alcohols[40] are found to fit the relationship $\log k/k_0 = -3.45 (E_\sigma)$, where k_0 is the rate constant for the formaldehyde acetal of methanol, and E_σ is the acyl substituent constant corresponding to the alkyl group in the acetal whose rate constant is k.

OBSERVED AND CALCULATED VALUES OF LOG k/k_0

Alcohol, ROH, of formaldehyde acetal where R is	$(\log k/k_0)$obsd.	$(\log k/k_0)$ calcd.	d
CH_3	0.00	0.00	0.00
C_2H_5	+ .93	+ .87	.05
n-C_3H_7	+ .97	+ .96	.01
i-C_3H_7	+1.67	+1.62	.05
n-C_4H_9	+0.97	+1.10	.13
i-C_4H_9	+1.11	+1.07	.04

This series is admittedly a limited one, but the fit is extremely good. The extension of this series to other alcohols, particularly those producing large polar effects would be desirable. The large negative proportionality constant, −3.45, indicates that this reaction is especially susceptible to polar substituents and is accelerated by electron release. The fact that steric factors are shown by these results to be of essentially no importance in determining relative reactivity indicates that there is probably essentially the same distribution of bond angles in the hydrolysis transition state as in the starting acetal.

To Reaction Series for which Steric Factors are not Constant.—If a method of evaluating the total steric effect of each substituent is available, subtraction of these quantities from relative free energy changes may yield results which parallel the E_σ values of Table IV. For example, values of the quantity $(\log k/k_0)_B - (\log k/k_0)_A$[41] obtained from the data for the base- and acid-catalyzed hydrolysis of thiolacetates in 43% (wt.) aqueous acetone at 30°[42] agree closely with values calculated from the relation $(\log k/k_0)_B - (\log k/k_0)_A = (+0.69)\ E_\sigma + 0.20$, where E_σ is the aliphatic acyl electron displacement parameter (for normal esters) corresponding to the alkyl group in the thiolacetate whose rate constant is k.

Substituent	$(\log k/k_0)_B - (\log k/k_0)_A$ Exptl.	Calcd.	d
CH_3	0.00	+0.20	0.20
C_2H_5	+ .06	+ .04	.02
i-C_3H_7	− .10	− .12	.02
i-C_4H_9	− .02	− .01	.01
t-C_4H_9	− .39	− .38	.01

The probable conclusions to be drawn from these results are that the base-catalyzed hydrolysis of thiolacetates is less susceptible (since $\rho_B - \rho_A = +0.69$; $\rho_B \cong 0.69$) to polar alkyl substituents than the glycerate ester reaction series previously referred to ($\rho_B - \rho_A = +1.45$; $\rho_B \cong +1.45$) and therefore that the inductive effect of alkyl groups is transmitted more effectively by the more polarizing oxygen than sulfur.

Acknowledgment.—The author wishes to express his thanks to Professor L. P. Hammett for numerous discussions relating to the effect of structure on reactivity. The suggestions of Dr. N. C. Deno and one of the Referees in the preparation of this and the previous manuscript are gratefully acknowledged.

STATE COLLEGE, PA.

[40] A. Skrabal and H. H. Eger, *Z. physik. Chem.*, **122**, 349 (1926).

[41] $(\log k/k_0)_A$ should be an approximate measure of steric factors associated with each thiolacetate.

[42] Data of ref. 32. The rate constant used for the base catalyzed hydrolysis of methyl thiolacetate in 43% (wt.) aqueous acetone at 30° was calculated from the corresponding rate constant at 20° using a value of 12.7 kcal. for the activation energy.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

Base Catalysis in the Decomposition of Diazomalonic Acid

BY CECIL V. KING AND PAULINE KULKA

RECEIVED NOVEMBER 14, 1951

Data are now available for the decomposition rates when potassium diazomalonate is dissolved in dilute strong acid (perchloric); in buffers of weak acids (trimethylacetic, acetic, glycolic, anilinium perchlorate); and in buffers of intermediate acids (chloroacetic, phosphoric, glycinium perchlorate). In all these solutions the rates may be explained as catalysis, by water and other bases, of the reactions of both the bivalent and univalent (acid) anions of diazomalonic acid.

It was shown in a previous paper[1] that diazomalonic acid decomposes at measurable rates in dilute perchloric acid, and that in acetate and aniline buffers the reaction is catalyzed by water and by the basic components of the buffers. The over-all reaction was assumed to be

$$N_2C(COO)^{=} + H_3O^+ \longrightarrow N_2 + CO_2 + CH_2OHCOO^- \quad (1)$$

The second ionization constant of diazomalonic acid was estimated (wrongly, later experiments show) from the rates.

In strong acid, the bimolecular reaction of hydrogen ion with the bivalent diazo ion was previously assumed to be rate controlling. Water catalysis and possible reaction of the acid diazo anion were not considered. However, if in weak acid buffers the entire reaction is one of water and anion catalysis, there seems no reason why water catalysis should not be present in solutions of strong acid. Further, in phosphate buffers, it was found that as increasing amounts of phosphoric acid were added to a fixed concentration of sodium primary phosphate, the rate increased too much to be explained by the increases in hydrogen ion and phosphate ion unless there were simultaneous reactions of the acid diazo ion. If this ion reacts in buffers, it is necessary to assume that it also reacts in perchloric acid solutions. The entire reaction in strong acid is then a water catalysis, and the effect of hydrogen ion, in addition to completing the reaction, is to shift the second ionization equilibrium of the diazomalonic acid.

In all solutions the rate-controlling steps are then

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[1] C. V. King, P. Kulka and A. Mebane, THIS JOURNAL, **72**, 1906 (1950).

the reactions of basic molecules or ions with one of the diazo ions. Since the ions are probably hydrated (see Experimental), the process may consist in removal of a proton rather than simple addition

$$N_2C(COO)_2^=, H_2O + B \rightleftharpoons \text{intermediate}$$
$$N_2C(COOH)(COO)^-, H_2O + B \rightleftharpoons \text{intermediate}$$

These steps are followed by rapid reaction with hydrogen ion, in solutions where its concentration is sufficiently high.

The Rate Equation

A general rate equation can be written as

$$dx/dt = k_1C_{N^=} + k_2C_{HN^-} + k_3C_AC_{N^=} + k_4C_AC_{HN^-} \quad (2)$$

where $N^=$ and HN^- indicate the diazo ions, k_1 and k_2 are the water constants (C_w considered constant), and A is any other base than water. In strong acid only the terms in k_1 and k_2 are present; in weak acid buffers ($K_A \gg 10^{-5}$) the terms in k_2 and k_4 vanish because C_{HN^-} is negligible. In buffers of intermediate acids ($K \gg 10^{-4}$) all four terms are important.

From the second ionization constant of the acid

$$KC_{HN^-} = C_{H^+}C_{N^=} \quad (3)$$

and the stoichiometric condition

$$C_{HN^-} + C_{N^=} = (a - x) \quad (4)$$

where $(a - x)$ is the total diazomalonate concentration at time t, it follows (neglecting salt effects) that

$$C_{N^=} = \frac{K(a - x)}{K + C_{H^+}} \text{ and } C_{HN^-} = \frac{C_{H^+}(a - x)}{K + C_{H^+}} \quad (5)$$

The observed rates, in all solutions used, are essentially first order and may be expressed by k' in the equation

$$dx/dt = k'(a - x) \quad (6)$$

From (2), (5) and (6)

$$k'(K + C_{H^+}) = k_1K + k_2C_{H^+} + k_3KC_A + k_4C_{H^+}C_A \quad (7)$$

Equation (7), with suitable values of the constants, can express most of the measured rates with an average deviation of ±0.0010 unit in k'.

Experimental

Rates were measured as described before,[1] at 25 ± 0.02°, using 50 ml. of solution and 0.0056 *M* potassium diazomalonate. Glycine solutions were standardized by titration using formaldehyde, and buffers were made by adding standardized perchloric acid. Phosphate buffers were made by adding standardized phosphoric acid to solutions of primary sodium phosphate. All chemicals were of Reagent grade.

The solid potassium diazomalonate, dried in air at room temperature, appears to be a sesquihydrate. Direct analysis gave: C, 10.6% (with residue, assumed below to be K_2CO_3); H, 1.27; H_2O, 11.4; N, 11.8. Calcd. for $N_2C(COOK)_2 \cdot 1.5H_2O$: C, 10.3; H_2O, 11.6; N, 12.0.

Direct dehydration *in vacuo* at 40° gave 11.5% weight loss. Nitrogen evolved on reaction with 2 *N* HCl, after absorbing CO_2 with KOH, = 11.1%. On reaction with 0.1 *N* $HClO_4$, 103 mg. of the salt used 0.409 mmole acid (92.5% of theoretical).

Application of Rate Equation

Weak Acid Buffers. Determination of k_1 and k_3.—As shown previously[1] the rate, at a given anion concentration, reaches a maximum at some acid concentration, about 0.04 *M* in the pertinent cases. In Fig. 1 rate constants k', averaged for 0.04, 0.06, 0.08 and 0.10 *M* acid, are plotted *vs.* base concentration. The slopes of the straight lines are the molar catalytic constants, k_3 in equation (7). The points for 0.0024 *M* and 0.0034 *M* glycolate ion, run in glycolic acid with no added glycolate, are corrected for appreciable terms in k_2 and k_4 (see Table I). The lines, except for aniline, extrapolate to about 0.0140. Experiments in acetic and trimethylacetic acids give about the same value (Table I) and in all calculations k_1 has been taken as 0.0140 min.$^{-1}$.

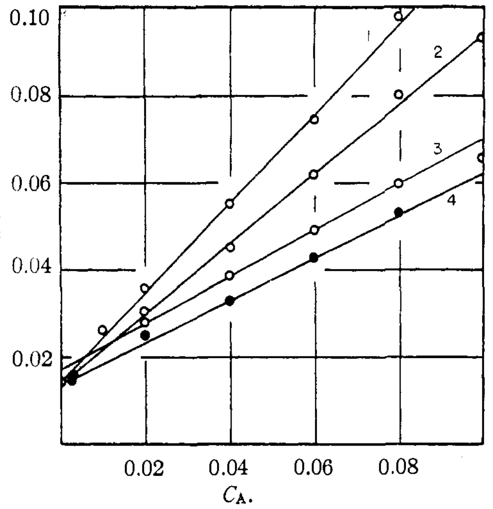

Fig. 1.—Rate constants in (1) trimethyl acetate, (2) acetate, (3) aniline and (4) glycolate buffers.

TABLE I

RATE CONSTANTS IN WEAK ACIDS ALONE

	C_{HA}	k'	k', cor.
Trimethylacetic	0.04*M*	0.0148	....
	.08	.0138	....
Acetic	.04	.0138	....
	.08	.0139	....
Glycolic	.04	.0175	0.0146
	.08	.0198	.0159

Strong Acid. Determination of K and k_2.—The rates in perchloric acid (Table I of the previous paper) can be expressed by equation (7), omitting terms in k_3 and k_4. It can be used in the form

$$\frac{k' - k_1}{C_{H^+}} = \frac{k_2}{K} - \frac{k'}{K} \quad (8)$$

for graphical evaluation of K and k_2, since k_1 is known. The following values are found: $K = 0.109$, $k_2 = 0.140$ min.$^{-1}$. Agreement with the data is shown better by plotting $k'(K + C_{H^+})$ *vs.* C_{H^+}, and this has been done in Fig. 2.

Intermediate Acid Buffers. k_3 and k_4.—Equation (7) may be rearranged as

$$\frac{k'(K + C_{H^+}) - k_1K - k_2C_{H^+}}{C_A} = k_3K + k_4C_{H^+} \quad (9)$$

After k' has been measured at various buffer compositions all terms on the left are known so that k_3 and k_4 may be determined graphically. The function used leads to considerable scatter of the points but the best straight line may easily be chosen. Table II gives the solution compositions and a comparison of observed and calculated rate constants for the phosphate buffers used. Values of C_{H^+} and $C_{H_2PO_4^-}$ were obtained from the equation

$$-\log K_c = 2.124 - 1.02\sqrt{\mu} + 0.1\mu \quad (10)$$

The data for glycine–glycinium perchlorate buffers were plotted in the same manner, to obtain $k_3 = 0.229$ liter mole^{-1} min.$^{-1}$ and $k_4 = 2.06$ liter mole^{-1} min.$^{-1}$. Table III gives solution compositions and observed and calculated rate constants. Salt effect is small with this type of buffer

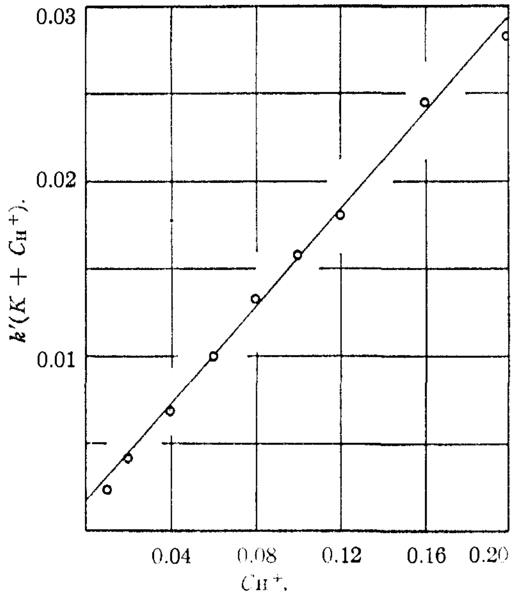

Fig. 2.—Data in perchloric acid compared with the equation $k(K + C_{H^+}) = k_1K + k_2C_{H^+}$; intercept $= k_1K = 0.00153$; slope $= k_2 = 0.140$.

equilibrium and C_{H^+} and C_{A} were calculated from the relation $K_c = K_A = 4.47 \times 10^{-3}$.

TABLE II

OBSERVED AND CALCULATED RATE CONSTANTS IN PHOSPHATE BUFFERS

$K = 0.109$, $k_1 = 0.0140$ min.$^{-1}$, $k_2 = 0.140$ min.$^{-1}$, $k_3 = 0.206$ liter mole^{-1} min.$^{-1}$, $k_4 = 1.35$ liter mole^{-1} min.$^{-1}$; stoichiometric concentrations of acid and salt are given.

$C_{H_3PO_4}$, M		$C_{NaH_2PO_4}$, M 0.02	0.04	0.06	0.08	0.10
0.0233	k', obsd.	0.0281	0.0304	0.0345	0.0383	0.0442
	k', calcd.	0.287	.0311	.0345	.0379	.0420
.0333	k', obsd.	.0331	.0340	.0382	.0405	.0469
	k', calcd.	.0325	.0346	.0376	.0411	.0453
.050	k', obsd.	.0373	.0389	.0432	.0437	.0513
	k', calcd.	.0381	.0399	.0425	.0454	.0497
.0667	k', obsd.	.0412	.0453	.0474	.0472	.0547
	k', calcd.	.0433	.0447	.0475	.0508	.0545
.100	k', obsd.	.0532	.0549	.0522	.0591	.0623
	k', calcd.	.0524	.0537	.0564	.0597	.0609

Average deviation = 0.0010

TABLE III

OBSERVED AND CALCULATED RATE CONSTANTS IN GLYCINE–GLYCINIUM PERCHLORATE BUFFERS

$K = 0.109$, $k_1 = 0.0140$ min.$^{-1}$, $k_2 = 0.140$ min.$^{-1}$, $k_3 = 0.229$ liter mole^{-1} min.$^{-1}$, $k_4 = 2.06$ liter mole^{-1} min.$^{-1}$; stoichiometric concentrations of salt and base are given.

$C_{Gl.ClO_4}$, M		C_{Gl}, M 0.01	0.02	0.04	0.06	0.08
0.02	k', obsd.	.....	0.0255	0.0269	0.0319	0.0359
	k', calcd.	.....	.0242	.0271	.0309	.0351
.04	k', obsd.	0.0282	.0292	.0313	.0324	.0345
	k', calcd.	.0291	.0289	.0308	.0342	.0378
.06	k', obsd.	.0322	.0339	.0336	.0371	.0398
	k', calcd.	.0334	.0340	.0341	.0371	.0406
.08	k', obsd.	.....	.0347	.0373	.0398	.0437
	$k,'$ calcd.	.....	.0366	.0376	.0401	.0435

Average deviation = 0.0009

The data for chloroacetic acid–sodium chloroacetate buffers were treated in the same manner. Because of the smaller contribution of the terms in k_3 and k_4, scatter of the points on the plot of equation (9) is more serious and the values of the constants are less certain. The following were chosen: $k_3 = 0.210$, $k_4 = 0.46$. The average deviation of $k'_{\text{calcd.}}$ from $k'_{\text{obsd.}}$ is 0.0005. Instead of tabulating these results the plot shown in Fig. 3 is given to illustrate. Values of C_{H^+} and C_A were obtained from the equation

$$-\log K_c = 2.855 - 1.02\sqrt{\mu} + 0.1\mu \qquad (11)$$

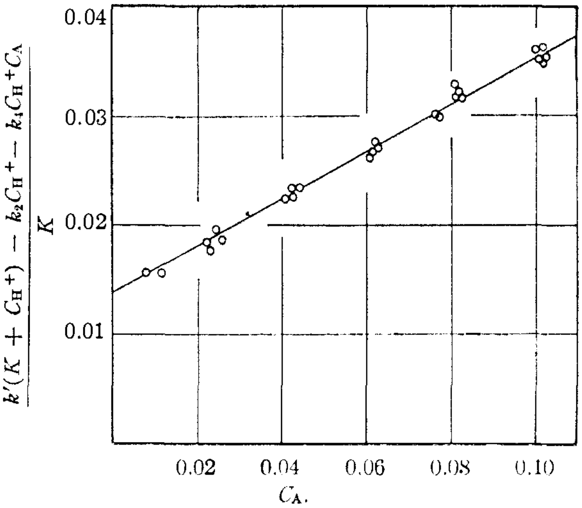

Fig. 3.—Graphical representation of rates in chloroacetate buffers.

Equation (7) does not represent the rates in solutions of perchloric acid to which phosphoric acid or glycinium perchlorate has been added, *i.e.*, where C_A and the increase in C_{H^+} are appreciable. With the former, catalysis by $H_2PO_4^-$ ion seems to be completely lost; with the latter the same is true with sufficient perchloric acid present. Table IV gives rate constants; the last column gives values calculated from equation (7) omitting terms in k_3 and k_4

$$k' = \frac{k_1K + k_2C_{H^+}}{K + C_{H^+}} \qquad (12)$$

TABLE IV

RATE CONSTANTS WITH PHOSPHORIC ACID AND GLYCINIUM PERCHLORATE ADDED TO PERCHLORIC ACID

C_{HClO_4}, M	$C_{H_3PO_4}$, M	k', obsd.	k', calcd. Eq. (7)	k', calcd. Eq. (12)
0.06	0	0.0590 .0605	0.0588	0.0588
.06	0.03	.0614	.0644	.0611
.06	.06	.0630	.0703	.0631
.06	.10	.0628	.0756	.0654
	$C_{Gl.ClO_4}$, M			
.02	0.08	0.0449	0.0479	0.0414
.04	.08	.0559	.0574	.0520
.06	.08	.0628	.0658	.0611
.08	.08	.0692	.0731	.0689

Salt Effects.—The effect on the rate of changing ionic strength is rather complex in the buffer systems, but fortunately is not large. The secondary effect on the buffer composition has been taken into account as described, but secondary effect on the diazomalonate equilibrium and primary effect on the rates have been ignored. Consequently the values of K, k_3 and k_4 are mean values which fit the data best at all ionic strengths used.

The constants k_1 and k_2 are subject to little salt effect since they apply to the reaction with water molecules. Salt effect in strong acid is then secondary and negative since C_{HN^-} decreases with ionic strength and $k_2 > k_1$. The numerical values of k_3 and k_4 should increase with μ if the base involved is an anion, and the secondary effect on equilibrium (3) will partly compensate in those buffers where C_{HN^-} is appreciable.

Table V shows some rates with added sodium perchlorate. In aniline buffers the effect is small as expected; in buffers of the three weakest acids the effect found is about 12%, between μ = 0.02 and 0.08.

TABLE V

SALT EFFECTS IN WEAK ACID BUFFERS

	C_{HA}, *M*	C_A, *M*	C_{NaClO_4}, *M*	*k'*
Trimethylacetate	0.06	0.02	..	0.0328
	.06	.02	0.06	.0369
Acetate	.06	.02	..	.0267
	.06	.02	.06	.0302
Glycolate	.06	.02	..	.0240
	.06	.02	.06	.0269
Chloroacetate	.062	.02	..	.0283
	.062	.02	.06	.0304
Aniline	.04	.11	..	.0702
	.04	.11	.04	.0708
	.04	.11	.08	.0705
	.04	.11	.12	.0718

Discussion

The values of k_3, collected in Table VI, may be compared with the Brönsted relation

$$k_3/q = G_B(K_B p/q)^\beta \qquad (13)$$

The values of k_4 are not sufficiently accurate to apply this equation. Using the factors p and q as suggested by Pedersen,[2] four anions show close agreement with the expression

$$\log k_3/q = -1.61 + 0.273 \log p/(qK_A) \qquad (14)$$

Bases like aniline and glycine usually follow similar equations with somewhat different constants. The value for water, *i.e.* log $k_1/55.5$, is too small by 1.5 units to fit equation (14). Usually water catalysis agrees within less than 1 log unit with the value calculated from anion catalysis (Bell, ref. 2, p. 92), but it is also true that β is usually larger than the value 0.273 found here.

TABLE VI

SUMMARY OF RATE AND STRENGTH CONSTANTS

Base	k_3	K_A
Me_3 acetate	1.02	8.91×10^{-6} [a]
Acetate	0.80	1.754×10^{-5} [b]
Aniline	.52	2.54×10^{-5} [c]
Glycolate	.48	1.475×10^{-4} [b]
Cl acetate	.210	1.396×10^{-3} [d]
Glycine	.229	4.47×10^{-3} [b]
Phosphate	.206	7.52×10^{-3} [b]
Water	2.52×10^{-4}	55.5

[a] J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938). [b] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 580. [c] K. J. Pedersen, *Det Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, XIV (9) (1937). [d] D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N.Y., 1939, p. 349.

NEW YORK 3, N. Y.

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[2] K. J. Pedersen, "Den Almindelige Syre-og Base-katalyse," Bianco Lunos Bogtrykkeri, Copenhagen, 1932; R. P. Bell "Acid-Base Catalysis," Oxford, Clarendon Press, Chapter V, 1941.

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XIII.[1] A Partial Resolution of Racemic Tartaric Acid by Means of Different Stabilities of Isomers of Complex Ions[2]

BY JOHN C. BAILAR, JR., HANS B. JONASSEN AND ALLAN D. GOTT

RECEIVED DECEMBER 6, 1951

When the cobalt complex made from levo-propylenediamine and racemic tartaric acid, $[Co(l\text{-pn})_2(rac\text{-tart})]Cl$, is heated in aqueous solution at 70° with an excess of levo-propylenediamine (1,2-diaminopropane), the levo-propylenediamine molecules preferentially displace the levo-tartrate ion. The dextro-tartrate ion appears to be more strongly held in the coördination sphere and is displaced only over a longer period of time at 70°. This paper presents experimental evidence to support this statement as well as other evidence which indicates that the isomers containing the levo-tartrate ion and the dextro-tartrate ion have different stabilities.

Introduction

When unsymmetrical or optically active groups coördinate with a metallic ion, several possibilities for isomerism arise. If, for example, an optically active bidentate coördinating group combines with a metallic ion having a coördination number of six, one might expect the eight stereoisomeric compounds D*ddd*, D*ddl*, D*dll*, D*lll*, L*lll*, L*lld*, L*ldd*, L*ddd*, where *d* and *l* represent the isomeric configurations of the coördinating molecules, and D and L the configurations around the metal nucleus. In the cases which have been studied, however, it has been found that only two of the eight compounds are stable enough to be isolated—D*lll* and L*ddd*. Two factors seem to be important in this. First, efforts to attach molecules of the *same* coördinating agent but of different configuration to the same metallic ion have not been successful; this eliminates the configurations represented by D*ddl*, D*dll*, L*lld* and L*ldd*. Secondly, the configuration of the coördinating agent seems to determine the configuration of the complex as a whole; in the cases studied, this has eliminated the configurations shown by D*ddd* and L*lll*.[3]

Consideration of the first phenomenon suggests that if a complex contains two optically active bidentate groups, a third optically active group might coördinate firmly if it has the same configuration as those already present. The enantiomorph of this third group should coördinate less readily, and the result would be a complex of lower

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[1] For the previous article in the series, see Sister Mary Martinette and Bailar, THIS JOURNAL, 74, 1054 (1952).

[2] Most of the work reported in this article was taken from the doctorate thesis of Hans Jonassen (1946), and Allan Gott (1952).

[3] See, however, the paper by Sister Mary Martinette and Bailar, ref. 1, where it is shown that this is not true for the complex ion $[Co(levo\text{-}pn)_2CO_3]^+$, which exists in both D- and L-forms. In this case, however, the complex contains only two molecules of the optically active coördinating agent.