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The reversible splitting of organomercuric cyanides with hydrogen chloride

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THE REVERSIBLE SPLITTING OF ORGANOMERCURIC
CYANIDES WITH HYDROGEN CHLORIDE

BY

Edward Carr

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Plant Chemistry

Approved

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Dean of Graduate College

Iowa State College

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INTRODUCTION

In the evolution of organic chemistry into a highly systematized body of knowledge it has been the common practice to classify compounds qualitatively in groups characterized by a type of structure. For example, the carboxylic acids, RCOOH , have been classified according to the type of structure of R. On this basis we have the aliphatic, aromatic and heterocyclic acids. Such classification developed very naturally from studies of the behavior of typical members of various classes. However, synthetic developments have yielded many compounds in these classes whose behavior departs more or less from that of "typical" members. In other words, a typical member may be so modified by substitution that its behavior in some respect becomes more like that of typical members of some other class. For example, the typical aliphatic acid $\text{CH}_3\text{CH}_2\text{COOH}$ having an ionization constant in the range of low values characteristic of such acids can, by chlorine substitution, be converted into a relatively strong acid with a constant comparable with that of alpha furoic acid. Thus, in so far as an ionization constant may be considered as an indicator, the radical CH_3CH_2- may be said to have been endowed through substitution with a heterocyclic property. On the basis of the magnitude of the ionization constant the chlorine-containing radical more logically should be classified with the heterocyclic radicals than with the aliphatic radicals. As a second example, if a methyl-

ene group is interposed between the phenyl radical and the amino group of aniline the magnitude of the ionization constant of the resulting amine, benzyl amine, is about 10^6 times that of aniline and lies in the range of values characteristic of typical aliphatic amines. A further modification produced by introducing a chlorine atom into the ortho position of benzyl amine decreases the value of the constant back toward that of aniline. Thus it would seem that an acid RCOOH or an amine RNH_2 might be made to have an arbitrary ionization constant within the limits for such compounds provided the proper radical R is attached to the functional group.

Such gradations of electrical properties from one typical class to another suggest that some property other than type of structure may better serve as a basis for systematizing organic chemistry. A point of attack that naturally suggests itself is a study of the relatively permanent aggregates of atoms designated as radicals. If some fundamental property common to organic radicals exists, capable of serving as a classifying index, the assaying of this property should yield a more natural and adequate means of systematizing organic chemistry.

This problem has been attacked in various ways by many investigators. A general survey of earlier theories and work

is given by Henrich, Johnson and Hahn (1).

An examination of the ionization constants of organic acids, RCOOH , where R contains no ionizable group, shows that the constants range in value from about 10^{-5} to about 10^{-1} . The range of the amine constants is from about 10^{-14} to about 10^{-4} . If a series of amines is arranged in the order of increasing ionization constants the radicals attached to the amino group should be arranged in the order of increase in the magnitude of some property of the radicals which is effective in producing a given magnitude of ionization. The ionization constants can be so placed relatively to each other as to give an orderly increase in their magnitudes. Corresponding to each ionization constant there would be a radical. If to each radical there were assigned a number the condition that a functional relation exist between the ionization constants and the numbers designating the radicals would be satisfied.

Such a functional relation was established by Hixon and Johns (2). They demonstrated that organic radicals fall into a significant series on plotting as ordinates on a smooth arbitrarily drawn curve the logarithms of the ionization constants of a series of primary amines. At the point on the ab-

- (1) Henrich, Johnson and Hahn, "Theories of Organic Chemistry", John Wiley and Sons, New York, 1922, pp. 75-167.
(2) Hixon and Johns, J. Am. Chem. Soc., 49, 1786-95 (1927).

scissa corresponding to log K for a given amine the radical was placed. This procedure fixed the radicals along the abscissa at points which must necessarily satisfy a functional relation. Added confidence in this procedure was immediately given when upon plotting log K of the carboxylic acids against the radicals thus fixed along the axis a smooth curve was obtained. Mathematical expressions of the form

$$\log K = ke^{ax+b} + c$$

were adjusted to the amine and acid curves.

The soundness of this procedure was more conclusively demonstrated and something of its significance revealed by subsequent work. The data obtained may be classified as follows:

1. In water the ionization constants of the organo mercuric nitrates (3), the α -substituted pyrrolidines (4,5), the α -substituted pyrrolines (5), and the N-substituted pyrrolidines (4).
2. In methanol the ionization constants of the carboxylic acids (6), the primary amines (6), and the substituted pyrrolidines (6).

- (3) Johns and Hixon, J. Phys. Chem., 34, 2218-25 (1930).
(4) Craig and Hixon, J. Am. Chem. Soc., 53, 4367-72 (1931).
(5) Starr, Bulbrook and Hixon, ibid., 54, 3971-76 (1932).
(6) Goodhue and Hixon, ibid., 56, 1329-33 (1934).

3. In ethanol the ionization constants of the carboxylic acids (6), the primary amines (6), and the equilibrium constants of the reaction



4. In benzene the equilibrium constants for the reaction $Cl_3CH(OH)SR \rightleftharpoons Cl_3CHO + RSH$ (8).

The logarithms of these constants were plotted against the radicals as they had previously been fixed on the abscissa.

Smooth curves were obtained.

Thus there is established for organic radicals a quantitative scale on which a radical has a characteristic constant value. This scale serves as the axis of an independent variable. In this systematization the guiding principle was that the only reliable information on affinity relations between chemical groups is given by the free energy change of reversible processes in which the influence of the groups is involved.

Attempts have also been made to systematize organic radicals in an electronegativity series on the basis of the splitting of unsymmetrical organomercuric (9) and organolead compounds (10). In the unsymmetrical organomercuric compounds

- (7) Johns and Hixon, *J. Phys. Chem.*, 34, 2226-35 (1930).
(8) Johns and Hixon, *J. Am. Chem. Soc.*, 56, 1333-36 (1934).
(9) Kharasch and Grafflin, *J. Am. Chem. Soc.*, 47, 1948-54 (1925).
Kharasch and Marker, *ibid.*, 48, 3130-43 (1926).
Kharasch and Flenner, *ibid.*, 54, 674-92 (1932).
(10) Gilman, Towne and Jones, *ibid.*, 55, 4689-93 (1933).

the relative electronegativity of the radical R' in the compound RHGR' was defined as follows (9): "The group R' which presumably first dissociates from the mercury and then combines with the hydrogen ion in solution to form the hydrocarbon R'H is defined as the more electronegative of the two radicals; that is, it has the greater attraction for electrons". The radicals studied in these cleavage experiments were arranged in a series. The interpretation placed on the series was that any radical in it is more electronegative than any below it and less electronegative than any above it. A comparison of this series of radicals with that obtained on the basis of ionization constants reveals that there is considerable difference in the relative positions of various radicals. In the series obtained by the splitting of the mercury compounds the nitro, bromo and chloro substituted phenyl radicals are listed as less electronegative than phenyl while the tolyl group is listed as more negative than phenyl. The benzyl radical is listed as less electronegative than the saturated aliphatic radicals. The opposite of these results is the case in the series based on ionization and equilibrium constants.

The question naturally arises as to the comparative significance of the results of the two methods of systematizing organic radicals. First of all, it is to be recognized that there is a fundamental difference between the reactions used in the two methods, in that one is reversible whereas the other is irreversible. It would seem that if each method is valid

in its own sphere it measures a different property than does the other. It was with a view to clarifying the comparative significance of the two methods that the work reported in this thesis was undertaken.

EXPERIMENTAL

Statement of the Problem

This thesis reports a study of the reaction of a few organomercuric cyanides with HCl in ethyl alcohol. There were two main purposes in carrying out the study:

1. To add to the series of reactions already studied, a true double decomposition reaction.
2. To obtain data on a reversible decomposition of an unsymmetrical type of organomercuric compound with HCl, with a view to lending to such a reaction amenability to thermodynamic treatment.

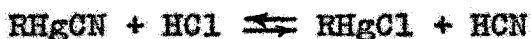
The reaction of the compounds RHgCN with HCl should be suited to these purposes for the following reasons:

1. The cyanide radical attached to mercury in the compounds RHgCN is removed by HCl in dilute solution to the exclusion of all but the most labile radicals R. As an example of the cleavage of a very labile radical from an RHgX compound we have the case of phenacyl mercuric chloride. This compound reacts with warm dilute HCl to give acetophenone (11). In the case of those radicals

(11) Dimroth, Ber., 35, 2870 (1902).

chosen for these measurements cleavage of the R-Hg bond could not have been significant as evidenced by the rapidity with which the reactions attained constant conductivity and by the length of time the conductivity remained constant.

In the splitting of the unsymmetrical organomercuric compounds RHgR' one or both of the radicals would be split off. The result was a heterogeneous system consisting of a solid phase of varying proportions of RHgCl and $\text{R}'\text{HgCl}$ and the homogeneous solution. In the absence of a tendency to reverse the reaction, the precipitate would account for a complete reaction minus the amount of organomercuric chlorides remaining in solution. Such a system does not lend itself to the determination of free energies. In the case of the organomercuric cyanides treated by Kharasch, namely, ethyl mercuric cyanide and orthoanisyl mercuric cyanide, apparently quantitative yields of RHgCl were obtained. But the solution above the solid phase must contain RHgCl to the extent of its solubility. If there is a tendency for HCN to react with RHgCl the solution should contain an equilibrium mixture of RHgCN , HCl , RHgCl and HCN . The equation for the reaction would be written as follows:



Thus, in the case of the cyanides by measuring only the amount of the solid phase the more important equilibrium in solution is ignored. Quite obviously, if the CN radical is cleaved off by HCl to the exclusion of R, practically all the cyanides will appear to give quantitative yields of RHgCl due to the great insolubility of these compounds.

Under certain conditions, compounds of the type RHgX are known to transform into R_2Hg and HgX_2 . But in the absence of reagents conducive to this transformation it probably does not take place to an appreciable extent. That this transformation does not take place to an appreciable extent in the case of the compounds studied is borne out by the following observations. The compounds methyl, ethyl, phenyl and tolyl mercuric chloride, alpha naphthyl mercuric acetate (12) and cyclohexyl mercuric bromide (13) when treated with soluble sulfides give immediate precipitates of stable white organomercuric sulfides of the formula $(\text{RHg})_2\text{S}$. An experiment with benzyl and o-chlorobenzyl mer-

(12) Whitmore, "Organic Compounds of Mercury", Chemical Catalog Co., (1921), pp. 50-59.

(13) ibid., p. 189.

curic chloride demonstrated that also these compounds behave in the same way. It seems likely, therefore, that the compounds RHgCN and RHgCl occurring in the reactions studied persist as such, and yield on ionization $\text{RHg}^+ + \text{X}^-$.

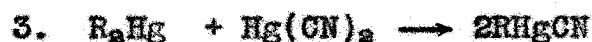
2. The conductivities of RHgCN , RHgCl and HCN are very low while that of HCl is comparatively high. Hence, a measurement of the conductivity of a reaction mixture should permit the calculation of equilibrium concentrations of all the components present. The corresponding equilibrium constant and the free energy of the reaction could be calculated in the usual way. These thermodynamic quantities would serve as a measure of that property of the radicals R which is effective in giving a characteristic extent of reaction. The energy of the reaction, not the radical split off, would in this case determine the position of any radical in a series.

Materials and Apparatus

The organomercuric chlorides were furnished by Dr. I. B. Johns. Several of these were recrystallized from appropriate solvents and the melting points of all of them determined.

The specific conductivity of 0.005N solutions in alcohol was determined. The purity of the compounds was assumed to be indicated by their melting points and conductivities. The data are given in table I.

In the preparation of the organomercuric cyanides three methods were employed depending on the starting materials available:



Cyclohexyl and o-chlorobenzyl mercuric cyanides were prepared by reaction 1. A solution of the bromide in acetone was shaken at intervals over a period of half an hour with excess silver cyanide at room temperature. The precipitate was allowed to settle and the solution filtered. The acetone was evaporated and the melting point of the solid determined. The treatment with silver cyanide was repeated until the solid recovered from the solvent had a constant melting point. Two such treatments were usually sufficient. A test for halogen was made by decomposing the compound with concentrated nitric acid and adding silver nitrate. Absence of opalescence was taken to be a negative test for halogen.

The benzyl, phenyl and naphthyl compounds were prepared by reaction 2 since the R_2Hg compounds were available. The reaction of R_2Hg with HgI_2 proceeded readily in acetone at room temperature. The reaction of the resulting iodides with silver cyanide was practically immediate in acetone as evidenced by the rapid change of the color of the solid phase from gray to yellow. Benzyl and naphthyl mercuric cyanides were crystallized from acetone by adding water. Phenyl mercuric cyanide was recrystallized from alcohol.

Ethyl mercuric cyanide was prepared by allowing a benzene solution of diethyl mercury to stand in contact with mercuric cyanide. At the end of three months the solid mercuric cyanide had disappeared. Evaporation of the benzene yielded a solid which on being crystallized from ether by adding petroleum ether melted sharply at $56.5^\circ C$.

Methyl mercuric cyanide was prepared by both reactions 1 and 3. Reaction 3 was carried out in water in a sealed tube at $120^\circ C$. The compound was crystallized from carbon tetrachloride by adding petroleum ether.

The p-tolyl compound was prepared by both reactions 2 and 3. It was recrystallized from acetone by adding water.

All the cyanides were tested for halogen as described above, and were analyzed for nitrogen by a micro-Dumas analysis. This analysis was chosen in preference to a mercury analysis due to the fact that the latter does not distinguish between a cyanide and a mixture of cyanide and chloride contain-

ing as high as twenty-five per cent chloride.

The specific conductivity of 0.005N solutions of the organomercuric cyanides in alcohol was determined. The procedure, as also for the chlorides, was as follows: Into a conductivity cell was introduced 25 ccm. of alcohol and its specific conductivity determined. The calculated amount of compound was then introduced and the specific conductivity of the resulting solution determined. The conductivity of the compound exclusive of the solvent was calculated by subtracting that of the solvent from that of the solution. The data on the compounds are given in table I. In the case of cyclohexyl, ethyl and phenyl mercuric cyanides no increase in conductance over that of the solvent was determinable. This merely means that the null point on the bridge was so great as not to permit distinguishing a very small increase in conductance at such low values.

The alcohol used was absolute ethyl alcohol obtained from the chemistry storeroom. The conductivity of the alcohol varied from 2×10^{-7} to 3.5×10^{-7} . Determination of the conductivity of HCl in samples of this alcohol obtained from the storeroom at various times showed that the conductivity varied from sample to sample. These variations were ascribed to varying amounts of water in the alcohol. As was shown by Goldschmidt (14) small variations in the water content of practi-

(14) Goldschmidt, Z. physik. Chem., 89, 129-144 (1914).

TABLE I

Melting Points, Analyses and Specific Conductivities
at 25°C. of Compounds

Compound	Melting Point	Analysis for N:		Conductivity	
		Calc.	Obs.	0.005N Soln.	Compound
C ₆ H ₁₁ HgCN Cl	146- 7°	4.52	4.66	2.8	0.0
	163- 4°			3.1	0.3
CH ₃ HgCN Cl	92- 3°	5.87	5.79	4.2*	0.7
	170°			6.4**	3.3
C ₂ H ₅ HgCN Cl	56.5°	5.48	5.47	2.8	0.0
	192°			3.4	0.6
C ₆ H ₅ CH ₂ HgCN Cl	127- 8°	4.41	4.36	3.0	0.2
	103- 4°				2.9 [∅]
o-ClC ₆ H ₄ CH ₂ HgCN Cl	138- 9°	3.98	4.11	3.0	0.2
	111-12°			4.7 [∅]	2.3
p-CH ₃ C ₆ H ₄ HgCN Cl	221- 2°	4.41	4.40	3.0	0.2
	233°			5.1 [∅]	2.7
C ₆ H ₅ HgCN Cl	209-10°	4.61	4.56	2.8	0.0
	251°			3.8	1.0
C ₁₀ H ₇ HgCN	236°	3.96	4.03	3.1	0.3
HCN				4.5 [∅]	1.5

The specific conductivity of the alcohol used unless otherwise stated was 2.8×10^{-7} .

* Specific conductivity of alcohol 3.5×10^{-7} .

** Specific conductivity of alcohol 3.1×10^{-7} .

[∅] Specific conductivity of alcohol 2.4×10^{-7} . The specific conductance of benzyl mercuric chloride at 0.005N was estimated by comparison with the value for o-chlorobenzyl mercuric chloride which was run at 0.006N.

∅ The value for HCN is the average of several values.

cally absolute alcohol appreciably affect the conductivity of HCl in solution. Experiment showed, however, that the values of the calculated equilibrium constants were the same when determined in samples of alcohol in which the conductivity of HCl was different. For this reason the alcohol was not subjected to further purification.

Dry hydrogen chloride was prepared by dropping concentrated sulphuric acid on to c. p. sodium chloride and passing the gas through sulphuric acid bottles and through a P_2O_5 tower.

Hydrogen cyanide was prepared by dropping 1:1 sulphuric acid onto potassium cyanide and passing the gas through long tubes of anhydrous calcium chloride and through a cotton plug.

The conductivity cells were of the usual type. A Leeds and Northrup student potentiometer was used as a Wheatstone bridge in conjunction with Leeds and Northrup resistance boxes.

Determination of Equilibrium Constants

Preliminary experiments on the reaction of $RHgCN$ with HCl in alcohol indicated that the reaction proceeded to a great extent in the direction of the production of $RHgCl$ and HCN, as shown by the great decrease in the conductivity of a solution of HCl into which was introduced an equivalent amount of $RHgCN$. The resulting conductivity, however, was of the order of a hundred times the sum of those of $RHgCl$ and HCN at the concentration that would be produced by a complete

reaction. Upon adding an equivalent amount of RHgCl to a solution of HCN the resulting conductivity was of the order of a hundred times the conductivity of a solution of the unreacted compounds. In view of the low conductivities of RHgCN , RHgCl and of HCN the relatively high conductivity of the reactions was attributed to the presence of HCl . This behavior indicates a reversal of the reaction.

The procedure followed in running the reactions was as follows: A solution of HCl of about 0.01N concentration was prepared in alcohol and analyzed for chloride. The analysis consisted of adding excess standard silver nitrate solution, filtering off the silver chloride, and titrating the filtrate for silver by the method of Sharwood (15). This method was selected in preference to the Volhard method due to the sharper endpoint in dilute solutions. A portion of this analyzed solution was diluted to 0.005N for running the reaction of RHgCN with HCl . A second portion was diluted to the range of concentration of the reactions and 25 ccm. of such solution introduced into a conductivity cell. Successive dilutions of this solution were made by pipetting portions of solution from the conductivity cell and replacing them with equal portions of alcohol. The conductivity was measured after each such dilution. In this way a series of concentrations and the corresponding conductivities were obtained in the range of concentration oc-

(15) Sharwood, J. Am. Chem. Soc., 19, 400-434 (1897).

curring in the reactions. The data are contained in table II.

TABLE II

Concentration-conductivity Data for HCl in Ethanol
t = 25°C.

	Normality	Specific Conductivity $\times 10^8$
I	0.000707	4.66
	0.000424	2.83
	0.000254	1.74
	0.000212	1.44
II	0.00100	6.31
	0.000600	3.91
	0.000120	0.803
III	0.000600	3.81
	0.000360	2.28
	0.000272	1.75
	0.000218	1.40
	0.000174	1.13
	0.000139	0.916
IV	0.000186	1.17
	0.000149	0.957
	0.000119	0.776

The specific conductivity values were plotted against the concentration of HCl. The graphs for data I, II and III are shown in figure 1. The data IV are not plotted in figure 1 due to the fact that the contracted scale would not permit distinguishing graph III from graph IV. The different plots are

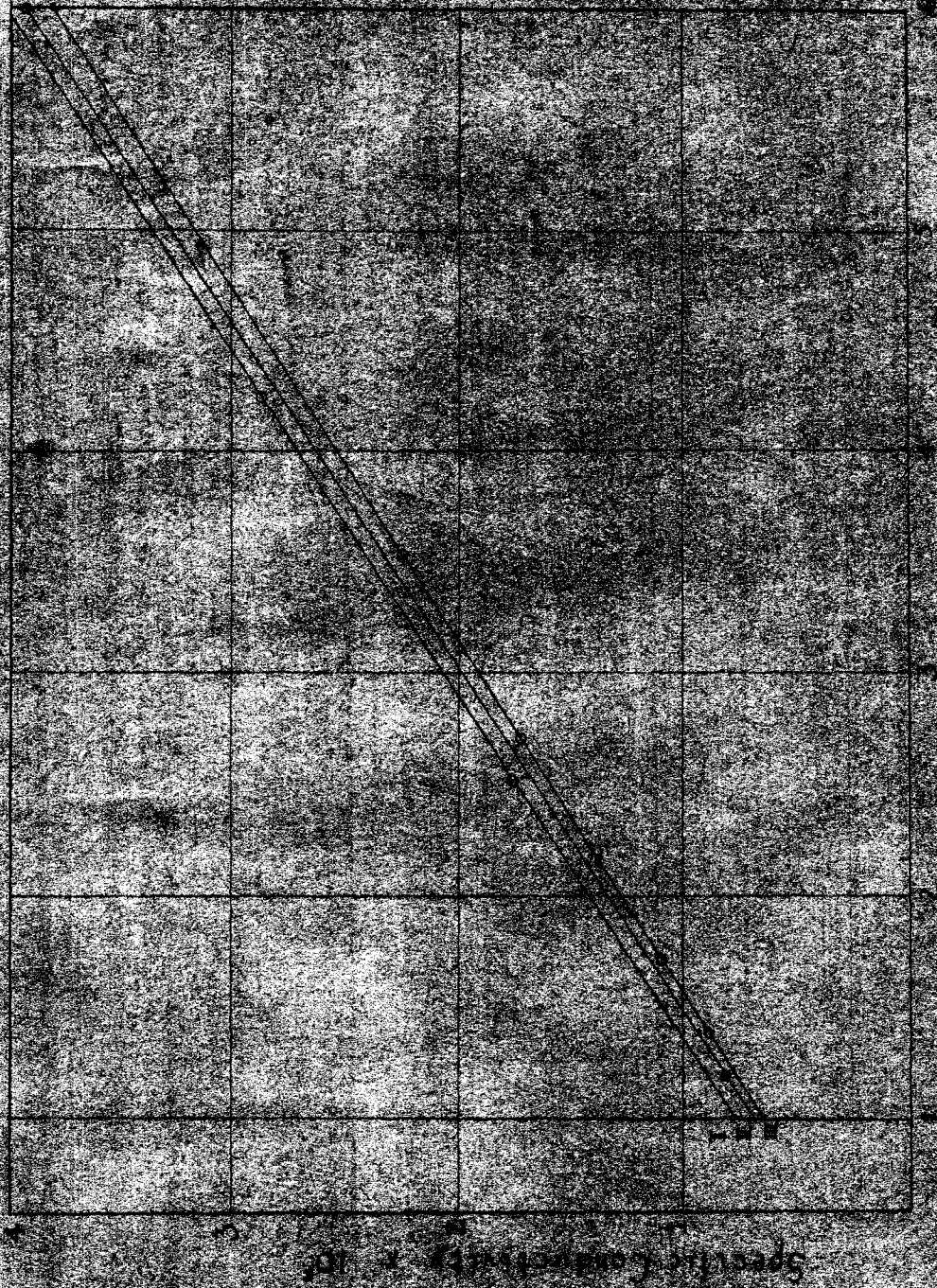


Fig. 1. Concentration-Conductivity graphs for data I, II, and III of Table II.

for different samples of alcohol or for the same sample which had stood long enough to require the determination of new conductivity data.

Into a clean cell was then introduced 25 ccm. of 0.005N HCl solution and into this an equivalent quantity of RHgCN. In practically all cases the conductivity of the reaction mixture had become constant by the time a measurement could be made which was a matter of not more than five minutes. A reaction mixture of o-chlorobenzyl mercuric cyanide and HCl remained constant in conductivity for eighteen hours, while one for ethyl mercuric cyanide remained constant for twenty-four hours. It is to be expected that HCl will react with the alcohol and hence constancy in conductivity for longer periods than this is not to be expected. The resulting conductivity was measured and a correction made for the conductivity of RHgCl and HCN, using the values of table I. The concentration of HCl corresponding to this corrected conductivity was determined from the conductivity-concentration graph for the sample of alcohol used as solvent. The concentrations of the remaining components were calculated from the equilibrium value for HCl and the initial concentration of HCl. The reverse reaction between RHgCl and HCN was run in a similar manner. The HCN solutions also were analyzed by the method of Sharwood (15). Test titrations showed that the cyanide did not need to be in the form of an alkali cyanide to give correct results in analysis. The data for all runs are tabulated in

table III. The values in column VI are $K \times 10^{-8}$, where

$$K = \frac{\frac{RHgCl}{HCN}}{\frac{RHgCN}{HCl}}$$

The correction for the conductance of $RHgCl$ and HCN , assuming them to be at 0.005N, is essentially correct since these compounds at equilibrium are very close to 0.005N in concentration and since the change of conductance of these compounds with change in concentration is very small. A reduction in the concentration of a solution of o-chlorobenzyl mercuric chloride from 0.01N to 0.006N, a reduction of forty per cent, produced a reduction in the specific conductivity of only 0.5×10^{-7} . The greatest deviation of the concentration of $RHgCl$ from 0.005N in table III is only twenty per cent. A forty per cent decrease in the concentration of HCN at 0.07N gave a change in the conductivity of only 0.3×10^{-7} . Hence, the error in the conductivity of the HCl due to this correction is not greater than 1×10^{-7} , which corresponds to an error in concentration of HCl of less than one per cent.

Certain limitations are inherent in the determination of the equilibrium constants for these reactions. The great extent of the reactions to the right diminishes the concentration of HCl to a very low value, thereby decreasing the accuracy with which the equilibrium constants can be calculated. The low solubility of the organomercuric chlorides limits the concentrations at which these compounds can be run. With a view to determining whether the equilibrium constants were in-

TABLE III

Equilibrium Data at 25°C. for the Reaction



Reactants Initially at 0.005N

Radical	I	II	III	IV	V	VI
$\text{C}_6\text{H}_{11}-$.85	.83	IV	1.27	48.7	14.7
	.85	.83	IV	1.27	48.7	14.7
C_2H_5-	1.13	1.11	II	1.68	48.3	8.3
	1.12	1.10	II	1.66	48.3	8.5
	1.11	1.09	III	1.68	48.3	8.3
CH_3-	1.69	1.64	III	2.56	47.4	3.4
	1.56	1.51	IV	2.39	47.6	4.0
	1.59	1.54	IV	2.45	47.6	3.8
	1.53	1.48	IV	2.36	47.6	4.1
	1.54*	1.49	I	2.15	47.9	5.0
$\text{C}_6\text{H}_5\text{CH}_2-$	1.47	1.43	I	2.06	47.9	5.4
	1.33	1.29	III	2.01	48.0	5.7
	1.33	1.29	III	2.01	48.0	5.7
	1.31*	1.27	II	1.93	48.1	6.2
$o\text{-ClC}_6\text{H}_4\text{CH}_2-$	1.58	1.54	I	2.24	47.8	4.5
	1.53	1.49	II	2.28	47.7	4.4
	1.46	1.42	IV	2.26	47.7	4.5
	1.43*	1.39	I	2.00	48.0	5.8
	1.43*	1.39	I	2.00	48.0	5.8
$p\text{-CH}_3\text{C}_6\text{H}_4-$	2.02	1.98	I	2.90	47.1	2.6
	2.01	1.97	II	3.00	47.0	2.5
	1.95	1.91	III	2.97	47.0	2.5
	1.85*	1.81	I	2.64	47.4	3.2
C_6H_5-	2.29	2.26	∅	2.90, 3.50	47.0	2.2
	2.02	1.99	I	2.91	47.1	2.6
	1.93	1.90	III	2.95	47.1	2.6
	1.82*	1.79	I	2.62	47.4	3.3
C_{10}H_7-	2.18	2.15**	∅	2.70, 2.90	37.1	1.8
	2.25	2.22**	I	3.28	46.7	2.0
	2.36	2.33**	II	3.56	46.4	1.7

I. Specific conductivity $\times 10^5$ of reaction mixture; II. Corrected conductivity obtained by subtracting from I the conductivity of RHgCl and HCN in table I; III. Conductivity-concentration data of table II; IV. Equilibrium concentration $\times 10^4$ of HCl and RHgCN obtained from graph of conductivity concentration data of table II; V. Calculated concentration $\times 10^4$ of RHgCl and HCN ; VI. $K \times 10^{-2}$.

* $\text{RHgCl} + \text{HCN}$ initially at 0.005N.

** Same correction as for phenyl.

∅ Extrapolated from graph for data not shown in table II.

∅ Initial $\text{C}_6\text{H}_5\text{HgCN}$.00505, HCl .00499
 $\text{C}_{10}\text{H}_7\text{HgCN}$.004, HCl .00398

dependent of the concentration a few runs were made at different concentrations of some components. The initial concentrations and the calculated K's are tabulated in table IV. Increase in concentration gave an increase in the value of the constant. Further study of the relation of concentration to the value of the equilibrium constant was not made. For purposes of comparison it was decided to tabulate runs made at one concentration. The concentration 0.005N was chosen since this is very nearly the limit of solubility of the aromatic mercuric chlorides.

TABLE IV

Change of Equilibrium Constants with Concentration

	$\text{o-ClC}_6\text{H}_4\text{CH}_2\text{HgCl}$	HgCN	K = $\frac{[\text{RHgCl}][\text{HgCN}]}{[\text{RHgCN}][\text{HCl}]}$
Initial Concentration	0.01 0.005 0.0131 0.005	0.0657 0.112 0.0131 0.005	14.2×10^2 12.8×10^2 9.15×10^2 5.8×10^2
<hr/>			
	$\text{C}_2\text{H}_5\text{HgCN}$	HCl	K
Initial Concentration	0.0131 0.005	0.0131 0.005	13.5×10^2 8.2×10^2
<hr/>			
	$\text{C}_{10}\text{H}_7\text{HgCN}$	HCl	K
Initial Concentration	0.005 0.005 0.004	0.005 0.005 0.00398	2.0×10^2 1.7×10^2 1.8×10^2

The values of $K \times 10^{-2}$ obtained for methyl are higher than would be expected. Whether this is due to the anomalous behavior often encountered in the case of the first member of a homologous series, or to the operation of some other factor is not known. No doubt factors besides potential determine the behavior of a given radical in a compound (2). Such a factor may be the mass. The extent of the operation of each factor determining the ability of a radical to share electrons would not be expected to remain constant for all combinations of the radical with other atoms.

The values of $K \times 10^{-2}$ recorded in table III, with the exception of those for methyl, decrease regularly from cyclohexyl to naphthyl. This order is in agreement with that of the radicals as previously determined by the ionization constants of acids and amines. Although the constants calculated for the reverse reaction are uniformly high they show the same order of decrease as do those calculated for the forward reaction. No detailed study of the HCN solutions used in running the reverse reactions was made. There can be no doubt that HCl is produced by the reverse reaction inasmuch as the conductivities developed are far in excess of those of the other components. In figure 2 is plotted $-\log K$ against x . The value of K used is the average for the forward reaction. The points on the curve satisfy the relation

$$-\log K = -0.58e^{-0.28x} - 2.12$$

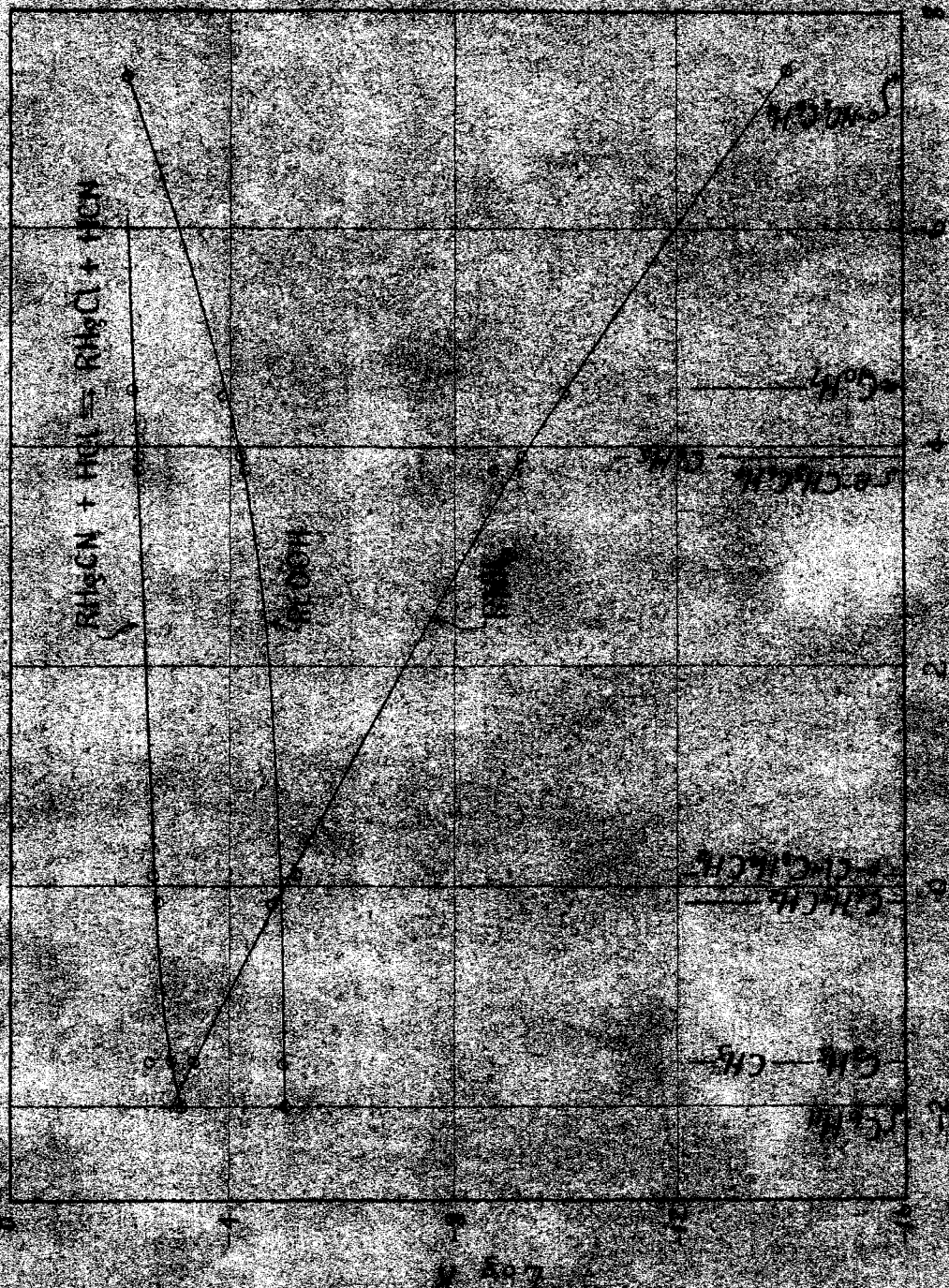


Fig. 21. Curves for the primary amines, carboxylic acids and the reaction $R_1H_2CN + HCl = R_1H_2Cl + HCN$. For the reaction the ordinate is $-\log K$.

On the same graph are plotted curves for the carboxylic acids and the primary amines.

Determination of Decomposition Temperatures
of the Organomercuric Cyanides

The approximate decomposition temperatures of the organomercuric cyanides, were determined by the following procedure. A small amount of a compound was put into a melting point tube and the tube immersed in an oil bath. The oil was heated and the temperature observed at which the first sign of darkening of the compound appeared. In all cases except that of the naphthyl compound the darkening occurred above the melting point. In the case of naphthyl mercuric cyanide both melting and darkening occurred at 236°C. In the case of the other compounds the heating was continued until the melted compound was distinctly black. The range of temperature during the observation was recorded. The values so determined are recorded in table V.

TABLE V

Approximate Decomposition Temperatures
of the Organomercuric Cyanides

Compound	: Decomposition Temperature
	: Degrees Centigrade
$C_6H_{11}HgCN$: 222-35°
C_2H_5HgCN	: 245-65°
CH_3HgCN	: 260-70°
$C_6H_5CH_2HgCN$: 208-16°
$o-ClC_6H_4CH_2HgCN$: 210-15°
$p-CH_3C_6H_4HgCN$: Above 250°
C_6H_5HgCN	: Above 250°
$C_{10}H_7HgCN$: 230-36°
$Hg(CN)_2$: Above 300°

DISCUSSION

The equilibrium data obtained establish that $\log K$ for the reaction $\text{RHgCN} + \text{HCl} \rightleftharpoons \text{RHgCl} + \text{HCN}$ is a function of the abscissa value of the radical. It should follow that, barring anomalous behavior, the logarithm of the equilibrium constant of the reversible splitting reaction involving any radical which has been fixed on the x-axis should satisfy the relation obtained above. Conversely it should be possible to place any radical on the x-axis by determining the equilibrium constant of the reaction in which it is involved.

Comparison of the Results of the Irreversible and Reversible Splitting of the Mercury-Carbon Bond

On the above basis it is interesting to compare the results of the reversible splitting of RHgCN with those of the irreversible splitting of unsymmetrical organomercuric compounds of the type RHgR' . A comparison of the series obtained by the two methods reveals that they do not agree in respect of the positions of many radicals. For example, by the irreversible splitting the benzyl radical is considered to be less electronegative than the saturated aliphatic radicals; the bromine, chlorine and nitro substituted phenyl radicals less electronegative than the phenyl radical; and the tolyl radical more electronegative than the phenyl radical. By the reversible splitting the opposite is true in each case.

In order to get at an understanding of these differences it is well at this juncture to consider the influence of R in the compounds RHgCN on the extent of the reversible splitting. We may assume that the CN group is more negative than any of the radicals R studied. As the negativity of R, that is, its attraction for electrons, is varied a concurrent variation in the negativity of CN should result. In the reaction with HCl different extents of reaction should be required in the case of different R's to establish electrical balance among all groups involved. But the extent to which the reaction must go in order to establish an electrical balance in the system will be a measure of the work done against forces which oppose the tendency of the system to become balanced. The characteristic extent of the reaction should be a function of the tendency of R to attract its valence electrons. The rate at which the reaction attains its limiting extent would be of no importance in determining the energy drop through which the system must fall in order to reach a balance. Experiment demonstrates that among the compounds RHgCN the CN radical is split off more rapidly than any radical R with possible exceptions previously mentioned. But there is no assurance that of two compounds RHgCN and R'HgCN the Hg-CN bond of one will react more rapidly with HCl than will that of the other, regardless of the negativity of the R's. In support of this statement we have the following data on the

esterification of various acids with ethyl alcohol (16):

Acid	Velocity Constant at 185°C.	Equilibrium Constant
Benzoic	0.63	0.40
3,4,5,-Tribromobenzoic	0.90	0.30
2,3,5,-Tribromobenzoic	0.37	0.12
2,4,6,-Tribromobenzoic	0.088	0.42
2,4,6,-Trichlorobenzoic	0.031	0.105
Propionic	0.95	2.24
Isobutyric	1.07	2.10
Trimethyl acetic	0.18	2.00

These data were determined under as nearly comparable conditions as could practically be established. In so far as they give any information on the relation of rates to extents they show that these properties of reactions are independent. Unfortunately, the reaction of RHgCN with HCl due to its rapidity is not suited to velocity measurements. Likewise, the irreversible splitting of RHGR with HCl proceeds too rapidly to permit of velocity measurements. But in view of available data on velocities and extents, and on consideration of the general theory of equilibrium constants we are led to believe that generally rate and extent are independent. A simple derivation of the equilibrium constant clearly shows this. For the metathetical reversible reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$,

$$s_1 = k_1(\text{A})(\text{B}), \quad \text{and} \quad s_2 = k_2(\text{C})(\text{D})$$

- (16) Rosanoff and Prager, J. Am. Chem. Soc., 30, 1895-1907, (1908); Z. physik. Chem., 66, 275-91 (1909).
Prager, J. Am. Chem. Soc., 30, 1908-13 (1908); Z. physik. Chem., 66, 292-99 (1909).

where s_1 is the rate of the forward reaction and s_2 that of the reverse reaction. At equilibrium the only condition that must be satisfied is that $s_1 = s_2$, which condition on being satisfied yields the relation

$$K_{eq} = \frac{(C)(D)}{(A)(B)} = \frac{k_1}{k_2}$$

This expression is quite independent of the rates and depends only on the specific velocity constants.

With these propositions in mind we are in a better position to consider the case of the irreversible splitting of $RHgR'$ compounds with HCl . Adopting the ionization scheme used by Kharasch (8)



we may grant that the ionization lies more to one side than to the other. Assuming that the radical which ionizes to the greater extent is the more negative there is, nevertheless, no assurance that it will combine with H^+ more rapidly than will the other radical. It is true that the proportions of $RHgCl$ and $R'HgCl$ in the solid phase indicate the relative velocities of the two ionic reactions with HCl , but we cannot say that the more highly ionized bond reacted with the greater velocity.

It is interesting to compare the thermal stabilities of

the compounds RHgCN with the reactivities of the compounds RHgR' . If we plot the temperature of decomposition against the radicals as they fall on the x-axis there is obtained the curve in figure 3. It is to be recognized, however, that the temperature of decomposition is only a rough approximation. Nevertheless, it is instructive to observe that this thermal stability curve passes through a minimum. The same order of stability was found in the case of the organomercuric nitrates (17). Moreover, a series of radicals based on thermal stabilities is essentially that of a series based on the irreversible splitting of RHgR' with HCl .

Refraction as a Measure of Electron Constraint

The so-called non-polar bond is conceived of by both physicists and chemists as consisting of two shared electrons. If to a given atom are attached successively different radicals the state of sharing between radical and atom should be different in each case and be characteristic of a particular combination. In other words we would not expect all radicals to be identical in respect of their affinity for the bonding electrons. Conceivably the extent of sharing exercised by various radicals could assume two extreme values, between which various degrees of sharing could exist, depending on the at-

(17) Johns, Peterson and Hixon, J. Phys. Chem., 34, 2218-2225 (1930).

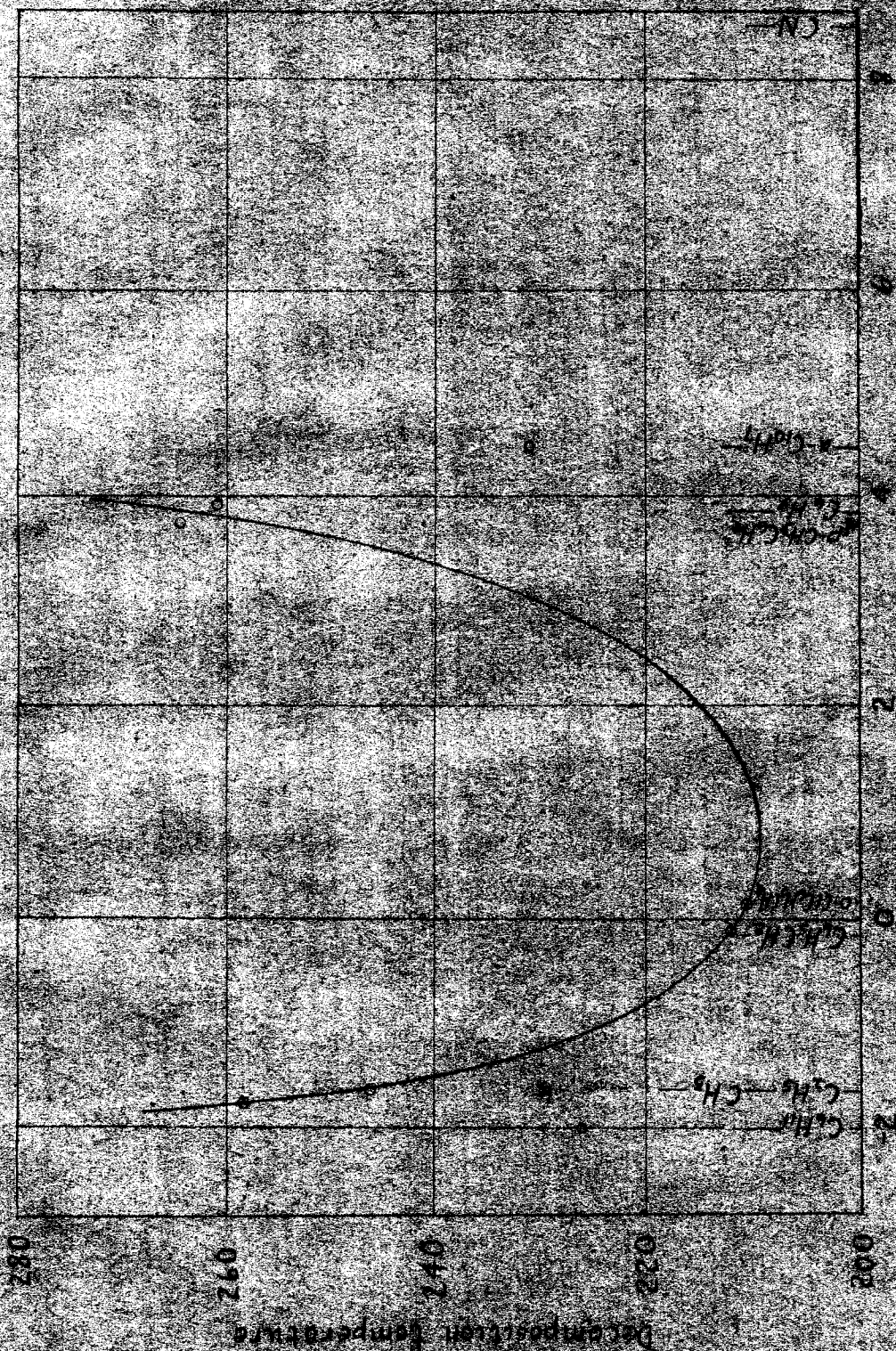


Fig. 3. Graph showing the relation between the thermal stability of the organomercuric cyanides and the position of the radicals on the abscissa.

traction of the radicals for the bonding electrons. At one extreme a radical would be positively ionized, at the other negatively ionized. If this attraction measures the negativity of the radicals the terms negativity and electron-sharing ability are identical. If the extent of ionization of a polar compound such as RNH_2 indicates the attraction of R for the electrons at the R-C bond a more intimate study of this bond should yield more exact information on the relation of negativity of radicals to polar properties.

Smyth (18) attacked the problem of the shared bond by using refraction as a means of calculating the constraint under which the outer electrons of atoms act when the atoms are combined in molecules. Born and Heisenberg (19) proceeded in a somewhat similar way to calculate the deformability of ions. The constraint calculated by Smyth is inversely proportional to and the deformability calculated by Born and Heisenberg is directly proportional to the molecular or ionic refraction. Fajans and Joos (20) have used refraction as a direct measure of the deformability of the electron shells. Krause and Fromm (21), assuming that the atomic refraction of carbon is constant in saturated aliphatic radicals, obtained the result that the atomic refraction of zinc in zinc di-alkyls experiences ex-

(18) Smyth, Phil. Mag., 50, 361-75 (1925).

(19) Born and Heisenberg, Z. Physik, 23, 388-410 (1924).

(20) Fajans and Joos, ibid., 399-410. 1-4/6

(21) Krause and Fromm, Ber., 59, 931-34 (1926).

altation as the size of the alkyl groups is increased. Krause (22) further showed that also the elements mercury, cadmium, tin and lead experience exaltation of atomic refraction when an ethyl group is substituted for a methyl group in the organic compounds of these metals.

All these results suggest that refraction studies can lead to a measure of the constraining force exerted by organic radicals. The use of refraction studies for this purpose would furnish the organic chemist with a method of quantitatively evaluating radicals which would be entirely independent of chemical reactions. The correlation between the results of refraction studies and those of chemical methods would greatly clarify the relation of organic radicals to the properties of their compounds.

(22) Krause, Ber., 59, 935-36 (1926).

CONCLUSIONS

1. The reaction in ethanol between HCl and the organomercuric cyanides studied is reversible.
2. For the reaction a functional relation exists between $\log K$ and the abscissa values of the radicals as determined by the ionization of acids and amines.
3. Irreversible splitting of the Hg-C bond measures a different property of the bond than does reversible splitting.

SUMMARY

1. The compounds o-chlorobenzyl, p-tolyl and α -naphthyl mercuric cyanide are reported for the first time.
2. The approximate decomposition temperatures are reported for cyclohexyl, methyl, ethyl, benzyl, o-chlorobenzyl, p-tolyl, phenyl and naphthyl mercuric cyanides.
3. The equilibrium constants at 25°C. for the reaction
$$\text{RHgCN} + \text{HCl} \rightleftharpoons \text{RHgCl} + \text{HCN}$$
 are reported for the above named organomercuric cyanides.
4. Log K for the reaction is expressed as a mathematical function of the abscissa values of the radicals as determined by the ionization constants of polar compounds.
5. It is pointed out that refraction may be used as a means of evaluating the constraining force exerted by organic radicals.