in total volume due to the drop in mercury level in the capillary is negligible) the results might not be too reliable due to the increased solubility of nitrogen with increasing pressure. Figure 4 shows the first-order plot for the process, log $[P_\infty/(P_\infty - P_t)]$ *versus* time yielding a straight line. The induction period and the scatter of points in this region probably can be explained by considering the time required to build up nitrogen saturation in the system and possible thermal equilibration effects. The value of k_d at 30.5° was calculated to be 1.31×10^{-7} and is included in Fig. 1.

Using all the available data for the decomposition of Azo I in solution the equation which best fits the experimental results is: $k_d = 1.58 \times 10^{15}$ exp$(-30.8$ kcal.$/RT)$.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Kinetics of the Exchange Reaction between Carbon-14-labeled Carbonate and Carbonato-bis-(trimethylenediamine)–Cobalt(III) Complex in Aqueous Solution. Effect of Steric Hindrance in a Ligand Substitution Process

BY JAMES E. BOYLE[1] AND G. M. HARRIS

RECEIVED AUGUST 29, 1957

The study of carbonate ligand exchange reactions of the carbonato-diamine–cobalt(III) series of complex ions has been extended to the bis-trimethylenediamine (tn_2) analog. The effects of changes in reactant concentration, *p*H and temperature have been determined. Comparisons are made between the behavior of the tn_2 complex and those previously investigated; *viz.*, the pentammine (N_5), tetrammine (N_4) and bis-ethylenediamine (en_2) types. The rates and mechanisms of the reactions which promote carbonate exchange are very similar for N_4 and en_2, but large variations from these are observed for the N_5 and tn_2 forms. The N_5 behavior can be reasonably attributed to hydrogen-bonding factors; for the tn_2, steric hindrance appears to play the predominant role.

Previous publications in this series have reported on the nature of the exchange reaction in aqueous solution between free (uncomplexed) carbonate ion and the corresponding ligand group in a number of carbonato–cobalt(III) complex ions. Included have been the tetrammine (N_4),[2a,b] the pentammine (N_5)[3] and the bis-ethylenediamine (en_2)[4] analogs. The mechanisms of the exchanges conform to a definite pattern of similarity, but some differences do occur both in the relative rates of the reactions and in details of the mechanisms. The present paper reports an extension of these studies to the bis-trimethylenediamine (tn_2) complex, which differs from the en_2 compound only in the insertion of one more CH_2 group in each of the diamine–cobalt chelate rings. Evidence accrues from this study concerning the effect of stereochemical factors on the rate and mechanism of the ligand replacement reaction.

Experimental

Preparation, Purification and Analysis of Materials.—Carbonato-bis-(ethylenediamine)-cobalt(III) chloride was prepared as described previously.[4] The corresponding tn_2 salt was prepared by an extension of the procedure of Bailar and Work.[5,6] $(Cotn_2Cl_2)Cl$ was first obtained, then aquated by allowing it to stand in dilute aqueous solution at room temperature for 45 minutes. Excess of Ag_2CO_3 was dispersed in the solution and kept in suspension by rapid stirring for three hours. The mixture was filtered and the filtrate retreated with silver carbonate for one hour and refiltered. Slight excess of $BaCl_2$ was added to the bright red filtrate containing $(Cotn_2CO_3)_2CO_3$. After standing overnight, the $BaCO_3$ was filtered off, and the filtrate evaporated to dryness in the open air at 70°, causing precipitation of the excess $BaCl_2$ as $BaCO_3$. The cobaltic complex was extracted from the residue with water, recrystallized twice from water, and air-dried at room temperature.

The purified dry solid $(Cotn_2CO_3)Cl \cdot H_2O$ remained completely stable at room temperature indefintely. Its complete analysis was carried out as follows: water of crystallization was determined by drying in air at 110°, cobalt by the method of Hillebrand,[7] and by direct ignition of the complex to Co_3O_4 at 700°, carbonate by a modification of the Fresenius vacuum baryta method,[8] chloride by standard gravimetric procedure,[9] and nitrogen by a modified Kjeldahl method.[10]

Anal. Calcd.: H_2O, 5.62; Co, 18.38; CO_3, 18.71; Cl, 11.06; N, 17.47. Found: H_2O, 5.75; Co, 18.26; CO_3, 18.73; Cl, 11.11; N, 17.54.

Carbon-14-labeled sodium carbonate was prepared by reaction of barium carbonate-C-14 with lead chloride and subsequent absorption of the active dioxide in carbonate-free sodium hydroxide.[11]

Apparatus and Technique.—The kinetic runs were made in a manner very similar to that of the previous studies.[2-4] A typical run was commenced by mixing rapidly a weighed portion of the anhydrous complex salt, 15.00 ml. of 0.0834 *M* sodium borate, 1.00 ml. of 0.3153 *M* inactive sodium carbonate, 7.00 ml. of CO_2-free water, and after temperature equilibrium was established, 2.00 ml. of 0.0321 *M* active sodium carbonate. A zero-time sample was removed and the free carbonate precipitated within 90 seconds. Subsequent samples were withdrawn at convenient time intervals, a stream of CO_2-free nitrogen being passed through the reaction flask during sampling. Assay was effected by end-window counting of the uniformly-spread $BaCO_3$ samples in nickel-plated planchets.

Half-times of exchange were obtained from the conventional log $(1 - f)$ *vs.* time plots,[12] using least-squares analy-

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(1) Work done as part of Ph.D. requirement of the University of Buffalo, 1956. Complete report available from University Microfilms, Ann Arbor, Michigan.

(2) (a) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952); (b) D. R. Stranks, *ibid.*, **48**, 911 (1952).

(3) D. R. Stranks, *ibid.*, **51**, 505 (1955).

(4) J. S. Holden and G. M. Harris, THIS JOURNAL, **77**, 1934 (1955).

(5) J. C. Bailar and J. B. Work, *ibid.*, **68**, 232 (1946).

(6) Experimental quantities of trimethylenediamine were obtained as a gift from the American Cyanamid Company.

(7) W. F. Hillebrand, *et al.*, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, New York, N. Y., 1953, p. 418.

(8) W. J. Johnson, *Roy. Aust. Chem. Inst. J. Proc.*, **17**, 327 (1950).

(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 307.

(10) A. Eisner and E. C. Wagner, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 473 (1934).

(11) N. Zwiebel, J. Turkevich and W. Miller, THIS JOURNAL, **71**, 376 (1949).

(12) Friedlander and Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 318.

TABLE I

DATA OF RUN NO. 6

Temperature = 50.5° (carbonate) = 0.01518 M
pH 9.50 (complex) = 0.03505 M
Half-time = 156 min. (borate) = 0.05 M

Time, min.	Wt. of $BaCO_3$, mg.	Spec. activity (A_t), cts./min./mg.	$(1 - f)$
0	4.94	785	1.000
60	4.21	675	0.790
120	4.73	570	.589
180	4.86	507	.468
240	4.72	440	.340
300	4.15	400	.264
350	4.75	375	.218
∞	4.19	262	.000

sis of the data to achieve best fit. The fraction of reaction is $f = (A_0 - A_t)/(A_0 - A_\infty)$, where the A's are specific activities at $t = 0$, $t = t$ and $t = \infty$, respectively. The final activity A_∞ was determined experimentally by allowing exchange to proceed for a minimum of 8 half-times. Data of a typical run are presented in Table I. pH measurements were made on a Beckman Model G pH-Meter, and were corrected for sodium ion concentration[13] and temperature.[14]

Results

A. Reinvestigation of the pH-Dependence of the Exchange of Carbonate Ion with $Coen_2CO_3^+$ Ion.—Holden and Harris[4] studied the pH-dependence of the $Coen_2CO_3^+$/carbonate exchange in absence of borate buffer. It appeared from other data that use of the buffer might have introduced a negative catalytic effect, but no test of the premise was made. It was considered worthwhile to repeat their pH-dependence study in presence of 0.05 M borate. Figure 1 records the results obtained and compares them with the earlier work. It is apparent that the buffer has no significant influence on the exchange rate. The 0.8 inhibition factor surmised by Holden and Harris is therefore spurious, and can in fact be abolished by a minor re-interpretation of the data (see Discussion).

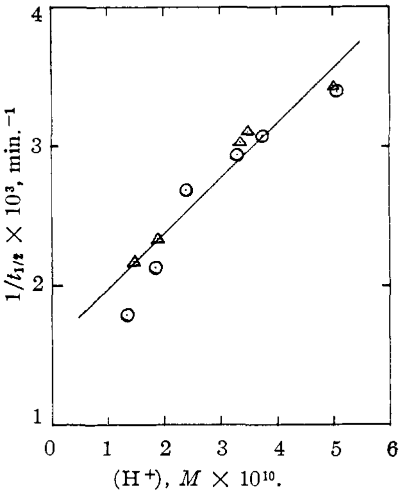

Fig. 1.—Variation of exchange half-time of en_2 complex with concentration of H$^+$: ○, present investigation, (borate) = 0.05 M; △, Holden and Harris, no borate; (complex) = 3.51 × 10^{-2} M; (carbonate) = 1.52 × 10^{-2} M; temperature, 25.00°.

B. Stability of Aqueous Solutions of Co tn_2CO_3-Cl.—Solutions of this tn_2 salt were found to be unaffected by heating at 50° for as long as three days in the presence of $BaCl_2$, NH_4OH, or both. Its absorption spectrum remained constant,[15] as did its pH and electrical conductivity. It is clear that not even the minor changes observed with the en_2 analog[4] take place here.

C. Kinetics of the Exchange Reaction.—A series of runs was made in which concentrations of the carbonato complex (a), total free carbonate (b), and hydrogen ion (h) were varied. In each run, pH control was achieved by a suitably adjusted 0.05 M sodium borate–boric acid buffer.[16] The half-times were determined as described above, and the various rates of exchange calculated according to the standard relation[12,17] $R = \ln 2/t_{1/2} \times ab/(a + b)$. The results so obtained are presented in Fig. 2. Some experiments were performed in which

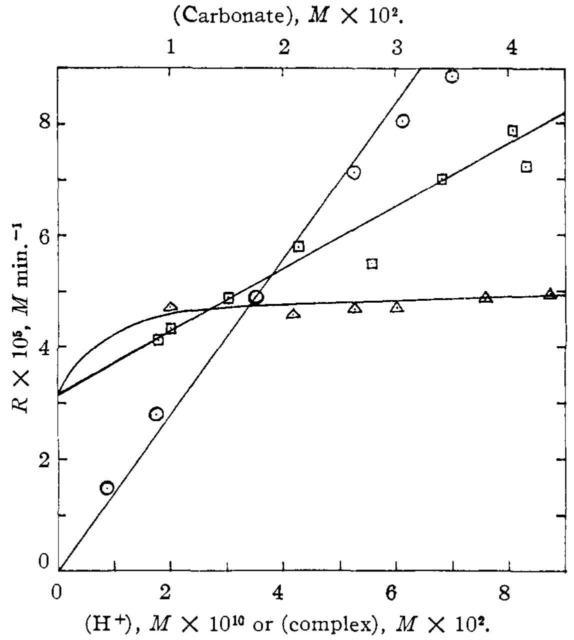

Fig. 2.—Variation of exchange rate of tn_2 complex with reactant concentration: △, (H$^+$) variable; (complex) = 3.51 × 10^{-2} M; (carbonate) = 1.52 × 10^{-2} M; ○, (complex) variable; (H$^+$) = 7.59 × 10^{-10} M; (carbonate) = 1.52 × 10^{-2} M; □, (carbonate) variable; (H$^+$) = 7.59 × 10^{-10}; (complex) = 3.51 × 10^{-2} M; (borate buffer) = 0.05 M; temperature, 50.5° in all cases.

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(13) H. F. Walton, "Principles and Methods of Chemical Analysis," McGraw-Hill Book Co., New York, N. Y., 1951.

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

(15) The spectrum was determined between 3000 and 6500 Å. on a Beckman D.U. spectrophotometer. Two peaks are observed, which compare with those for the en_2 complex as follows: ($E = (\log I_0/I)/Cl$ = molar extinction coefficient): en_2: 5200, E = 127.4; 3600, E = 119.8; tn_2: 5200, E = 108.5; 3600, E = 127.7.

(16) Several runs were made in which all factors remained constant except the borate concentration, and no rate differences were observed showing that borate has no influence on the exchange in the concentration used. Likewise duplicate control experiments in light and dark or in glass-bead-packed and unpacked vessels ruled out possible photochemical or surface effects.

(17) This relation ignores isotope effects. The equilibrium isotope effect in the tn_2 system is about 7% (see forthcoming publication), and only very small errors in the rate constant values will be introduced by neglecting it (see G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951)).

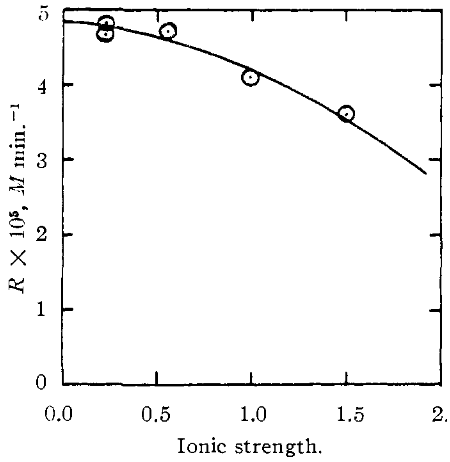

Fig. 3.—Variation of exchange rate of complex with ionic strength: (Complex) = 3.51×10^{-2} M; (carbonate) = 1.52×10^{-2} M; (borate) = 0.05 M; pH 9.12; temperature, 50.5°.

the ionic strength was varied over a wide range by addition of sodium chloride, as shown in Fig. 3. The temperature dependence of the exchange was studied under three different sets of concentration conditions, and the results were analyzed by means of the usual Arrhenius plots (see Fig. 4). The activation energies were identical in all three cases, 24.8 ± 0.9 kcal./mole.

Discussion

Figure 2 indicates that the tn_2 complex exchange reaction is essentially independent of pH. It is first-order in complex concentration and appears to be part zero-order and part first-order in total free carbonate concentration ($HCO_3^- + CO_3^=$). A mechanism which satisfies these conditions and develops logically from the concepts deduced in the previous studies of the series[1-4] is ($L = tn_2$)

$$CoLCO_3^+ + H_2O \rightleftharpoons CoLCO_3 \cdot H_2O^+ \quad (1)$$

$$CoLCO_3 \cdot H_2O^+ + HC^*O_3^- \rightleftharpoons CoLC^*O_3 \cdot H_2O^+ + HCO_3^- \quad (2)$$

$$CoLCO_3 \cdot H_2O^+ + H_2O \rightleftharpoons CoL(H_2O)_2^{+++} + CO_3^= \quad (3)$$

$$CoL(H_2O)_2^{+++} + C^*O_3^= \rightleftharpoons CoLC^*O_3 \cdot H_2O^+ + H_2O \quad (3')$$

$$CoLC^*O_3 \cdot H_2O \rightleftharpoons CoLCO_3^+ + H_2O \quad (1')$$

The rate law corresponding to this mechanism is[17]

$$R = \frac{k_2K_1(H_2O)}{K_1(H_2O) + 1}\, ab \left(\frac{h}{h + K_4}\right) + \frac{k_3K_1(H_2O)^2}{K_1(H_2O) + 1}\, a \quad (A)$$

In this, the small k's are forward-reaction rate constants and the large K's equilibrium constants. K_4 refers to the reaction

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \quad (4)$$

Using "best-fit" values of

$$k' = \frac{k_2K_1(H_2O)}{K_1(H_2O) + 1} = 3.5 \times 10^{-2} \text{ l.mole}^{-1} \text{ min}^{-1}$$

and

$$k'' = \frac{k_3K_1(H_2O)^2}{K_1(H_2O) + 1} = 9.0 \times 10^{-4} \text{ min.}^{-1}$$

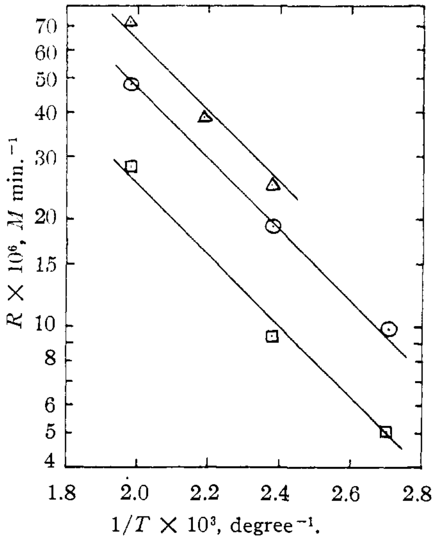

Fig. 4.—Temperature dependence of the exchange: □, Series 1 (complex) = 1.75×10^{-2} M; (carbonate) = 1.52×10^{-2} M; ○, Series 2 (complex) = 3.51×10^{-2} M; (carbonate) = 1.52×10^{-2} M; △, Series 3 (complex) = 3.51×10^{-2} M; (carbonate) = 4.16×10^{-2} M; (borate) = 0.05 M; (H^+) = 7.59×10^{-10} M in all series.

respectively, the curves of Fig. 2 have been plotted. Excellent agreement with the experimental points is seen to be obtained.[18]

The variation of R with ionic strength is slight (Fig. 3), a small decrease occurring at high μ-values. Under the conditions of the study, about $^1/_3$ of R is contributed by the second-order ion–ion reaction, and $^2/_3$ by the first-order aquation. This corresponds closely to the situation discussed in detail previously for the CoN_4CO^{3+} species,[2b] and the tn_2 results may be dealt with similarly.

It remains to compare the carbonate exchange behavior of the four analogous carbonato-cobalt-(III) salts for which data are now at hand. The relevant experimental results appear in Table IIA.

TABLE IIA

SUMMARY OF EXPERIMENTAL RATE DATA

Complex	k', l. mole^{-1} min.$^{-1}$	k'', l. mole^{-1} min.$^{-1}$	Temp., °C.	E', cal./deg./mole	E'', cal./deg./mole	Ref.
N_5	8.7×10^{6a}	7.8×10^5	0	15.8	19.9	3
N_4	1.3×10^{-2}	9.0×10^5	20.3	16.7	20.6	2a
en_2	1.6×10^{-2}	6.0×10^5	25	..[b]	..[b]	4
tn_2	3.5×10^{-2}	9.0×10^{-4c}	50.5	24.8	24.8	Present work

[a] Includes equil. const. K_5. Units are l.^{2} mole^{-2} min.$^{-1}$ for this k'. [b] Not adequately studied for this compound. [c] Does not include K_5. Units are min.$^{-1}$ for this k''.

TABLE IIB

RATE DATA RECALCULATED TO 25°

Complex	k'	k''	k_6[a]
N_5	1.0×10^8	9.3×10^6	0.07
N_4	0.021	1.7×10^6	.2
en_2	.016	6.0×10^5	.7
tn_2	.0012	3.3×10^{-5}	..

[a] See text below.

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[18] Since $K_4 = 6.7 \times 10^{-11}$ at 50° (Harned and Scholes, This Journal, **63**, 1706 (1941)), $h/(h + K_4)$ is nearly constant in the pH range of the study. Hence the near independence of pH of the rates of exchange observed.

Table IIB shows the same data computed to the common temperature 25°, utilizing the known activation energy information.

The results for the tetrammine have been recalculated on the basis of the mechanism suggested for the $\mathrm{en_2}$ complex,[4] which consists of reactions 1, 2 and 1′ above (L = $\mathrm{N_4}$ or $\mathrm{en_2}$), together with

$$\mathrm{CoLCO_3{\cdot}H_2O^+ + H^+ \rightleftarrows CoLHCO_3{\cdot}H_2O^{++}} \qquad (5)$$

$$\mathrm{CoLHCO_3{\cdot}H_2O^{++} + H_2O \rightleftarrows CoL(H_2O)_2{}^{+++} + HCO_3{}^-} \qquad (6)$$

$$\mathrm{CoL(H_2O)_2{}^{+++} + HC^*O_3{}^- \rightleftarrows CoLHC^*O_3{\cdot}H_2O^{++} + H_2O} \qquad (6')$$

$$\mathrm{CoLHC^*O_3{\cdot}H_2O^{++} \rightleftarrows CoLC^*O_3{\cdot}H_2O^+ + H^+} \qquad (5')$$

The corresponding rate law is

$$R = \frac{k_2K_1(\mathrm{H_2O})}{K_1(\mathrm{H_2O}) + 1}\,ab\left(\frac{h}{h + K_4}\right) + \frac{k_6K_5K_1(\mathrm{H_2O})^2}{K_1(\mathrm{H_2O}) + 1}\,ah \qquad (\mathrm{B})$$

so that for $\mathrm{N_4}$ and $\mathrm{en_2}$, k' is the same as for $\mathrm{tn_2}$ and $k'' = k_6K_5K_1(\mathrm{H_2O})/(K_1(\mathrm{H_2O}) + 1)$. This law not only fits the $\mathrm{N_4}$ data much better than that originally proposed,[2a] but also eliminates the unexplained arbitrary intercept found necessary to make the older expression conform to the *p*H dependence data. For the $\mathrm{en_2}$ complex, k' and k'' have been altered slightly from those given in the earlier publication[4] in order to fit the *p*H variation data more satisfactorily, while eradicating the spurious 0.8 borate inhibition factor mentioned above (see Experimental). The mechanism for the pentammine[3] consists of reactions 5, 5′, 6 and 6′ (reading $\mathrm{N_5}$ for $\mathrm{L{\cdot}H_2O}$), together with

$$\mathrm{CoN_5HCO_3{}^{++} + HC^*O_3{}^- \rightleftarrows CoN_5HC^*O_3{}^{++} + HCO^{3-}} \qquad (7)$$

The rate law is

$$R = k_7K_5hab\left(\frac{h}{h + K_4}\right) + k_6K_5(\mathrm{H_2O})ah \qquad (\mathrm{c})$$

so that for $\mathrm{N_5}$, $k' = k_7K_5$ and $k'' = k_6K_5(\mathrm{H_2O})$.

Of the various values for k', the "direct" exchange rate constants given in Table IIB, only those for the $\mathrm{N_4}$, $\mathrm{en_2}$ and $\mathrm{tn_2}$ compounds are strictly comparable. For the first two, the values differ but little, as would be expected, since in going from $\mathrm{N_4}$ to $\mathrm{en_2}$, one merely replaces ammonia by $\mathrm{NH_2R}$ (neglecting chelation effects). However, the value for $\mathrm{tn_2}$ is anomalously low, since $\mathrm{tn_2}$ differs little from $\mathrm{en_2}$ in their most significant chemical properties.[19] The only possible explanation must be a steric hindrance which can reduce the magnitudes of k_2 or K_1 or both, in the case of $\mathrm{tn_2}$. There is evidence, based on the lack of an equilibrium isotope effect, that K_1 is large for the $\mathrm{en_2}$ compound,[4] and this probably is also true for $\mathrm{N_4}$.[20] A much smaller K_1 for the $\mathrm{tn_2}$ complex would justify the observations, and comparison of molecular models of the $\mathrm{en_2}$ and $\mathrm{tn_2}$ forms does in fact support a spacial interpretation, since it is sterically much more difficult to carry out reaction 1 with the $\mathrm{tn_2}$ than with the $\mathrm{en_2}$ compound.

One must explain the large discrepancy in the $\mathrm{N_5}$ behavior as regards "direct" exchange. This has been attempted previously in terms of ligand electronegativity variations.[3] A more reliable approach now appears to be to consider hydrogen-bonding factors. In the $\mathrm{N_5}$ compound, only $\mathrm{NH_3}$ groups are *cis* to the $\mathrm{CO_3}$, while the exchanging species in aqueous solutions of the $\mathrm{N_4}$, $\mathrm{en_2}$ and $\mathrm{tn_2}$ forms have $\mathrm{H_2O}$ *cis* to $\mathrm{CO_3}$. It is well known that the O–H . . . . O hydrogen bond is much stronger than N–H . . . . O.[21] Hence the $\mathrm{CO_3}$ group in $\mathrm{CoLCO_3{\cdot}H_2O^+}$ (L = $\mathrm{N_4}$, $\mathrm{en_2}$, $\mathrm{tn_2}$) retains considerable bidentate character and has a rather smaller tendency to accept a further proton than does the $\mathrm{N_5}$ type. The latter readily becomes protonated,[22] and it is the bicarbonato form that undergoes rapid "direct" exchange,[23] accounting for the *p*H dependence of this process, in which it contrasts with the $\mathrm{N_4}$, $\mathrm{en_2}$ and $\mathrm{tn_2}$ complexes.

Turning now to the k'' values, the rate constants for the "aquation" mechanism of exchange, only those for $\mathrm{N_5}$, $\mathrm{N_4}$ and $\mathrm{en_2}$ are comparable ($k'' = k_6{\cdot}K_5(\mathrm{H_2O})$).[24] The k_6's should be in the approximate ratio 1:3:10 for $\mathrm{N_5}$, $\mathrm{N_4}$ and $\mathrm{en_2}$, respectively.[25] Since K_5 for $\mathrm{N_5}$ is 2.5×10^6 at 25°,[22] the various k_6's are as given in Table IIB, corresponding to K_5 values of 1.7×10^5 and 1.5×10^4 for $\mathrm{N_4}$ and $\mathrm{en_2}$, respectively. The $\mathrm{tn_2}$ reaction is not only much slower but proceeds by a *p*H-independent mechanism. Again, a steric explanation is reasonable—the models show that hydrogen bonding is so favored in the compound $\mathrm{Cotn_3CO_3{\cdot}H_2O^+}$ that reaction 5 has a much smaller tendency to occur than it has for $\mathrm{en_2}$ and K_5 is in consequence smaller by perhaps a few more orders of magnitude. The main path for aquation of the $\mathrm{tn_2}$ complex is thus by direct replacement of water for $\mathrm{CO_3{}^=}$, according to reaction 3. The latter reaction is also sterically difficult, thereby contributing, along with the small K_1, to the smallness of k''.

Finally, the activation energy data, though incomplete, offer some further support of the arguments advanced above. For $\mathrm{N_5}$, $E' = E_7 + \Delta H_5$. The temperature coefficient of reaction 5 for $\mathrm{N_5}$ suggests $\Delta H_5 \sim -10$ kcal./mole.[22] Thus, $E_7 \cong 26$ kcal./mole, somewhat higher than E_2 for $\mathrm{N_4}$ (17

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[19] For example, their basicities (G. Bredig, *Z. physik. Chem.*, **13**, 309 (1894)).

[20] An equilibrium isotope effect has been observed for the tetrammine (D. R. Stranks and G. M. Harris, *J. Phys. Chem.*, **56**, 906 (1952)) though this has been questioned (E. Saito and B. Lazard, *J. Inorg. Nuclear Chem.*, **1**, 218 (1955)). In any case, reaction 1 need not be *complete* for $\mathrm{N_4}$—with K_1 only of the order of unity, $K_1(\mathrm{H_2O})/K_1(\mathrm{H_2O}) + 1 \cong 1$.

[21] C. A. Coulson, *Research*, **10**, 149 (1957).

[22] A. B. Lamb and K. Mysels, THIS JOURNAL, **67**, 468 (1945), report $K_5 = 2.5 \times 10^6$ at 25° for $\mathrm{N_5}$.

[23] Using Lamb and Mysels' K_5 value, it is seen that $k_7 = 40$ l. mole^{-1} min.$^{-1}$, about 200 times as great as k_2 for the $\mathrm{N_4}$ species.

[24] Assuming K_1 at least as great as the order of unity (see ref. 20) for $\mathrm{N_4}$ and $\mathrm{en_2}$.

[25] The following rate constants of aquation have been observed for chloro-cobaltic complexes: $\mathrm{Co(NH_3)_4Cl{\cdot}H_2O^{++}}$ – $k = 1.3 \times 10^{-4}$ min.$^{-1}$ at 20° (J. N. Brönsted, *Z. physik. Chem.*, **122**, 383 (1926)); $\mathrm{Co\ en_2\ Cl{\cdot}H_2O^{++}}$ – $k = 2.0 \times 10^{-3}$ min.$^{-1}$ at 30° (data of J. P. Mathieu, *Bull. soc. chim.*, [5] **3**, 2121 (1936), re-interpreted in the manner of Brönsted, above); $\mathrm{Co(NH_3)_5Cl^{++}}$ – $k = 4.0 \times 10^{-4}$ min.$^{-1}$ at 35° (R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955)). Brönsted's temperature dependence study for the corresponding nitrato salt (*ibid.*) indicates $E_{\mathrm{act}} \sim 25$ kcal./mole for this type of reaction. Thus, it can be estimated that at 25° the k values are roughly in the ratio 1:3:10 for the $\mathrm{N_5}$, $\mathrm{N_4}$ and $\mathrm{en_2}$ types of chloro–cobaltic ions, and one would expect a similar ratio for the bicarbonato salts of reaction 6.

kcal./mole). However, reaction 2 is rather more complicated than (7), since it involves both carbonate replacement and H^+ transfer, precluding direct comparisons between them. $E'' = E_6 + \Delta H_5$ for both N_4 and N_5, making $E_6 \sim 30$ kcal./mole for both ammines, in acceptable agreement with Brönsted's data for the corresponding reaction of the nitrato salt.[25] For tn_2, E' lies between E_2 and $E_2 + \Delta H_1$, depending on how small K_1 is. Similarly, E'' lies between E_3 and $E_3 + \Delta H_1$ for tn_2. ΔH_1 is not known but is probably quite small, so that $E_2 \cong E_3 \cong 25$ kcal./mole in this case.

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BUFFALO, N. Y.

[CONTRIBUTION NO. 1463 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Investigation of the Catalytic Mechanism of Catalase and Other Ferric Compounds with Doubly O^{18}-labeled Hydrogen Peroxide

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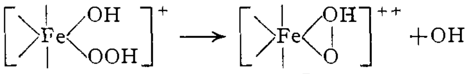
A method for determining the origin of molecular oxygen in the catalytic decomposition of hydrogen peroxide is developed and applied to the catalytic decomposition of hydrogen peroxide by catalase, polyamine–Fe(III) chelates and ferric hydroxide. In all cases studied, the oxygen molecule originates from the intact O–O bond in hydrogen peroxide.

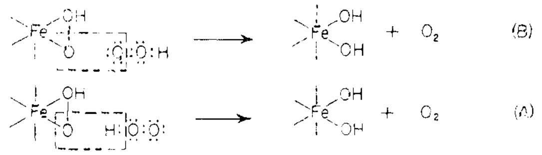
One method of approach to the study of catalysis is *via* the synthesis and investigation of relatively simple model molecules of known structure. By this means Wang[2] discovered the remarkably high catalytic efficiency of triethylenetetramine-Fe(III) chelate for the decomposition of hydrogen peroxide. The postulated mechanism of catalysis involves the metathetical displacement of a bound OH^- by OOH^-, followed by the displacement of another bound OH^- by the second oxygen atom of the same OOH^- as illustrated below.



I II

Since the O–O bond in compound II is under strain, it becomes more reactive and reacts subsequently with a second OOH^- to produce O_2 and regenerate the catalyst.

There are two alternative mechanisms for this last reaction step to take place. These are depicted below as mechanisms (A) and (B), respectively.



It is of particular interest to find out whether the catalytic decomposition of hydrogen peroxide by triethylenetetramine–Fe(III) chelate takes place through mechanism (A) or (B).

In general even for cases in which the detailed mechanism is unknown, it is still of interest to know whether the two O-atoms in each O_2 liberated came from the same H_2O_2 molecule or from two separate H_2O_2 molecules.

Principle of the Method

Suppose O^{18}-enriched hydrogen peroxide is made directly by an electric discharge through O^{18}-enriched water vapor. If the isotopic atom-fraction of O^{18} in the resulting H_2O_2 is X, the mole-fraction of $HO^{18}O^{18}H$ should be approximately equal to X^2. (Here it is assumed that the isotope-effect due to the difference in zero point energies of light and heavy O-atoms in H_2O_2 is negligible.) When this H_2O_2 is catalytically decomposed, the mole-fraction of $O^{18}O^{18}$ in the oxygen gas liberated should also be X^2 no matter whether the decomposition takes place through mechanism (A) or mechanism (B), because the isotopic distribution in this H_2O_2 is in accordance with natural probabilities. However, when each mole of this O^{18}-enriched hydrogen peroxide is mixed with q moles of ordinary hydrogen peroxide, the isotopic atom-fraction of O^{18} and the mole-fraction of $HO^{18}O^{18}H$ in the mixed H_2O_2 become $[X + q(0.0020)]/(1 + q)$ and $[X^2 + q(0.0020)^2]/(1 + q)$, respectively, where 0.0020 is the isotopic atom-fraction of O^{18} in ordinary H_2O_2. This last isotopic distribution is unnatural, for had this H_2O_2 been made directly from enriched water vapor with atom-fraction of O^{18} equal to $[X + q(0.0020)]/(1 + q)$, then the mole-fraction of $HO^{18}O^{18}H$ in the resulting H_2O_2 would be $[X + q(0.0020)]^2/(1 + q)^2$. Now if this O^{18}-enriched H_2O_2 with unnatural isotopic distribution is catalytically decomposed by, say, triethylenetetramine–Fe(III), the mole-fraction of $O^{18}O^{18}$ in the liberated O_2 will be different for mechanisms (A) and (B), respectively. Mechanism (B) involves a reshuffling of the O-atoms, *i.e.*, restoration to the natural distribution of the isotopic species, and hence predicts a mole-fraction of $[X + q(0.0020)]^2/(1 + q)^2$ for $O^{18}O^{18}$ in the liberated O_2 gas. But a mechanism such as (A), which produces all the O_2 from the intact O–O bonds, leaves the original isotopic distribution undisturbed, and hence predicts the mole-fraction of $O^{18}O^{18}$ to be $[X^2 + q(0.0020)^2]/(1 + q)$.

If $X = 0.10$ and $q = 1.0$, we have $[X^2 + q(0.0020)^2]/(1 + q) \approx 0.0050$ and $[X + q(0.0020)]^2/(1 + q)^2 \approx 0.0026$. Consequently a mass-spectrometric analysis of the O_2 produced by the catalytic decomposition of hydrogen peroxide could

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[1] National Science Foundation Predoctoral Fellow, 1957–1958.

[2] J. H. Wang, THIS JOURNAL, **77**, 4715 (1955).