Anal. Calcd. for $C_{15}H_{25}O_8P_2Co$: C, 39.65; H, 5.55. Found: C, 39.77; H, 4.96.

Acetylcobalt Carbonyl Tris-(Trimethylolpropane Phosphite).—A solution of 0.81 g. of methylcobalt carbonyl bis-(trimethylolpropane phosphite) in 5 ml. of methylene chloride was treated with 2.0 ml. of 1.0 M trimethylolpropane phosphite in ether. After 30 minutes at room temperature, the solution was evaporated to 3 or 4 ml. and 5 ml. of ether was added. The product immediately crystallized as clusters of fine colorless needles. Two more recrystallizations from methylene chloride–ether gave 0.65 g. of acetylcobalt carbonyl tris-(trimethylolpropane phosphite). The complex had no definite melting point but decomposed gradually as it was heated.

Anal. Calcd. for $C_{21}H_{36}O_{11}P_3Co$: C, 40.92; H, 5.89. Found: C, 40.96; H, 5.90.

Methylcobalt Carbonyl Tris-(Trimethylolpropane Phosphite).—A solution of 0.60 g. of acetylcobalt tris-(trimethylolpropane phosphite) in tetrahydrofuran (not all dissolved) was mixed with 1.0 ml. of 1.0 M sodium ethoxide in tetrahydrofuran under nitrogen. The mixture was shaken for about an hour and then the insoluble sodium cobalt carbonyl tris-(trimethylolpropane phosphite) formed was separated by centrifuging and washed with two 5-ml. portions of fresh tetrahydrofuran. Then, to a slurry of this sodium salt in 5 ml. of tetrahydrofuran, 0.5 ml. of methyl iodide was added at 0° under nitrogen. The mixture was allowed to warm up slowly, and in 30 minutes nearly all the solid had dissolved. Evaporation of the solution left an oil and sodium iodide. The oil was separated by extraction with methylene chloride. Evaporation of the extracts to a few milliliters followed by the addition of ether gave crystals of the product. Several more crystallizations from methylene chloride–ether gave a nearly colorless powder, m.p. ~185° dec.

Anal. Calcd. for $C_{20}H_{36}O_{10}P_3Co$: C, 40.85; H, 6.17. Found: C, 40.73; H, 6.19.

This compound did not react with more trimethylolpropane phosphite in methylene chloride even on heating to 100°.

Cobalt Dicarbonyl Bis-(Trimethylolpropane Phosphite) Hydride.—A solution of 0.95 g. of acetylcobalt dicarbonyl bis-(trimethylolpropane phosphite) in 30 ml. of tetrahydrofuran was placed in a 110-ml. hydrogenation vessel and pressured to 3000 p.s.i. with hydrogen. The solution was heated to 60° and rocked for 12 hours. After cooling, the excess hydrogen was vented and the clear brown reaction mixture was removed by means of a hypodermic syringe to protect the product from the air. Evaporation of the solution under vacuum at room temperature left a tan solid. The product was taken up in methylene chloride and pentane was added dropwise until a black amorphous material separated. The solution was centrifuged to remove the black material and, on cooling, tan crystals of the hydride were obtained. Several recrystallizations from methylene chloride–pentane gave a sample, m.p. 155–160° dec.

Anal. Calcd. for $C_{14}H_{23}O_8P_2Co$: C, 38.20; H, 5.27. Found: C, 38.58; H, 5.40.

Acetylcobalt Tricarbonyl Tris-(p-anisyl)-phosphine.—A solution of 0.34 g. of dicobalt octacarbonyl in 5 ml. of methylene chloride at 0° was treated with a solution of 0.8 g. of tris-(p-anisyl)phosphine (prepared from p-anisylmagnesium bromide and phosphorus trichloride) in 5 ml. of methylene chloride. Evaporation of the solution after an hour left a dark oil which was probably bis-[tris-(p-anisyl)phosphine] cobalt tricarbonyl cobalt tetracarbonylate. The oil was diluted with 5.0 ml. of ether in a capped tube and heated at about 100° for an hour to convert the compound into the tri-p-anisylphosphine cobalt tricarbonyl dimer. The ether-insoluble solid brown dimer was filtered off and air-dried. There was obtained 0.74 g. of product.

Sodium cobalt tricarbonyl tris-(p-anisyl)-phosphine was prepared by shaking 0.74 g. of the above dimer with 12 ml. of tetrahydrofuran and 5.0 g. of 1% sodium amalgam in a capped tube under nitrogen overnight. The solution was centrifuged and the clear ~0.1 M solution of the sodium salt was transferred to another nitrogen-filled tube, where it was cooled to 0° and 0.5 ml. of methyl iodide was added. After an hour at 0°, the infrared spectrum showed that methylcobalt tricarbonyl tris-(p-anisyl)phosphine had been formed (bands at 4.91 (w) μ and 5.10 (vs) μ. An attempt was made to measure the rate of uptake of carbon monoxide by this compound at 0° under one atmosphere of pressure, but the reaction was much too fast under these conditions. From the reaction mixture, by evaporation and recrystallization several times from methylene chloride–pentane, a good yield of acetylcobalt tricarbonyl tris-(p-anisyl)-phosphine, as yellow prisms, m.p. 125–126° dec., was obtained.

Anal. Calcd. for $C_{26}H_{24}O_7PCo$: C, 58.00; H, 4.49. Found: C, 58.35; H, 4.90.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT BUFFALO, BUFFALO 14, N. Y.]

Carbonate Ligand and Hydrogen Exchange Studies of Some Carbonatoamine Cobalt(III) Complex Ions: A General Mechanism for the Ligand Carbonate Exchange Reaction in Aqueous Solution

BY GABRIEL LAPIDUS[1] AND GORDON M. HARRIS

Several studies have been made in recent years of the carbonate substitution reactions in aqueous solution of carbonatocobalt(III) complex ions of the general type $Co \, L \, CO_3^-$, where L represents an amine ligand grouping. This paper reports the results of a detailed study of the kinetics of the carbonate exchange reactions of $Co(pn)_2CO_3^+$ (pn = propylenediamine), and includes a complete reassessment of earlier data on the reactions of the analogs in which the group L is pentaammine (N_5), tetraammine (N_4), ethylenediamine (en$_2$), cis-diamminoethylenediamine (N_2en), and trimethylenediamine (tn$_2$). New data on the acidity dependence of the reactions has confirmed that the whole series react by a common dual mechanism involving both second-order carbonate/carbonate exchange and pseudo-first-order aquation. The rate law is of the form: $R = k'\alpha\beta ab + k''\alpha a$, where a and b are the total concentrations of complex and free carbonate, respectively, and α and β are functions of the form $Kh/Kh + 1$, with h = hydrogen ion concentration, and K a protonation equilibrium constant. Much of the variation in reactivity between members of the series appears to be of stereochemical origin, in which intramolecular O–H–N hydrogen-bonding may play a significant role. Evidence concerning this latter factor has been adduced from rate studies of the deuterium exchange between the amine hydrogens of several of these complexes and the solvent water. An important conclusion from the study is that it is only a protonated species, whether of complexed or free carbonate, which takes part in the reactions at an appreciable rate.

The exchange reaction in aqueous solution between free (uncomplexed) carbonate ion and the corresponding ligand group in various monocarbonatoaminecobalt(III) complex ions has been the subject of a number of investigations.[2-6] Since the complexes studied all have the same total charge and an identical central metal ion, unequivocal evidence is provided concerning the effect of different but related uncharged substitution-inert ligands on the kinetics of the displacement reactions of the adjacent dibasic carbonato ligand. The preceding paper in our own series[2] dealt

(1) Work done as part of Ph.D. requirement of University of Buffalo, 1961; complete report available from University Microfilms, Ann Arbor, Mich.

(2) J. E. Boyle and G. M. Harris, *J. Am. Chem. Soc.*, **80**, 782 (1958).

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

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

(5) J. S. Holden and G. M. Harris, *J. Am. Chem. Soc.*, **77**, 1934 (1955).

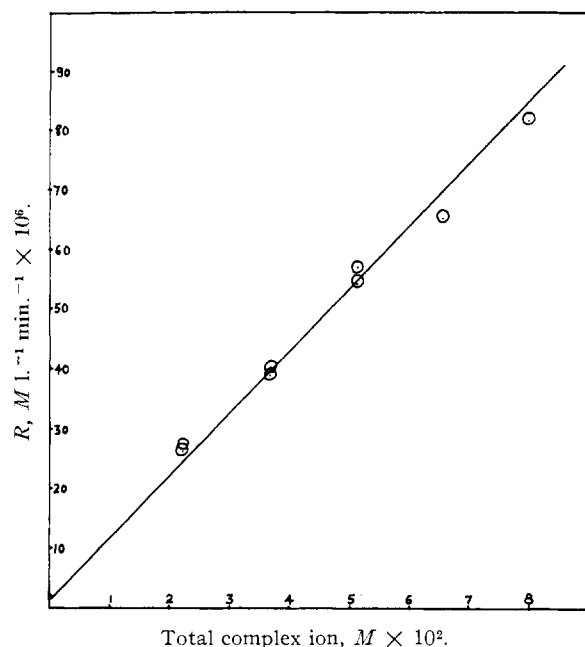(6) R. A. W. Pratt, E. Sherwin and G. J. Weston, *J. Chem. Soc.*, 476 (1962).

Fig. 1.—Exchange rate vs. total complex ion concentration for (pn)₂; 30.10°; total free carbonate = 0.0262 M; pH 9.65.

Fig. 2.—Exchange rate dependence of (pn)₂ on total free carbonate concentration: A, temperature 30.10°, pH = 9.90[a]; A', temperature 30.10°, pH = 8.71[a]; B, temperature 36.12°, pH = 9.90[a]; C, temperature 41.95°, pH = 9.90[a]. [a] pH determined at room temp.; (complex) = 0.041 M.

with the kinetics and mechanism of the reactions of the ion $Co(tn)_2CO_3^+$ (tn = trimethylenediamine), and included a reassessment of the previous work on the tetraammine[3] (N_4), pentaammine[4] (N_5), and ethylene-diamine[5] (en_2) analogs. Recently, other workers[6] studied the "mixed" species cis-$Co(en)(NH_3)_2CO_3^+$-(N_2en), and have interpreted their data strictly in accordance with the earlier proposals.[2] None of the analogous complexes so far studied contain side-chain-substituted amine ligands, so one aim of the present study was to obtain evidence on the kinetic effect of this type of factor by use of the bis-propylenediamine complex ion, $Co(pn)_2CO_3^+$. Also, uncertainties concerning the role of acidity in these exchanges needed to be resolved, and questions raised[6,7] with respect to the relative magnitudes of the various exchange rate parameters required further consideration. Finally the suggestion[2] that intramolecular hydrogen bonding is an important factor in the chemistry of these complexes called for possible confirmation by means of hydrogen-deuterium exchange studies of the amine ligands.

Experimental

A. Preparation, Purification and Analysis of Materials.— Carbonato-bis-(propylenediamine)-cobalt(III) chloride may occur in several stereoisomeric forms, although studies of the resolution of this system have never been completely definitive.[8] For the present work, the reasonable assumption is made that the possible isomers occur in statistical proportions and differ but little insofar as carbonate ligand exchange rates are concerned. A racemic preparation of the salt was therefore used throughout. The cis-dichloro chloride was prepared by the method of Bailar, $et\ al.$[9] The necessity of preparing the intermediate carbonato-carbonate was eliminated by allowing a saturated solution of the cis-dichloro chloride to aquate for about 12 hr., and then triturating with a stoichiometric amount of Ag_2CO_3 for about 1 hr. The precipitated AgCl was filtered off and the filtrate concentrated by evaporation. The near-saturated solution containing the impure carbonato chloride was then filtered free of lint and other solid contaminants and transferred to an erlenmeyer flask fitted with an air condenser. Recrystallization was accomplished by adding 3 volumes of 95% ethanol to one volume of the carbonato chloride solution, and heating on a hot-plate to effect solution. On cooling, partial crystallization ensued, provided the initially impure aqueous carbonato chloride was close to satura-

tion before treatment with ethanol. Further crystallization was assured by the addition of varying amounts of near-freezing ether. The precipitated carbonato chloride was filtered off on a coarse sintered-glass filter, washed with warm ethanol and then with ether, and the material air-dried for at least 3 hours. Potentiometric chloride and Kjeldahl nitrogen analysis corresponded very well with the previously reported formulation[8] Co-(pn)₂CO₃Cl·2H₂O; calcd. Cl, 10.46; found: Cl, 10.40; calcd. N, 16.54; found N, 16.47. The visible spectrum determined in the range $8 < pH < 10$ was experimentally almost indistinguishable from that of the (en_2)[10] and quite similar to that of the (tn_2)[11] analogs, as shown by the data:

Complex	(en₂)		(pn₂)		(tn₂)	
λ_{max}, mμ	358	512	357	515	360	520
E_{max} (log I_0/I)/Cl	120	127	122	133	128	109

It should be mentioned that E_{max} for the 357 peak of (pn₂) was not constant for $pH > 10$, increasing on standing to 127 at pH 10.2. However, no precipitation of Co_2O_3 was observable at this or higher basicities even on heating.[12]

The pentaammine, tetraammine, bisethylenediamine and bis-trimethylenediamine carbonato complexes were prepared as previously described,[2-5] as were samples of $Co(en)_2C_2O_4Cl$,[13] $Co(en)_3Cl_3$[14] and $Co(tn)_3Cl_3$.[15] Deuterated material for use in the hydrogen exchange studies was prepared $in\ situ$ by equilibration of the protiated complex in excess pure D_2O for 1–2 days at 25°, and carbon-14-labeled sodium carbonate stock solution was prepared as before.[2] All standard chemicals were of reagent grade.

B. Apparatus, Technique, and Results.—Carbonate exchange runs were carried out in the manner described previously.[2] pH control was achieved by the combined buffering action of the borate and carbonate present in the reaction mixtures. Exchange rates were obtained in the standard manner, making use of half-times, $t_{1/2}$, obtained from log ($A_t - A_\infty$)/($A_0 - A_\infty$) vs. time plots (A = specific radioactivity of the free carbonate); R, the exchange rate, is then obtained from the relation: $R = (0.693/t_{1/2})(ab/(a + b))$, where "$a$" and "$b$" are molar concentrations of complexed and free carbonate, respectively. The variation of R was studied at 30.10° as a function of

(7) D. R. Stranks and R. G. Wilkins, *Chem. Rev.*, **57**, 802 (1957).

(8) (a) Sr. M. Martinette and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **74**, 1055 (1952); (b) A. Sargeson, private communication, 1962.

(9) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis and E. H. Huffman, *J. Am. Chem. Soc.*, **61**, 2402 (1939).
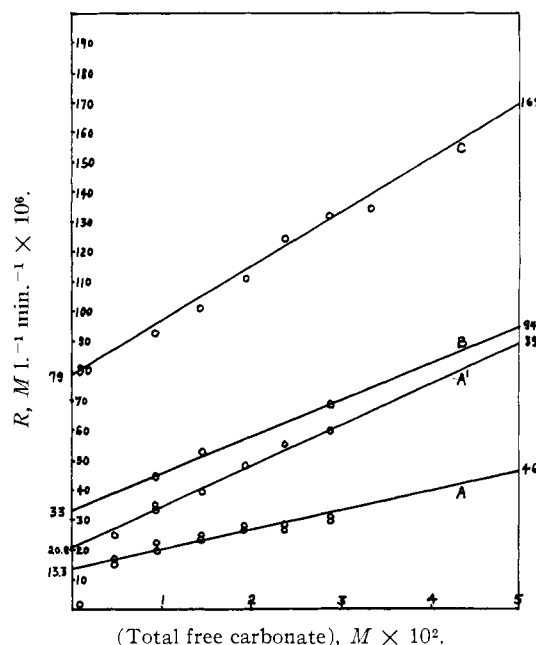
(10) J. S. Holden, M.Sc. Thesis, University of Melbourne, 1953.

(11) J. E. Boyle, Ph.D. Thesis, University of Buffalo, 1956.

(12) This contrasts with the behavior of N₄, which is quite unstable outside the pH range 8.5–10. However, both en₂ and tn₂ are similar to pn₂ in stability.

(13) A. Werner and A. Vilmos, *Z. anorg. Chem.*, **21**, 145 (1899).

(14) "Inorganic Syntheses," W. C. Fernelius, Ed., Vol. II, McGraw–Hill Book Co., Inc., New York, N. Y., 1946, p. 221.

(15) Prepared by substituting trimethylenediamine for ethylenediamine in the directions of ref. 14.

(complex), (total free carbonate), and (H$^+$), with the results represented by the points in Fig. 1, 2 and 3. Figure 2 also includes data obtained at 36.12° and 41.95° from which the temperature dependence parameters of the pn$_2$ reaction were determined as detailed later. In Figure 4 are given some new data on the tn$_2$ complex, obtained in a manner designed to determine more satisfactorily the acidity dependence of this reaction than was previously possible.[2]

The deuterium exchange rate was studied as follows. A calibration curve for each complex was constructed by determining the infrared spectrum of precipitated samples of complex of predetermined equilibrium D-content, brought down as the HgCl$_2$ double salt or as the tetraphenylborate from known D$_2$O–H$_2$O mixtures. These were incorporated in KBr disks and the "G-function" of Block and Gold[16] was plotted out by use of the N–H band near 3 μ or the N–D band near 4 μ, and of the deuterium-insensitive carbonate band near 6 μ. Exchange runs were made in light water using previously completely deuterated complex salt samples, which were precipitated at appropriate time intervals and examined for fraction of exchange, F, by use of the calibration data. All runs were made at 25° using a phosphate buffer at pH 5.9 and (complex) = 5 × 10^{-2} M. Exchange half-times were obtained from the conventional log (1 − F) $vs.$ time plots. The exchanges of Co(enD)$_3^{+3}$ (enD = ND$_2$CH$_2$CH$_2$ND$_2$), Co(tnD)$_3^{+3}$ (tnD = ND$_2$(CH$_3$)$_3$ND$_2$) and Co(ND$_3$)$_4$CO$_3^+$ were found to be too rapid to measure accurately by the present technique under the specified conditions (half-times of the order of a few minutes or less). However, readily measurable half-times of 1.1, 6.3 and 9.8 hr. were obtained for Co(enD)$_2$CO$_3^+$, Co(enD)$_2$C$_2$O$_4^+$ and Co(tnD)$_2$CO$_3^+$, respectively.
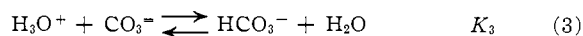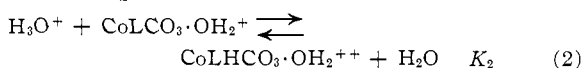
Discussion

The mechanism previously proposed[2] to account for the carbonato/carbonate exchange data was in fact threefold—one to account for the reactions of the tn$_2$ complex, a modified form for the N$_4$ and en$_2$ species, and a third variation for N$_5$. Over the widened range of acid dependence studies of the present work, none of the previous rate interpretations is entirely satisfactory. It turns out that in the earlier postulations, incomplete account was taken of the fact that the acid–base equilibria of the carbonato complexes are closely related to that of free carbonate. A revised general reaction scheme which takes cognizance of each of these acid–base equilibria on similar terms is
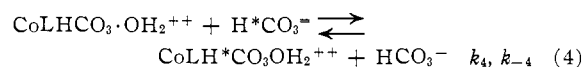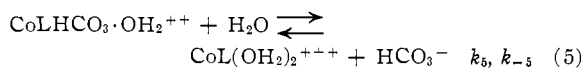
(a) *Aquo-dechelation equilibria*[17]

$$CoLCO_3^+ + H_2O \rightleftarrows CoLCO_3 \cdot OH_2^+ \qquad K_1 \qquad (1)$$

(b) *Acid–base equilibria*

$$H_3O^+ + CoLCO_3 \cdot OH_2^+ \rightleftarrows$$
$$CoLHCO_3 \cdot OH_2^{++} + H_2O \qquad K_2 \qquad (2)$$

$$H_3O^+ + CO_3^= \rightleftarrows HCO_3^- + H_2O \qquad K_3 \qquad (3)$$

(c) *Direct carbonate exchange*

$$CoLHCO_3 \cdot OH_2^{++} + H^*CO_3^= \rightleftarrows$$
$$CoLH^*CO_3OH_2^{++} + HCO_3^- \qquad k_4, k_{-4} \qquad (4)$$

(d) *Exchange by aquation*[18]

$$CoLHCO_3 \cdot OH_2^{++} + H_2O \rightleftarrows$$
$$CoL(OH_2)_2^{+++} + HCO_3^- \qquad k_5, k_{-5} \qquad (5)$$

This mechanism proposes that *only the protonated complex and free carbonate species* undergo reactions leading to carbonate exchange, and that equilibria

(16) H. Block and V. Gold, *J. Chem. Soc.*, 966 (1959).

(17) The product of this reaction may also be symbolized CoLHCO$_3$·OH$^+$, the choice depending upon which coördinated group, CO$_3$ or OH, is deemed to be the strongest base. Of the corresponding aqueous free ions, the latter is more basic than the former by a factor of over 10^5. This difference may be much less pronounced or even reversed in the complexed species, but from the kinetics point of view in the pH range of this work, the argument is of no consequence, provided the over-all pK of the aquo complex exceeds 11, as is undoubtedly true here. Reaction 1 is not, of course, applicable to N$_5$, since NH$_3$ already occupies five of the six coördination positions. In reactions 2, 4 and 5, –OH$_2$ does not appear in the complex when L = N$_5$ for the same reason.

(18) The extent of carbonate release in this equilibrium is negligible, as proved by the constancy of the spectra of the complexes over the pH range of the study, and the fact that there is no CO$_2$ liberation or other chemical evidence of decomposition down to pH < 4 for the bis-diamine complexes (en$_2$, pn$_2$ and tn$_2$). However, see footnote 12.
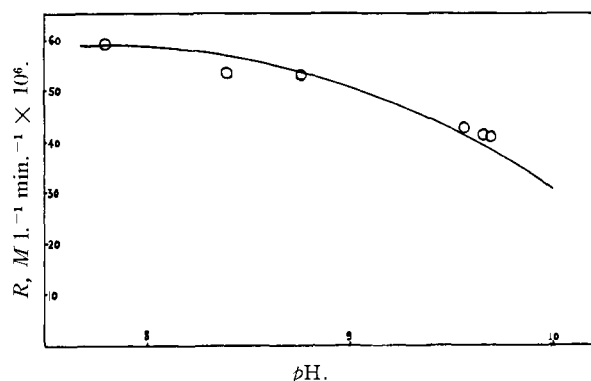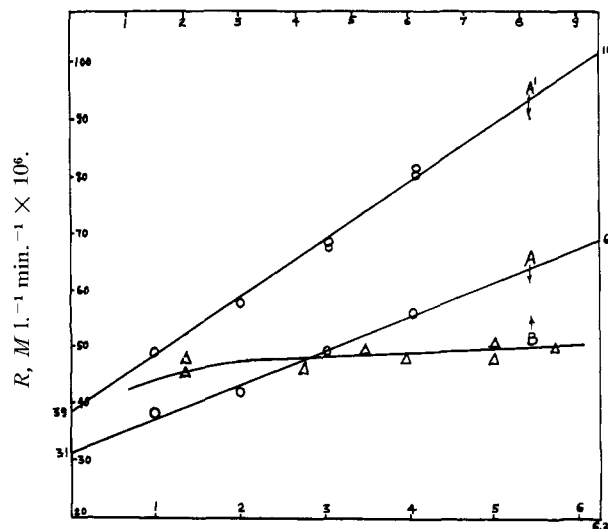
Fig. 3.—Calculated (solid line) and observed variation of exchange rate with acidity for (pn)$_2$; temp., 30.10°; (complex) = 0.04 M; (carbonate) = 0.026 M.

(Total free carbonate), M × 10^2, or (H$^+$), M × 10^{10}.

Fig. 4A.—Exchange rate $vs.$ total free carbonate concentration for (tn)$_2$; temp. 50.50°; (complex) = 0.0351 M; (carbonate) = 0.0152 M; A, pH 9.90^a; A′, pH 8.68.^{a} 4B.—Calculated (solid line) and observed variation of exchange rate with acidity^a for (tn)$_2$. ^{a}Acidity measured at room temp.

1, 2, and 3 are non-rate-determining. Representing the total concentrations of carbonato complex, free carbonate and hydrogen ion by a, b and h, respectively, the rate law is

$$R = k_4 \left(\frac{K_1(H_2O)}{K_1(H_2O) + 1} \right) \left(\frac{K_2h}{K_2h + 1} \right) \left(\frac{K_3h}{K_3h + 1} \right) ab +$$
$$k_5 \left(\frac{K_1(H_2O)}{K_1(H_2O) + 1} \right) \left(\frac{K_2h}{K_2h + 1} \right) a$$

The term $K_1(H_2O)/K_1(H_2O) + 1$, an indeterminate constant for each complex, is most conveniently included in the rate constants, leading to the simplified expression

$$R = k'\alpha\beta ab + k''\alpha a \qquad (6)$$

where α and β symbolize the bracketed expressions involving K_2 and K_3, respectively. With K_3 known[19] and a fixed, the ratio of the slopes and intercepts of plots of R $vs.$ b at two different values of h (Fig. 2 and 4) enable two independent evaluations of K_2 at a given temperature. The magnitudes of k' and k'' are then readily determined for each set of conditions, and may be used together with the other known constants to calculate R-values. The smooth curves in Fig. 1 through 4 are the result of such calculations, based on the set of experimental constants given in Table I.

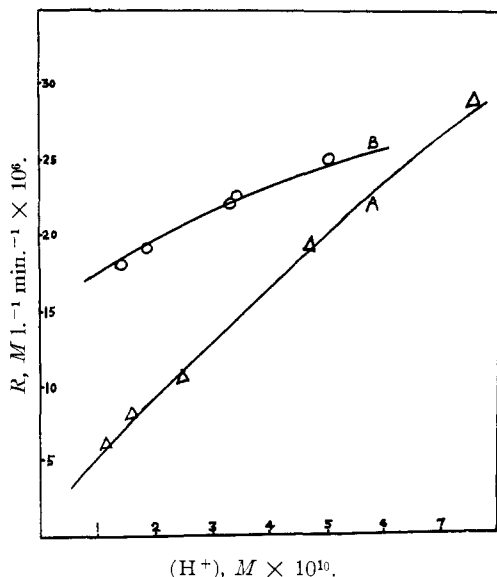(19) H. Harned and S. Scholes, *J. Am. Chem. Soc.*, **63**, 1706 (1941).

Fig. 5.—Calculated (solid line) and observed variation of exchange rate with acidity[a]: A = $(N)_5$: temp. 0.00°; (complex) = 0.0392 M; (carbonate) = 0.0189 M; B = (en)$_2$: temp. 25.00°; (complex) = 0.0351 M; (carbonate) = 0.0152 M.
[a] Acidity measured at room temp.

Making use of the temperature variation data on k' and k'', the Arrhenius activation energies E and frequency factors A have been determined in the usual manner for Co(pn)$_2$CO$_3{}^+$ from the linear log kv s. $1/T$ plots.[20] It is then possible to calculate k' and k'' values at 25° for comparison purposes. These, together with other rate parameters, are recorded in Table II. The figures given for the other carbonato analogs were obtained by recalculation of the data in the earlier papers,[2-6] as follows. New plots were made of the data for R $vs.$ b and R $vs.$ h variation. Then by com-

TABLE I

RATE CONSTANT DATA ON THE EXCHANGE REACTIONS OF
Co(pn)$_2$CO$_3{}^+$ AND Co(tn)$_2$CO$_3{}^+$

Complex	Temp., °C.	$10^{-10}K_3$,[a] M^{-1}	$10^{-10}K_2$, M^{-1}	$10^2k'$, M^{-1} min.$^{-1}$	$10^4k''$, min.$^{-1}$
Co(pn)$_2$CO$_3{}^+$	30.10	1.95	1.4[b]	3.6[b]	4.9[b]
	36.12	1.75	1.3[c]	7.1	13.3
	41.95	1.62	1.2[c]	11.2	32.6
Co(tn)$_2$CO$_3{}^+$	50.50	1.48	4.3[b]	3.1[b]	11.0[b]
	50.50	...	...	3.6[d]	9.4[d]

[a] Taken from data of ref. 19. [b] Mean of two independent experimental values. [c] Calculated from data at 30.10° on assumption of same temperature dependence as for K_3. [d] Values extracted from Boyle and Harris data (ref. 2), using present K_2 and K_3 figures.

TABLE II

RATE PARAMETERS FOR CARBONATE EXCHANGE REACTIONS AT 25°

Complex	$10^2k'$, M^{-1} min.$^{-1}$	$10^4k''$, min.$^{-1}$	$10^{-3}K_2$,[a] M^{-1}	E' (kcal. mole^{-1})	E''	log A'	log A''
N$_5$	32	470	0.26	16	20	11.1	13.3
N$_4$	4.2	7.5	6	17	21	11.1	12.3
N$_2$en[b]	3.8	2.9	9	..	..	...	...
en$_2$	1.4	6.5	9	17	23	10.6	13.7
pn$_2$	2.2	1.9	16	17	29	10.8	17.6
tn$_2$	0.11	0.39	61	25	25	15.4	14.0

[a] Calculated to 25° assuming same temperature coefficient as for K_3. [b] Ref. 6 (insufficient data to enable calculation of E's and A's).

(20) The E-values relate directly to k' and k'' since the factors α and β involving K_2 and K_3 (eq. 6) are independent of temperature within the experimental error of the E determinations.
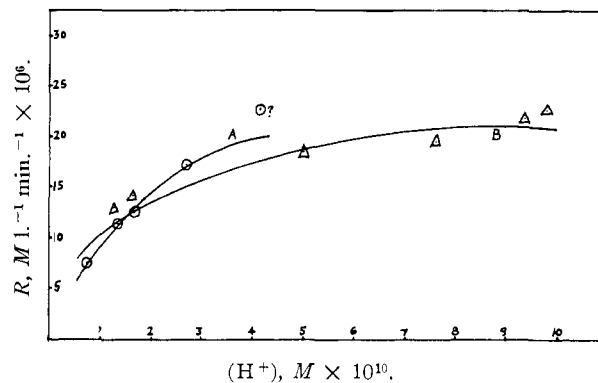

(H$^+$), M × 10^{10}.

Fig. 6.—Calculated (solid line) and observed variation of exchange rate with acidity: A, (N)$_4$, temp. 20.30°; (complex) = 0.0339 M; (carbonate) = 0.0146 M; B, (N$_2$en), temp. 25.80°; (complex) = 0.0296 M; (carbonate) = 0.0144 M.

bining the observed intercept and slope values of the b-variation plots with data from the smoothed h-variation plots, enough equations can be provided from which to calculate K_2, k' and k''. These first-approximation values are then adjusted to get "lines of best fit" for all the available data in terms of eq. 6. Figures 5 and 6 illustrate how this works out for various experimental "acidity profiles." The activation energies and frequency factors were estimated from the published temperature dependence studies, making the valid assumption in all cases but that of N$_5$ that α, like β, is essentially independent of temperature in the experimental pH range. For N$_5$, $K_2 << K_3$ and the assumption does not hold. A small allowance must be made in this case for the change of α with temperature.[21]

One might first question the inclusion of reaction 1 in the proposed mechanism for the carbonato chelates. A valid reason is the recently reported study[23] of the crystal structure of Co(NH$_3$)$_4$CO$_3$Br, which shows how distorted chelated carbonate has to be. This makes it very likely that in a strongly coördinating solvent such as water one end of the carbonato group will be displaced to allow a solvent molecule to occupy the sixth coördination position. A further necessity for the postulation of reaction 1 derives, as proposed in earlier papers,[2,24] from data on the equilibrium isotope distribution in the reaction

$$CoLCO_3{}^+ + C^{14}O_3{}^= \rightleftarrows CoLC^{14}O_3{}^+ + CO_3{}^= \qquad K_7 \quad (7)$$

Little or no isotope discrimination is observable for N$_4$[25] and en$_2$[26,27] over the pH range 9–10, while for the

(21) The data (ref. 4) at 0° are fitted well by $k' = 2.7 × 10^{-2} M^{-1}$min.$^{-1}$, $k'' = 2.1 × 10^{-3}$ min.$^{-1}$, and $K_2 = 5 × 10^3$. Lamb and co-workers (ref. 22a) predicted a value of ≤2.5 × 10 from K_2 at 0° from aquation kinetics data, but in later work (ref. 22b) reported a value of 1.3 × 10^4 at 0° and 2.5 × 10^6 at 25°. These correspond to a much greater temperature coefficient for K_2 than seems likely, since the corresponding constant K_3 for free-carbonate ion changes by a factor of less than two over this same range (ref. 19). Our value for K_2 at 25° has been estimated from our 0° value using the K_3 temperature coefficient, and this leads to more reasonable k' and k'' values than either of Lamb's limiting possibilities, between which ours lies.

(22) (a) A. B. Lamb and R. G. Stevens, J. Am. Chem. Soc., 61, 3229 (1939); (b) A. B. Lamb and K. J. Mysels, ibid., 67, 468 (1945).

(23) G. A. Barclay and B. F. Hoskins, J. Chem. Soc., 586 (1962).

(24) G. M. Harris, "Radioisotopes in the Physical Sciences and Industry," I.A.E.A., Vienna, 1962, Vol. III, p. 407.

(25) Earlier work (D. R. Stranks and G. M. Harris, J. Phys. Chem., 56, 906 (1952)) using carbon-14 tracer indicated K_7 for N$_4$ to be 0.9 at 25°. However, E. Saito and B. Lazard (J. Inorg. Nuclear Chem., 1, 218 (1955)) were unable to confirm this result, reconciling the apparent contradictions by the assumption of a non-exchanging impurity. More recent experiments (S. Sheel and G. M. Harris, unpublished results, 1958) indicate that the isotope effect is indeed only apparent, and results from the instability of N$_4$ and the probable formation of colloidal cobalt carbonates which tie up a small percentage of the highly-radioactive and initially "free" carbonate in a non-exchangeable form.

(26) P. E. Yankwich and J. E. McNamara, J. Chem. Phys., 20, 1325 (1952).

(27) D. R. Stranks, Trans. Faraday Soc., 51, 492 (1955).

tn_2 species, $K_7 = 0.93$ at $50.5°$ and pH $10.$[11] This indicates that the CO_3 groups in the first two complexes mentioned differ very little thermodynamically from free $CO_3^=$ or HCO_3^- (the latter two ions have practically identical C^{14}/C^{12} partition function ratios[28]). Monodentate carbonate, as in N_5, shows no equilibrium isotope effect,[27] so for N_4 and en_2 it is assumed that K_1 is relatively large and the fraction $K_1(H_2O)/K_1(H_2O) + 1$ close to unity. But for tn_2, K_1 must be small enough that most of the coördinated carbonate remains bidentate due to H-bonding and other stereochemical hindrances. Then, since chelated carbonate resembles the carbonyl grouping $X_2C{=}O$, an isotope effect is observed.[25,28]

Support of this concept is also provided by the spectral data recorded in the Experimental section. It is noted that the tn_2 peaks are shifted slightly but significantly toward longer wave lengths as compared to en_2 and pn_2. This is the expected behavior if the latter are in the form $CoLCO_3 \cdot OH_2$ and not the former, since $CO_3^=$ undoubtedly falls below H_2O in the spectrochemical series.[29,29a]

An alternative view that acid-catalyzed dechelation by a one-step process combining reactions 1 and 2

$$CoLCO_3^+ + H_3O^+ \rightleftharpoons CoL \cdot HCO_3 \cdot OH_2^{++} \qquad (8)$$
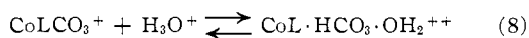
eliminates the isotope effect in the pH range 9–10 is untenable. The K_2 data show that the fraction of protonated and presumably dechelated complex varies from 0.4 to 0.9 for N_4 and en_2 over this pH range but stays close to unity for tn_2. This would predict no isotope effect for tn_2 and a pH-dependent isotope effect for N_4 and en_2, contrary to observation.

Hydrogen bonding has been invoked[2] as a factor in the aquo-dechelation reactions of the carbonato complexes. The data now available allow for at least a qualitative appraisal of this factor, since it is logical to assume that the rate of exchange of labile hydrogens of a compound with those of the water solvent is diagnostic of its extent of intramolecular hydrogen bonding.[30] Table III presents our amine–H exchange data

TABLE III

RATES OF AMINE HYDROGEN EXCHANGES OF SOME COBALT(III) COMPLEXES AT 25°

Complex	pH	$k_{OH-},$ M^{-1} sec.$^{-1}$	Reference
$Co(ND_3)_6^{+3}$	Variable	1.2×10^6	16
$Co(NH_3)_6^{+3}$	5.3	1.6×10^6	31
$Co(en)_3^{+3}$	5.3	2.5×10^6	31
$Co(pn)_3^{+3}$	5.3	4.5×10^6	31
$Co(tn)_3^{+3}$	5.3	1.1×10^7	31
$Co(ND_3)_4CO_3^-$	5.9	$>10^5$	This work[a]
$Co(ND_3)_4C_2O_4$	Variable	6.2×10^4	16
$Co(enD)_2CO_3^+$	5.9	2×10^4	This work
$Co(enD)_2C_2O_4^+$	5.9	4×10^3	This work
$Co(tnD)_2CO_3^-$	5.9	2.5×10^3	This work

[a] Half-time less than 0.3 hr.

in the form of second-order rate constants, calculated on the assumption of a completely OH^--catalyzed mechanism as confirmed by Block and Gold.[16] Also included in the tabulation are other significant data published by Basolo, et al.[31]

(28) D. R. Stranks and G. M. Harris, J. Am. Chem. Soc., **75**, 2015 (1953).

(29) The position of carbonate in the series has not been determined, but both formate and oxalate precede water (T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 266).

(29a) See also C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 110.

(30) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 184 et seq.

In the case of the tris-amine complexes, the rate of H-exchange is very rapid and increases as one changes from NH_3 to en to pn to tn, consistent with a suggested correlation[31] with acidity variation of the complexes as one goes down the series. It is obvious that another factor determines the relative rates of the amine–H exchanges of the carbonato and oxalato series, where a reversal of the order occurs. Hydrogen-bonding stabilization of these species by formation of N—H—O—C bridges is a possible explanation, and molecular models suggest that the geometry favors H—O interaction more for oxalato than for carbonato, and more for tn_2 than for en_2 than for N_4.

It is now convenient to consider in more detail the trends evident in the data of Table II. The bimolecular carbonate exchange process (reactions 1, 2, 3 and 4), described by the rate constant k', exhibits no serious discontinuities as one goes through the series N_4, N_2en, en_2 and pn_2. This suggests a rather unspecific type of activated complex in these cases, where the entering HCO_3^- ion is perhaps bonded by simple ion-pair formation rather than in some more sterically discriminatory seven-coördinate complex. A discontinuity does appear, however, in the rates of the aquation process (reactions 1, 2, 3 and 5) for the same series between N_4 and en_2 on the one hand and N_2en and pn_2 on the other. Here conformational factors may be involved. These may derive partially from the nature of the solvation sheath, since it is clear that aquation promotion by this sheath would be less effective for the methyl group-shielded pn_2 ion than for N_4 or en_2. The solvation sheath argument does not apply to cis-N_2en, and it is difficult to see what other conformation factor is involved, unless it is the different type of distortion of the octahedral symmetry engendered by the presence of only one diamine chelate rather than two. A study of the trans-diammine analog should provide interesting and important evidence concerning the effect of such stereochemical modifications.

One notes that the magnitudes of E'' for the N_4, en_2 and pn_2 series increase in the same order as does the protonation equilibrium constant K_2, suggesting that the same electromeric effects which increase the basicity of the carbonato ligand decrease the ease with which the water molecules can replace it. The studies by Taube and co-workers[32] of acid-catalyzed aquation of N_4 and N_5 suggest that in the former (and its amine analogs) the last bond to be broken in aquation is the C–O bond adjacent to the metal ion. It thus appears that the more basic is the carbonato-aquo intermediate, the stronger is the C–O bond under consideration. This seems quite reasonable in terms of electron density distribution requirements.

The N_5 species exhibits greatly enhanced reactivity over the bidentate series for both types of carbonate substitution processes. This occurs in spite of the reduced basicity of N_5, for which K_2 is smaller by an order of magnitude than for the other complexes. This contrast cannot be ascribed to small values of K_1 for the bidentates, at least for N_4 and en_2, since these do not exhibit an exchange equilibrium isotope effect, as explained above. In the N_5 species, all sites adjacent to the reactive $-OCO_2H$ group are occupied by non-labile $-NH_3$, while one of these sites is occupied by $-OH_2$ in the other complexes, in the protonated form in which they react. The labilization of the bicarbonato group for aquation by the additional NH_3 of N_5 is paralleled by a similar effect for rates of aquation of

(31) F. Basolo, J. W. Palmer and R. G. Pearson, J. Am. Chem. Soc., **82**, 1073 (1960).

(32) J. P. Hunt, A. C. Rutenberg and H. Taube, ibid., **74**, 268 (1952); F. A. Posey and H. Taube, ibid., **75**, 4099 (1953).

$Co(NH_3)_5Cl^{++}$ as compared to $Co(NH_3)_4OH_2 \cdot Cl^{++}$, but the former undergoes chloride release in aqueous solution at a rate only a few times greater than the latter,[33] as against a factor of 60 or more in the corresponding carbonato compounds. The explanation must be that, while each substitution event (whether by HCO_3^- or H_2O) results in carbonate exchange in N_5, H_2O substitution for H_2O in the bicarbonato-aquo species, which results in no carbonate exchange, may well be the favored path.[34] Furthermore, the dynamic

(33) D. R. Stranks in "Modern Co-ordination Chemistry" (ref. 29), p. 129.

(34) Since only the immediately adjacent water molecules of the solvent sheath can take part in the substitutions, the geometry of the transition states for the H_2O/H_2O and H_2O/HCO_3^- reactions may be almost identical, differing only by small shifts in the O–H, O–C and O–Co bond distances. The more easily attainable orientation, assumed here to be that for H_2O/H_2O exchange, will thus be favored at the expense of the other, especially as labilization of the OH_2 ligand by the adjacent basic O_3CH ligand[35] will assist in formation of this "more favorable" transition state.

(35) It is significant that water exchange between water solvent and the cis-Co(en)$_2$OH·H$_2$O^{-+} ion occurs at 25° at a rate over 50 times greater than

equilibrium of reaction 1 provides an additional non-carbonate-exchange reaction path which is not available to the N_5 complex.

The tn_2 complex undergoes carbonate exchange an order of magnitude more slowly than do the other bidentate carbonato complexes. This is logically explained in terms of the reduced value of K_1 for tn_2, since the rate constants of both types of carbonate substitution reactions include the factor $K_1(H_2O)/K_1(H_2O) + 1$. Equilibrium isotope effects, hydrogen-bonding and spectral evidence for a relatively small K_1 value in tn_2 have been discussed above.

the rate of the corresponding reaction of the cis-Co(en)$_2$(H$_2$O)$_2$$^{+3}$ ion (W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961)), and over 400 times greater than for cis-Co(en)$_2$NH$_3$·H$_2$O^{-3} (D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962)). This commonly observed hydroxide-induced labilization of the adjacent ligand (see ref. 33) can be expected to be paralleled by a similar effect by the strongly basic bicarbonate group.

The Photochemistry of Methylamine[1]

BY JOE V. MICHAEL[2] AND W. ALBERT NOYES, JR.

RECEIVED SEPTEMBER 29, 1962

Hydrogen, methane, nitrogen, ethane, ammonia, ethylenimine, dimethylamine, azomethane and a polymer have been identified as products in the photochemical decomposition of methylamine. Quantum yields of most of these products have been determined under a variety of experimental conditions at room temperature. By use of CH_3ND_2 and of CD_3NH_2 as well as by use of scavengers it has been shown that the main primary process is the elimination of a hydrogen atom. This is followed by abstraction from the substrate to form hydrogen gas. Other steps in the mechanism are suggested and evidence for some of them presented.

The photochemistry of methylamine has been extensively studied.[3] The results were not always in good agreement.

Methylamine is a photochemically interesting molecule. There is some direct production of molecular hydrogen in the primary process following absorption by methanol vapor.[4] An analogous reaction in methylamine would be possible.

Methylamine probably shows a predissociation type spectrum.[5] By analogy with NH_2 the reactions of CH_3NH with oxygen and with nitric oxide might also prove to be interesting.[6,7]

The photochemistry of methylamine is complex, a fact to be expected from the difficulties in interpreting results on the photolysis of ammonia.[8] The main primary process is the formation of hydrogen atoms, but there may be small amounts of dissociation to

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Contract AF49(638)-679.

(2) National Science Foundation Coöperative Fellow, 1959–1960; Eastman Kodak Company Fellow, 1960–1961; National Science Foundation Predoctoral Fellow, 1961–1962.

(3) H. J. Emeléus and H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 3370 (1931); H. J. Emeléus and L. J. Jolley, *J. Chem. Soc.*, 1612 (1935); O. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, **12**, 61 (1944); C. I. Johnson and H. A. Taylor, *ibid.*, **19**, 613 (1951); J. S. Watson and B. deB. Darwent, *ibid.*, **20**, 1041 (1952). For reviews see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 382, and E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 244, 636.

(4) R. P. Porter and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 2307 (1959).

(5) See H. J. Emeléus and L. J. Jolley, ref. 3. A. B. F. Duncan, *Phys. Rev.*, **47**, 822 (1935), and R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935), have discussed ammonia spectrum and bands.

(6) H. Gesser, *J. Am. Chem. Soc.*, **77**, 2626 (1955).

(7) A. Serewicz and W. A. Noyes, Jr., *J. Phys. Chem.*, **63**, 843 (1959).

(8) Cf. C. C. McDonald and H. E. Gunning, *J. Chem. Phys.*, **23**, 532 (1955).

methyl and amine radicals as well as to form molecular hydrogen.

Experimental

An unfiltered Hanovia S-100 was used for all experiments. Since polymer formed on the front window of the cell, it was necessary to clean the cell after each run.

The radiation was not monochromatic. All of the wave lengths between 1940 and 2440 Å. are probably absorbed by methylamine.

Actinometry measurements were made by the hydrogen bromide–mercury vapor system in tandem with the photolysis cell. This actinometer is described in detail elsewhere.[9,10] One molecule of hydrogen is assumed to be formed per photon when mercury is present to react with the bromine. Quantum yields should be valid within 5%.

Reagents.—Methylamine was prepared from Eastman Kodak Co. White Label methylamine hydrochloride. It was recrystallized three times from water, and the amine was liberated by anhydrous calcium oxide.[11] The purity was 99.9%.

Methylamine-C-d_3 was prepared in the same manner as methylamine. Methylamine-C-d_3 hydrochloride was supplied by Dr. R. J. Cventanović of the National Research Council, Ottawa, Can., to whom the authors are indebted. The purity determined by vapor phase chromatography of the final sample was 99.9% and the isotopic purity determined by mass spectrometry was at least 93%.

Methylamine-N-d_2 was obtained from Merck, Sharp, and Dohme of Canada, Ltd., and had a purity of 99.5%. The principal impurity was ND_3. The isotopic purity was at least 99%.

Ammonia was obtained from the Matheson Co., Inc. A middle third was taken from a bulb-to-bulb distillation. Vapor phase chromatography and mass spectrometry showed it to be 99.9% pure.

Azomethane was prepared by the method of Jahn and was purified by vapor phase chromatography.[12]

Research grade methane and ethane (Phillips Petroleum Co.) were used without further purification.

(9) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 83.

(10) W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937).

(11) A. P. Gray and R. C. Lord, *ibid.*, **26**, 690 (1957).

(12) F. P. Jahn, *J. Am. Chem. Soc.*, **59**, 1761 (1937).