[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Electron-sharing Ability of Organic Radicals. IX. The Reversible Splitting of Organomercuric Cyanides[1]

BY EDWARD CARR, I. B. JOHNS AND R. M. HIXON

The present work was suggested by the work of Kharasch and co-workers[2] on the irreversible splitting by hydrochloric acid of unsymmetrical organomercurials of the type RHgR′, where R and R′ are bound to mercury by carbon.

The work of Kharasch led to a series of radicals arranged in the order of increasing ease of cleavage from mercury, the series ending in the most easily cleaved radical, namely, -CN.

These authors found that RHgCN in no case was cleaved at the R–Hg bond by HCl, but only at the Hg–CN bond. A series of RHgCN compounds treated with HCl according to the method of Kharasch would give quantitative yields of RHgCl according to the equation

$$\mathrm{RHgCN + HCl \longrightarrow \underset{\substack{\downarrow \\ RHgCl(s)}}{RHgCl} + HCN}$$

The analytical method used required forcing the reaction to completion by removing RHgCl as an insoluble compound. Since hydrogen cyanide is distinctly more reactive than HR, where R is a hydrocarbon radical, it is to be expected that the reaction represented above actually is not irreversible but should be represented as

$$\mathrm{RHgCN + HCl \rightleftarrows \underset{\substack{\downarrow\uparrow \\ RHgCl(s)}}{RHgCl} + HCN}$$

If this reaction is reversible as represented and is carried out at such concentrations that RHgCl cannot precipitate, the reaction mixture will represent a case of homogeneous equilibrium, and will be amenable to the methods available for studying such systems.

In a series of compounds of the type RHgCN the Hg–CN bond should be affected differently by the electron "pull" of different radicals, R, exerted through the mercury atom. The influence of R on the Hg–CN bond should be reflected in the cleavage energy of this bond. A variation of the cleavage energy of the Hg–CN bond with a variation in R should serve as a basis for arranging various R's in a series according to their relative electron "pulls."

The present paper demonstrates that the reaction between RHgCN and hydrochloric acid is reversible, that the equilibrium constant for the reaction varies with R, and that the order of the radicals is the same as previously established for other reversible processes.[3]

Experimental

Ethanol was purified by refluxing the 95% alcohol with calcium oxide for twenty-four hours and distilling. The middle one-third was retained. The conductivity of this ethanol was 2.8×10^{-7}.

Hydrogen chloride was prepared from C. P. sodium chloride and concentrated sulfuric acid and was passed through concentrated sulfuric acid and phosphorus pentoxide, thence into ethanol. Hydrogen cyanide was prepared by dropping 1:1 sulfuric acid onto potassium cyanide and was passed through long tubes of calcium chloride, thence into ethanol. The hydrogen chloride solutions were analyzed for chlorine by the Volhard method. The hydrogen cyanide solutions were analyzed for cyanide by the method of Sharwood.[4]

The organomercuric cyanides and chlorides were prepared by methods described in the literature[5] and were recrystallized at least twice. The cyanides were tested for halogen and were analyzed for nitrogen by the micro-Dumas method.

The specific conductivity of ethanol solutions of RHgCN, RHgCl and hydrogen cyanide are recorded in Tables I and II, and of hydrochloric acid solutions in Table III. Conductivity measurements were made at 25 ± 0.1°, using a Leeds and Northrup student potentiometer and resistance boxes with the usual type conductivity cell. The null point was determined by means of ear phones.

The reaction between RHgCN and hydrochloric acid in ethanol was shown to be quantitatively reversible by preparing separate solutions of these reactants and of the compounds RHgCl and hydrogen cyanide, at a given initial concentration and comparing the resultant specific conductivities. Identical conductivities were obtained in both cases as shown for the benzyl and

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[2] Kharasch, THIS JOURNAL, **47**, 1948 (1925); Kharasch and Marker, *ibid.*, **48**, 3130 (1926); Kharasch and Flenner, *ibid.*, **54**, 674 (1932).

[3] Hixon and Johns, *ibid.*, **49**, 1786 (1927); Johns and Hixon, *J. Phys. Chem.*, **34**, 2226 (1930); Johns, Peterson and Hixon, *ibid.*, **34**, 2218 (1930); Johns and Hixon, THIS JOURNAL, **56**, 1333 (1934); Craig and Hixon, *ibid.*, **53**, 4367 (1931); Goodhue and Hixon, *ibid.*, **56**, 1329 (1934).

[4] Sharwood, *ibid.*, **19**, 400 (1897).

[5] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, N. Y., 1921.

TABLE I

MELTING POINTS, ANALYSES, AND CONDUCTIVITIES OF RHgCN AND RHgCl

Compound	M.p., °C.	N Content, % Calcd.	N Content, % Obsd.	Conductivity[a]
$C_6H_{11}HgCN$	146	4.52	4.66	0.0
Cl	163			.3 × 10^{-7}
C_2H_5HgCN	56.5	5.48	5.47	.0
Cl	192			.6 × 10^{-7}
$C_6H_5CH_2HgCN$	127	4.41	4.36	.2 × 10^{-7}
Cl	103			2.5 × 10^{-7}
o-$ClC_6H_4CH_2HgCN$	138	3.98	4.11	0.2 × 10^{-7}
Cl	111			2.3 × 10^{-7}
p-$CH_3C_6H_4HgCN$	221	4.41	4.40	0.2 × 10^{-7}
Cl	233			2.3 × 10^{-7}
C_6H_5HgCN	209	4.61	4.56	0.0
Cl	251			1.0 × 10^{-7}
α-$C_{10}H_7HgCN$	236	3.96	4.03	0.3 × 10^{-7}

[a] Specific conductivity of 0.005 *N* solution minus the specific conductivity of the solvent (2.8 × 10^{-7}).

TABLE II

CONDUCTIVITY OF ETHANOL SOLUTIONS OF HCN AND *o*-$ClC_6H_4CH_2HgCl$. SPECIFIC CONDUCTIVITY OF ETHANOL: 2.8 × 10^{-7}

HCN normality	Specific conductivity of soln.
0.112	7.5 × 10^{-7}
.0657	6.0 × 10^{-7}
.0131	4.8 × 10^{-7}
.005	4.3 × 10^{-7}
o-$ClC_6H_4CH_2HgCl$	
.01	6.0 × 10^{-7}
.006	5.1 × 10^{-7}
.0036	4.0 × 10^{-7}

phenyl compounds in Table IV. The conductivity reported for the forward and reverse reactions was established immediately upon mixing the reactants and remained constant for twenty-four hours, which is as long as the conductivity of alcoholic hydrochloric acid remains constant. The constancy of the conductivity proves that no irreversible side reactions occur such as the cleavage of the R–Hg bond. Further evidence that the reaction comes to equilibrium is the constancy of the expression for *K* in Table V.

In the reaction between RHgCN and HCl as formulated by the equation

$$\text{RHgCN} + \text{HCl} \rightleftarrows \text{RHgCl} + \text{HCN}$$

only one of the components of the reaction mixture, namely, hydrogen chloride, is highly ionized and therefore the conductivity should be preponderantly due to hydrogen chloride. The magnitude of the conductivities of RHgCN, RHgCl and hydrogen cyanide is shown in Tables I and II. If the conductivities of the components of the mixture other than hydrogen chloride were actually exerted to an extent within the precision of these measurements in the presence of highly ionized hydrochloric acid it would be necessary to correct for these in order to obtain the conductivity of hydrochloric acid alone. But a highly ionized acid tends to suppress the ionization of a weaker acid, the more so the greater the difference between the strengths of the two acids. Assuming a dissociation constant for hydrogen cyanide in alcohol of the order of magnitude[6] of 10^{-10}, it can easily be calculated that hydrogen cyanide at a concentration of 10^{-1} *N* furnishes a hydrogen-ion concentration of only 10^{-7} *N* in the presence of hydrochloric acid at a concentration as low as 10^{-4} *N*. This contribution of hydrogen cyanide to the hydrogen-ion concentration is below the precision of the present measurements, which precision corresponds to a difference in hydrochloric acid concentration of 1 × 10^{-6} *N*. It would require a concentration of hydrogen cyanide of 1 *N* in the presence of hydrochloric acid at a concentration of 10^{-4} *N* to contribute a detectable concentration of hydrogen ion. The same situation exits in the case of RHgCl, the ionization of which would be suppressed by the common ion action of the chlorine ion.

The independence of the conductivity of hydrochloric acid was verified for a mixture containing hydrogen cyanide at 0.1 *N* and hydrochloric acid at 0.005 *N*. The constancy of *K* in Table V indicates that the contribution of RHgCN, RHgCl and hydrogen cyanide to the conductivity of the reaction mixture is not greater than the precision of determining the hydrochloric acid concentration.

The procedure for carrying out a measurement consisted of preparing an ethanol solution of either RHgCN and HCl or of RHgCl and hydrogen cyanide, and measuring the specific

TABLE III

CONDUCTIVITY OF HYDROGEN CHLORIDE IN ETHANOL 25 ± 0.1°. SP. COND. OF ETHANOL 2.8 × 10^{-7}

Normality of HCl	Conductivity Specific	Conductivity Equivalent
7.07 × 10^{-4}	4.66 × 10^{-5}	65.5
4.24	2.83	66.0
2.54	1.73	66.9
2.12	1.45	66.9
1.50	1.03	66.6

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[6] The value in water is of the order of 10^{-10} and would be somewhat less in ethanol.

conductivity of the solution. The concentration of hydrochloric acid in the reaction mixture was then taken as that corresponding to the measured conductivity by referring to the concentration–conductivity data of Table III, which represent a straight line.

Most of the reactions were carried out with RHgCN and hydrochloric acid as the reactants due to the greater facility and safety of working with hydrochloric acid than with hydrogen cyanide. An initial concentration of 0.005 *N* was chosen for the reactions reported in Table IV since this concentration is very nearly the limit of solubility of the aromatic mercuric chlorides.

Reactions of the benzyl and phenyl compounds were carried out starting with RHgCl and hydrogen cyanide at 0.005 *N* as recorded in Table IV.

Table IV

Equilibrium Data at 25° for the Reaction $RHgCN + H^+ + Cl^- \rightleftarrows RHgCl + HCN$

Reactants Initially at 0.005 *N*

Radical	Sp. conductivity of soln.	$\frac{[HCl]}{[RHgCN]}$	$\frac{[RHgCl]\,[HCN]}{[RHgCN][H^+][Cl^-]}$
C_6H_{11}—	0.85×10^{-5}	1.18×10^{-4}	1.45×10^{7}
	$.85 \times 10^{-5}$	1.18×10^{-4}	1.45×10^{7}
C_2H_5—	1.12×10^{-5}	1.59×10^{-4}	5.83×10^{6}
	1.13×10^{-5}	1.60×10^{-4}	5.71×10^{6}
$C_6H_5CH_2$—	1.33×10^{-5}	1.91×10^{-4}	3.32×10^{6}
	1.33×10^{-5}	1.91×10^{-4}	3.32×10^{6}
	1.32×10^{-5}[a]	1.90×10^{-4}	3.37×10^{6}
	1.33×10^{-5}[a]	1.91×10^{-4}	3.32×10^{6}
o-$ClC_6H_4CH_2$—	1.52×10^{-5}	2.20×10^{-4}	2.15×10^{6}
p-$CH_3C_6H_4$—	2.02×10^{-5}	2.98×10^{-4}	8.35×10^{5}
	2.01×10^{-5}	2.97×10^{-4}	8.44×10^{5}
C_6H_5—	2.02×10^{-5}	2.98×10^{-4}	8.35×10^{5}
	2.03×10^{-5}	3.00×10^{-4}	8.17×10^{5}
	2.03×10^{-5}[a]	3.00×10^{-4}	8.17×10^{5}
α-$C_{10}H_7$—	2.25×10^{-5}	3.34×10^{-4}	5.84×10^{5}

[a] Initial reactants RHgCl and HCN. Percentage conversion to RHgCl ranges from 97% for cyclohexyl to 93% for α-naphthyl.

Table V records the reaction between *o*-$ClC_6H_4CH_2HgCl$ and hydrogen cyanide at various initial concentrations.

The equilibrium constant has been formulated as follows

$$K = \frac{[RHgCl]\ [HCN]}{[RHgCN]\ [H^+]\ [Cl^-]}$$

This formulation is in accord with the high degree of ionization of hydrochloric acid indicated by the constancy of the equivalent conductance in Table III, and is verified by the constancy of *K* in Table V.

Table V

Constancy of Expression for Equilibrium Constant *o*-$ClC_6H_5CH_2HgCl + HCN \rightleftarrows$ *o*-$ClC_6H_4CH_2HgCN + HCl$

Initial concn. RHgCl	Initial concn. HCN	Sp. cond. reaction mixt.	*K*
0.00500	0.00500	1.52×10^{-5}	2.15×10^{6}
.0100	.0657	4.31×10^{-5}	2.17×10^{6}
.0131	.0131	2.80×10^{-5}	2.17×10^{6}
.00500	.112	4.05×10^{-5}	2.08×10^{6}

The equilibrium constants recorded in Table IV vary in a regular manner from radical to radical and are in the order previously established in this Laboratory.

In Fig. 1 are plotted curves for (1) the reaction $2RHgI \rightleftarrows R_2Hg + HgI_2$, (2) the ionization of primary amines, (3) the reaction $RHgCN + HCl \rightleftarrows RHgCl + HCN$. The ordinate measures log *K* while the abscissa is the axis of radicals established by Hixon and Johns.[3]

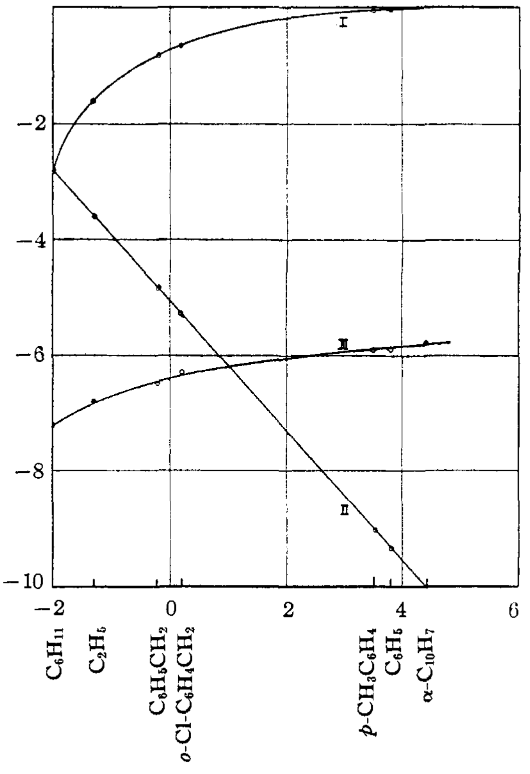

Fig. 1.—Radicals plotted against log *K* for the reactions (I) $2RHgI \leftrightarrows R_2Hg + HgI_2$; (II) ionization of RNH_2; and against $-\log K$ for the reaction (III) $RHgCN + H^+ + Cl^- \leftrightarrows RHgCl + HCN$.

The range of *pK* variation in the reaction involving RHgCN is 1.3 units which is a much smaller range of variation than in the case of the ionization of amines. The narrow range of variation in the case of RHgCN is entirely in accord with the conception that the mercury atom is so large that it absorbs much of the electron "pull" of the radical which otherwise would be more pronouncedly imparted to the -CN bond. The wide range of *pK* variation in the case of the amines is in agreement with the fact that the nitrogen atom, through which the effect of the radical is transmitted, is small.

Summary

1. It is shown that the cleavage of -CN from RHgCN by hydrochloric acid in ethanol is reversible.

2. Equilibrium constants at 25° have been determined for this reaction in the case of the radicals cyclohexyl, ethyl, benzyl, 2-chlorobenzyl, *p*-tolyl, phenyl and alpha-naphthyl.

3. The equilibrium constants vary from radical to radical.

4. The order of the radicals is that previously established for other reversible processes.

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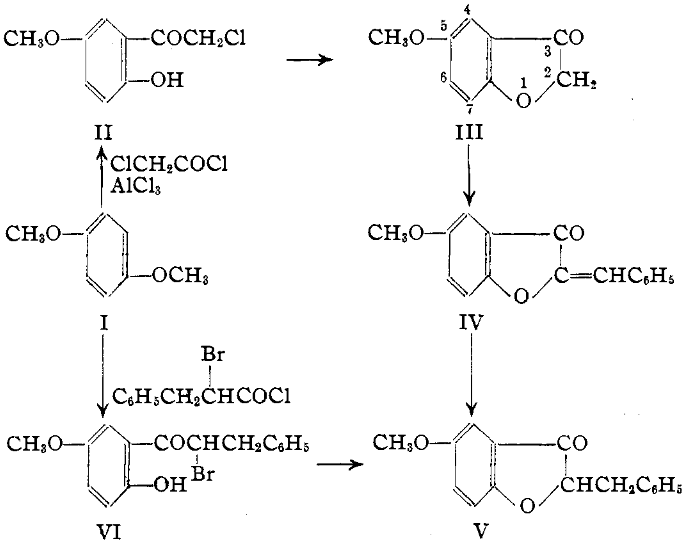
Derivatives of Coumaran. I. 2-Benzyl-5(and 6)-methoxycoumaran-3-one

BY R. L. SHRINER AND R. E. DAMSCHRODER

The synthesis of coumaran derivatives is of interest as bearing on the problem of the structure of certain naturally occurring substances, such as tectorigenin, which may be a substituted coumaran-3-one[1] or an isoflavone,[2] quebracho tannin, which may be a substituted coumaran-3-ol[3] or a flavpinacol.[4] Rotenone[5] contains a coumaran nucleus with an unsaturated side chain in one portion of its structure.



Since coumaran-3-ones contain active methylene groups, they readily condense with aromatic aldehydes.[6] If these unsaturated ketones could be reduced readily at the double bond, a useful method for the synthesis of coumaran-3-ones substituted in the 2-position would be available. The reduction of benzalcoumaranones has been reported in which platinum was used as the catalyst[7] but Freudenberg[8] found that side reactions occurred with platinum as the catalyst and hence used nickel on kieselguhr.

The present paper is concerned with the catalytic reduction of 2-benzal-5-methoxycoumaran-3-one IV, which was prepared by the method of von Auwers and Pohl.[9] Hydroquinone dimethyl ether (I), chloroacetyl chloride and aluminum chloride yielded ω-chloro-2-hydroxy-5-methoxyacetophenone (II). The latter underwent ring closure upon treatment with alcoholic sodium acetate and the resulting 5-methoxycoumaran-3-one (III) was then condensed with benzaldehyde to yield IV. It was found that, in glacial acetic acid solution, the latter was reduced readily by platinum and hydrogen to the saturated ketone (V). An independent synthesis of V was carried out not only to establish the fact that reduction occurred as indicated

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(3) Nuñez, *Anales asoc. quim. argentina*, **24**, 159 (1936).

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(8) Freudenberg, Fikentscher and Harder, *Ann.*, **441**, 157 (1925).

(9) Von Auwers and Pohl, *ibid.*, **405**, 243 (1914); *Ber.*, **48**, 85 (1915).