH, that is when most of the racemization is occurring through the diaquo ion, that neutral salt addition has any pronounced influence (compare Tables I and II). This is seemingly almost independent of the type of salt used. Probably for  $Coen_2(H_2O)_2^{+++}$ , reagents which tend to compete with the complex ion for water of solvation considerably accelerate its inversion. Further investigation of this point would be of considerable interest.

Financial assistance through Contract No. AT-(30-1)-1578 between the University of Buffalo and the U.S.A.E.C., which facilitated completion of this study, is gratefully acknowledged.

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## The Effect of X-Rays on Solutions which Contain Formic Acid and Ceric Ion

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RECEIVED JUNE 14, 1954

If ceric sulfate and formic acid are dissolved in 2.8 N sulfuric acid, they do not react appreciably under ordinary conditions. If such a solution is exposed to the radiation from an X-ray tube operated at 50 kv. and 45 ma., reaction occurs at a readily measurable rate. The principal products are cerous ion, carbon dioxide, hydrogen and oxygen. In the experiments reported in this paper it was found that these products alone sufficed to give a material balance within 10% except at high formic acid concentrations. Under the latter conditions some deviations were found which are believed to be caused by the formation of formaldehyde, although the amount of that substance formed was never enough to obtain a positive test. The effects of varying the concentrations of formic acid and of ceric ion and of adding oxygen have been studied. A mechanism has been formulated which gives a quantitative description of the experimental facts. On the basis of this mechanism the yield of radicals from the action of the radiation on water can be estimated. The yield calculated from these experiments has been compared with one calculated from some similar experiments on ferrous sulfate solutions, assuming the validity of Hart's mechanism, and the agreement found to be good.

In the study of the effects of ionizing radiations on dilute aqueous solutions it is generally assumed that the primary action of the radiation is to produce hydroxyl radicals and hydrogen atoms. The other reactions which occur are the result of reactions of these substances (or substances derived from them) with the solutes present. Normally the hydrogen atoms act as reducing agents and the hydroxyls as oxidizing agents although the latter may act as a reducing agent through some mechanism such as the formation of hydrogen peroxide. It follows that usually a solute will react with only one of the radicals. In the work described in this paper we have attempted to get clear cut reactions with both radicals by introducing two solutes, one being an oxidizing agent and the other being primarily reducing in character.<sup>1</sup>

The system selected for study is a solution of ceric sulfate and formic acid in 1.4 M sulfuric acid. In

the absence of ionizing radiations there is no appreciable reaction in this solution even if it is kept for several weeks. However, if the solution is treated with X-rays from a 50 kv. tube reaction occurs with the formation of cerous ion, carbon dioxide, hydrogen and oxygen. No other products were found in detectable amounts although there was some reason to believe that a small amount of formaldehyde might have been formed in some of the experiments.

### Experimental Details

**Materials.**—The water used in all irradiations was twice distilled, first from a tin still and then from an alkaline permanganate solution in a Pyrex still. J. T. Baker 90.5% C.P. analyzed formic acid, G. F. Smith reagent grade ceric hydroxide, Baker and Adamson 95–96% C.P. sulfuric acid, and Mallinckrodt analytical grade ferrous sulfate were used without further purification.

**Solutions.**—Enough ceric hydroxide to make an approximately 0.2 molar stock ceric solution was dissolved in an appropriate amount of concentrated acid to make the final solution 1.4 molar sulfuric acid after dilution with twice

(1) Cf. W. M. Garrison and G. K. Rollefson, *Discs. Faraday Soc.*, **12**, 155 (1952).