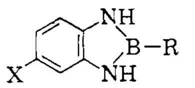
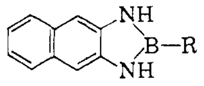
TABLE I



I-XII



XIII

No.	Substituents R	X	M.p., °C.[a]	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Ultraviolet absorption λ_{max}, mμ	Ultraviolet absorption $\epsilon_{max} \times 10^{-4}$	Ultraviolet absorption λ_{max}, mμ	Ultraviolet absorption $\epsilon_{max} \times 10^{-4}$	Yield,[b] %	Procedure[c]
I	*n*-Propyl	H	92–94	$C_9H_{13}N_2B$	17.51	17.62	232	0.543	284	0.553	53	A
II	*n*-Propyl	Methyl	99–101	$C_{10}H_{15}N_2B$	16.10	16.02	233	0.550	290	0.659	72	A
III	Phenyl	H	212–214	$C_{12}H_{11}N_2B$	14.44	14.15	245	0.865	296	1.74	91	A
IV	*p*-Methoxyphenyl	H	242–243	$C_{13}H_{13}ON_2B$	12.50	12.40	248	1.73	295	2.38	85	A
V	*p*-Chlorophenyl	H	219–221	$C_{12}H_{10}N_2BCl$	12.26	12.28	249	0.952	298	1.95	92	A
VI	*m*-Nitrophenyl	H	218–219	$C_{12}H_{10}O_2N_3B$	17.58	17.24	256	1.28	297	1.68	84	B
VII	*p*-Carboxyphenyl	H	281–282	$C_{13}H_{11}O_2N_2B$	11.77	11.50	235	2.18	289	0.377	79	B
VIII	Phenyl	Methyl	224–225	$C_{13}H_{13}N_2B$	13.47	13.31	248	0.897	302	1.86	89	A
IX	Phenyl	Methoxy	138–140	$C_{13}H_{13}ON_2B$	12.50	12.39	249	0.818	308	1.77	59	A
X	Phenyl	Chloro	183–184	$C_{12}H_{10}N_2BCl$	12.26	12.20	245	1.40	301	2.09	79	A
XI	Phenyl	Nitro	203–204	$C_{12}H_{10}O_2N_3B$	17.58	17.33	236	1.49	267	2.19	53	B
XII	Phenyl	Carboxy	209–210	$C_{13}H_{11}O_2N_2B$	11.77	11.68	222	2.70	308	1.41	95	B
XIII	Phenyl	......	327–328	$C_{16}H_{13}N_2B$	11.48	11.40	245	5.33	377	1.63	95	B

[a] Melting points are uncorrected and were determined in capillary tubes immersed initially in an unheated bath. [b] Recrystallized material. [c] This refers to the methods of preparation described in the Experimental part.

tinued and the mixture was evaporated to dryness *in vacuo*. The residue was suspended in 5 to 10 ml. of cold toluene, filtered, washed with petroleum ether and dried. The amorphous residue then was recrystallized from toluene.

Adduct of *o*-Phenylenediamine and Phenylboronic Acid.—In 25 ml. of 90% methanol was added 2.44 g. of phenylboronic acid and 2.16 g. of *o*-phenylenediamines. The solution was warmed at 60° for one hour and then concentrated *in vacuo*, to near dryness without warming above 60°. The solution was filtered, washed with a small volume of water and dried; a yield of 1.9 g., m.p. 70–72°, was obtained. At its melting point, the product resolidified and melted at 206–207°. This is the 2-phenylborobenzimidazoline, characterized by infrared spectra.

Infrared Spectra.—One mg. of twice-recrystallized substances was made up with 150 mg. of anhydrous potassium bromide[27] to a disk in the usual manner. All spectra were taken with a Perkin–Elmer model 21 recording spectrophotometer.

Ultraviolet Spectra.—The absorption spectra of twice-recrystallized materials were determined in freshly-prepared methanolic solutions, approximately 10^{-4} molar. All spectra were recorded with a Beckman DK-2 automatic spectrophotometer.

Acknowledgments.—The authors are very grateful to Drs. William H. Sweet, Gordon L. Brownell and E. A. Balazs for their great interest and encouragement in this work. It is a pleasure to acknowledge the technical assistance of Mr. Paul Szabady. We wish to thank Miss Mary Ellen Collins and Mr. E. T. Kaiser for their coöperation in obtaining the infrared spectra.

BOSTON 14, MASS.

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[27] Harshaw Chem. Co., Cleveland 6, Ohio.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Mechanism of the Reaction of Some Dialkyl and Diaryl Mercury Compounds with Hydrogen Chloride

BY RAYMOND E. DESSY, G. F. REYNOLDS[1] AND JIN-YOUNG KIM

RECEIVED AUGUST 12, 1958

The rates of reaction of diphenyl-, dimethyl-, diethyl-, di-*n*-propyl-, di-*i*-propyl-, divinyl- and dicyclopropylmercury with hydrogen chloride in dimethyl sulfoxide have been measured by a convenient conductometric method at various temperatures. The sequence of reactivities found is $(\Delta)_2$ Hg > $(H_2C{=}CH)_2$ Hg > $(C_6H_5)_2$Hg >> Et_2Hg > *i*-Pr_2Hg > *n*-Pr_2Hg > Me_2Hg. The effect of addition of dioxane, water, various inorganic salts and acids, the results of experiments involving DCl and the observed second-order kinetics all point to a four-center mechanism involving attack by molecular HCl.

In 1935, Ingold[2] in his classical series on S_N reactions, proposed what he termed S_E reactions—electrophilic substitution at a carbon center. This class of reactions could be divided, as the S_N reactions, into two categories—S_E1 and S_E2. Without experimental evidence, Ingold predicted what sequence of reactivities might be expected from each reaction path. Since that time many investigations have been initiated which involve a study of S_E reactions. Most of these have involved the use of organomercury compounds as the substrate providing the nucleophilic carbon for various practical reasons.

Earlier qualitative work by Marvel[3] with the reaction

$$R{-}Hg{-}R + HCl \longrightarrow RHgCl + R{-}H \quad (1)$$

indicated the sequence of reactivity to be *t*-Bu > *s*-Bu > *n*-Bu. No attempt at a rate or kinetic investigation was made.

In 1932, Kharasch[4] published the results of an

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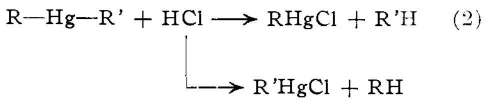
[1] Procter and Gamble Research Fellow 1957–1958.

[2] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

[3] C. S. Marvel and H. O. Calvery, THIS JOURNAL, **45**, 820 (1923).

[4] M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 675 (1932).

intensive investigation of the reaction



$$\mathrm{R{-}Hg{-}R' + HCl \longrightarrow RHgCl + R'H} \quad (2)$$
$$\longrightarrow \mathrm{R'HgCl + RH}$$

By analyzing the products he was able to show that the ease of cleavage of the $-\overset{|}{\underset{|}{C}}-Hg$ bond under these conditions is Me > Et > *i*-Pr > *t*-Bu. Again no attempt at a rate or kinetic investigation was made. In addition it must be recognized that comparison of the cleavage of the unsymmetrical compounds and symmetrical compounds is not valid. The sequence found in each series need not, and indeed *is* not, the same—in fact it is essentially reversed.

A rather complete investigation of the reaction

$$(C_6H_5)_2Hg + HA \longrightarrow C_6H_5HgA + C_6H_6 \quad (3)$$

has been reported by Corwin.[5] Unfortunately the reaction was run under pseudo-first order conditions and therefore difficult to interpret mechanistically. The dilatometric method used has obvious handicaps in an extensive program.

The acetolysis of dialkylmercury compounds

$$\mathrm{R{-}Hg{-}R + AcOH \longrightarrow R{-}Hg{-}O{-}Ac + RH} \quad (4)$$

has been investigated by Winstein[6,7]; the sequence of reactivities reported is C_6H_5 > *sec*-Bu > *n*-Bu. The authors reported extreme difficulty in the analytical method used to follow the reaction.

The purpose of this paper is to present a simple experimental method for following reactions of the type illustrated by equation 1, and to introduce some data concerning reactions in dimethyl sulfoxide, data from which a mechanism for the reaction can be established.

Experimental

Organomercury Compounds.—Dimethyl-, diethyl-, di-*n*-propyl-, di-*i*-propyl- and diphenylmercury were prepared by treating the corresponding Grignard reagent with mercuric chloride in ether or tetrahydrofuran, depending upon the boiling point and isolation properties of the organomercury. The divinyl- and dicyclopropylmercury compounds were prepared as previously described.[8] All of these compounds apparently were stable over very long periods of time when kept refrigerated, with the exception of di-*i*-propylmercury. This material over the period of a few hours showed a slight black deposition of mercury. It was therefore distilled immediately before use.

Solvents.—Dimethyl sulfoxide suitable for conductometric purposes was obtained by redistillation of commercial material, b.p. 54–56° (4 mm.). It had a specific resistance greater than 10^6 ohms. 1,4-Dioxane was purified by passage through alumina followed by distillation from sodium.

Measurement of Rates of Reaction with HCl.—The most convenient method for following the hydrochloric acid cleavage of organomercury compounds is by the use of conductivity. This method is applicable provided that (1) there is a considerable difference in conductance between the initial and final systems, and (2) the change in conductivity is proportional to the progress of the reaction. The use of a solvent with a high dielectric constant which is a good solvating medium for the materials employed is a necessity for such a method. Dimethyl sulfoxide (DMSO), with a dielectric constant of about 30 and high solvating capacity for compounds of mercury, was chosen as a solvent for this work.

The bridge consisted of a variable frequency oscillator capable of supplying from 10 to 100,000 c.p.s. at a level of from 0–10 v., a general utility impedance bridge equipped with compensating condensers, a VTVM serving as both a rough detector for the bridge signal and as an amplifier feeding to an oscilloscope used as a visual detector in the manner described by Fuoss.[9] In general 1,000-cycle current was used for the measurements. Five different conductivity cells were used, depending upon the concentrations employed. The cells constants ran from 0.01 to 30. Bright platinum electrodes were used.

A mineral oil thermostat operating at temperatures from 25 to 65° was used; the temperature was controlled in the higher regions at about ±0.01°, but in the lower regions to only ±0.050°.

Preliminary results obtained from the measurement of the resistance of the organomercury-HCl solutions indicated that the resistance increased linearly with time when the reactants were initially present in equal concentrations. Since it was verified that under the conditions of these experiments all the products and reactants except the hydrogen chloride contribute negligible amounts to the conductance, the problem of translating conductivity data into kinetics expressions was not unduly difficult.

If we define L_0 as the specific conductance at time zero, and L_∞ as the specific conductance at time infinity, then the difference $L_0 - L_\infty$ is equivalent to the complete path length of the reaction. The assumption is made that any distance along this path length, $L_0 - L_t$, is proportional to the amount of reaction that has taken place in time t. This assumption is supported by the data shown in Table I, where the conductance is shown to be an approximate linear function of added HCl over the concentration range employed in this study. Then the initial concentration of reacting HCl, a, and the concentration of product formed at any time, t, x, can be expressed in terms of conductances as

$$a = c(L_0 - L_\infty) \text{ and } x = c(L_0 - L_t) \quad (1)$$

The fact that resistance increases linearly with time is indicative of a second-order reaction. Substitution into the second-order rate equation gives

$$1/c(L_t - L_\infty) = kt + C \quad (2)$$

where k is the reaction rate constant and C is a constant.

Since the products of the reaction contribute negligibly to the conductance this reduces to

$$1/cL_t = kt + C \quad (3)$$
$$\text{or } R_t/c = kt + C$$

Therefore a plot of R_t *versus* t should be linear.

A more accurate expression may be obtained which does not involve the approximation $L_\infty = 0$ by solving for the integration constant in equation 2. This yields

$$L_t = (1/ka)[(L_0 - L_t)/t] + L_\infty \quad (4)$$

This relationship was used in determining rate constants when the reactants were present in equal concentration.

For reactions involving unequal concentrations of starting materials, the concentrations of which initially are a and b, respectively, substitution and integration gives

$$1/(a - b) \ln [f - [(L_0 - L_t)/(L_0 - L_\infty)]]/[1 - [(L_0 - L_t)/(L_0 - L_\infty)]]$$

where b represents the reactant present in the limiting amount and $f = a/b$. Thus a plot of log $(f - y)/(1 - y)$ *vs.* t, where $y = (L_0 - L_t)/(L_0 - L_\infty)$, should be linear.

Kinetic Runs.—Because of the slow reaction of hydrogen chloride with DMSO, it proved expedient to use standardized solutions of HCl in dioxane as a source of hydrogen chloride for the experiments. The hydrogen chloride was purified by passing through phosphorus pentoxide, and dissolved in the dioxane. It was standardized against sodium carbonate in a large excess of water using a *p*H meter to determine the end-point. A solution 0.7 *N* in HCl was found convenient.

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(5) A. H. Corwin and M. A. Naylor, Jr., THIS JOURNAL, **69**, 1004 (1947).

(6) S. Winstein, T. G. Traylor and C. S. Garner, *ibid.*, **77**, 3741 (1955).

(7) S. Winstein and T. G. Traylor, *ibid.*, **77**, 3747 (1955); **78**, 2597 (1956).

(8) G. F. Reynolds, R. E. Dessy and H. H. Jaffé, *J. Org. Chem.*, **23**, 1217 (1958).

(9) R. M. Fuoss and D. Edelson, *J. Chem. Ed.*, **27**, 610 (1950).

The kinetic runs were made by dissolving a calculated amount of organomercury compound in 10.0 ml. of DMSO and allowing the solution to equilibrate in the bath. Then 1.0 ml. of the dioxane–HCl solution was added and readings of the resistance of the solution taken over about 75% of the reaction.

Second-order fits were obtained for over 66% of the reaction. Reproducibility was approximately 1.5%. It is estimated that the entropies of activation are good to about ±2 e.u., and energies of activation to about ±0.5 kcal.

The initial concentration of organomercury compound usually ran from 0.035 to 0.21 M, while the acid concentration ranged from 0.035 to 0.07, depending upon the rate of the reaction.

All runs were made in duplicate.

Acidity Function Measurements.—The acidity functions of the HCl in DMSO–dioxane (10:1) over the concentration range employed in the kinetics were measured by the technique reported by Braude,[10] using *p*-nitroaniline as the proton acceptor. The results are reported in Table I. (The acidity function H, as defined here, is the negative of Hammett's acidity function H_0. This definition is preferred because H, unlike H_0, increases with increasing proton availability.) Over the range studied a plot of H *vs.* log (HCl) is linear.

TABLE I

SPECIFIC CONDUCTIVITY AND H-VALUES OF HCl *versus* CONCENTRATION IN DMSO–DIOXANE (10:1)

N_{HCl}	L, ohm^{-1} cm.$^{-1}$ $\times 10^3$	H
0.081	1.08	−2.15
.065	0.91	−2.20
.048	.77	−2.25
.032	.60	−2.37
.016	.38	−2.45

Results and Discussions

Previous investigations of the kinetics of the acid cleavage of organomercury compounds have

$$\text{RHgR} + \text{HCl} \longrightarrow \text{RHgCl} + \text{RH} \quad (5)$$

dealt almost exclusively with the diarylmercury compounds, which in general react about 10^3 times more rapidly than the saturated dialkyl compounds. Thus reactions of the dialkyl compounds in 91% methanol–9% water would have to be followed for several days in order to obtain good kinetics, using the concentrations available. Dioxane, seemingly the best of the common solvents available, was found in a 2:1 mixture with water to yield rates one-fifth as fast as that of the aqueous methanol and was not a good solvent for the mercury compounds. Obviously, if one were to embark on an extensive program, the cleavage reactions would have to be speeded up either by (1) increasing concentration, (2) increasing temperature or (3) finding a more suitable solvent. Both 1 and 2 have their obvious limitations. The cleavage of diphenylmercury in 91% dimethylsulfoxide (DMSO)–9% water was therefore investigated, and the rate of reaction found to be in the same range as that in aqueous methanol. However, completely anhydrous DMSO resulted in rates some twenty times faster than those in 66% dioxane–water. Because of the slow reaction of DMSO and hydrogen chloride, it was found convenient to use a standard solution of hydrogen chloride in dioxane as a source of acid. Except where the solvent composition was varied the ratio of DMSO–dioxane was kept constant at 10:1.

The rates of reaction were followed by a conductometric method. It was found that the conductivity of HCl in DMSO–dioxane (10:1) was a linear function of the concentration over the concentration range used, and that the other reactants and products contributed negligible amounts to the conductivity. This linear relationship is rather surprising, and could be due to either complete dissociation of the HCl, or to a very low dissociation, where the deviation from linearity would be smaller than the experimental error. An investigation of the acidity functions,[10] H, in the concentration range employed in the kinetic measurements indicated that H could be represented in the form $H = 0.5 \log (\text{HCl}) - 1.6$. If α, the dissociation constant of the acid, is small, it can be shown[10] that H should take the form $H = \log (K_B^S/K_B^{HOH}) + 0.5 \log K_a c_a$; where K_y^x represents the equilibrium constant of the reaction $\text{XH}^+ + \text{Y} \rightarrow \text{YH}^+ + \text{X}$ in the solvent X, K_a is the dissociation constant of the acid, c_a is its concentration, and S and B the solvent and indicator, respectively. This indicates that the degree of dissociation of HCl in the solvent system DMSO–dioxane is small at concentrations above 0.01 M.

From the very first reactions that were studied—using equal concentrations of diphenylmercury and HCl—it was evident that the resistance of the solution increased approximately linearly with time, clearly indicative of a second-order reaction. Comparison of rate constants involving a twentyfold variation in the concentration of the mercury compound or a twofold variation in the acid concentration indicated that the reaction was also second order between runs. The observed variation in k between runs was ±2%.

Effect of Varying R.—Table II shows the specific reaction rate constants, k, as determined for a series of bis-organomercury compounds reacting with hydrogen chloride in DMSO–dioxane at the temperatures indicated.

TABLE II

$$\text{R}_2\text{Hg} + \text{HCl} \xrightarrow{\text{DMSO–Dioxane (10:1)}} \text{RHgCl} + \text{RH}$$

R	Temp. = 25° k, l. mole^{-1} sec.$^{-1}$	Temp. = 40° k, l. mole^{-1} sec.$^{-1}$	E‡, kcal. mole^{-1}	ΔS‡, e.u.
Cyclopropyl	6.6×10^{-2}	2.5×10^{-1}	16.5	−11
Vinyl	1.4×10^{-2}	4.2×10^{-2}	13.6	−23
Phenyl	9.3×10^{-3}	2.5×10^{-2}	12.2	−29
	Temp. = 40° k, l. mole^{-1} sec.$^{-1}$	Temp. = 50° k, l. mole^{-1} sec.$^{-1}$		
Ethyl	3.8×10^{-4}	8.2×10^{-4}	15.5	−27
i-Propyl	2.6×10^{-4}	5.6×10^{-4}	15.4	−28
n-Propyl	2.3×10^{-4}	5.1×10^{-4}	16.5	−25
Methyl	Too slow to measure	1.3×10^{-4}		

From the specific reaction rates it is apparent that the nature of the R group has a marked effect upon the rate of reaction. Assigning an arbitrary value of 100 to the reaction of diphenylmercury with hydrogen chloride we obtained several relative rates of reaction—dimethylmercury, 0.2; di-*n*-propylmercury, 0.9; di-*i*-propylmercury, 1.0; diethylmercury, 1.5; diphenylmercury, 100; divinylmercury, 170; and dicyclopropylmercury,

[10] E. A. Braude, *J. Chem. Soc.*, 1971 (1948).

1000. Roughly the rates of reaction can be divided into two groups, slow and fast, with the dimethyl-, di-*n*-propyl-, di-*i*-propyl- and diethylmercury falling into the slow group, and diphenyl-, divinyl- and dicyclopropylmercury into the fast group. It is interesting to note that the fast group is made up of groups possessing π-electrons, or groups which are known to behave as pseudo-unsaturated functions, while the slow group contains the saturated aliphatic mercury compounds.

An examination of the thermodynamic calculations for the slow-reacting organomercurials, *i.e.*, di-*n*-propyl-, di-*i*-propyl- and diethylmercury, does not reveal the reason for their order of reactivity, as there is no significant trend in either the activation energy or entropy. However, it seems reasonable to conclude that the increased rate of cleavage of the diphenylmercury relative to the slow group is due to a decrease in activation energy. In the case of dicyclopropylmercury there seems to be no doubt that the very rapid rate of reaction is due to a more positive entropy of activation. The organometal produced was shown to be cyclopropylmercuric chloride by a mixed melting point determination and examination of the infrared absorption spectrum. The evolved hydrocarbon was shown to be cyclopropane, by comparison of the spectrum with the known spectra of cyclopropane. Propylene, if it is present, must occur in only trace amounts. There seems to be no obvious reason for the increased entropy term.

Effect of Varying DMSO–Dioxane Ratio.—In order to test the effect of lowering the dielectric constant of the media upon the reaction rate, the mole fraction of dioxane was increased, while keeping the concentrations of reacting substances unchanged. This was done with both diphenyl- and diethylmercury. The results are given in Table III. It is evident that the effect of added dioxane is to increase the rate of reaction; all of this increase in the reaction rate is difficult to explain on the basis of an electrostatic effect alone, unless the reacting species are both in the form of ions. The large negative entropy values observed in most cases would seem to make completely ionic reaction highly improbable.

TABLE III

$$\underset{0.068\,M}{R_2Hg} + \underset{0.068\,M}{HCl} \xrightarrow[\text{Dioxane}]{\text{DMSO–}} RHgCl + RH$$

R	Temp., °C.	Mole fract. dioxane	k, l. mole^{-1} sec.$^{-1}$	Increase in k, %
Diphenyl	32	0.0765	1.52×10^{-2}	0.0
		.322	1.78×10^{-2}	17.1
		.500	2.35×10^{-2}	54.6
		.729	3.76×10^{-2}	147.4
Diethyl	40	.0765	3.80×10^{-4}	0.0
	40	.0857	4.00×10^{-4}	5.3
	50	.0765	8.15×10^{-4}	0.0
	50	.143	1.06×10^{-3}	31.3
	65	.0765	5.27×10^{-3}	0.0
	65	.500	1.01×10^{-2}	89.8

The actual extent of ionization of HCl and its subsequent dissociation in DMSO–dioxane is unknown, but as pointed out earlier the degree of dissociation must be very low. Unfortunately there are no data available from which calculations of K_B^S can be made, either in dioxane or DMSO, and attempts at obtaining values for the specific conductances of HCl in these solvents at infinite dilution, values necessary for calculating K_a, have thus far failed. However, it is not unlikely that the addition of dioxane to DMSO could increase the amount of undissociated HCl present.

Effect of Added Water.—To find out the effect of small increments of added water, and to determine whether or not the ratio of (moles of water)/(moles of acid) was significant, small amounts of water were added systematically in place of dioxane to diphenylmercury reaction solutions. The results are given in Table IV. It is evident that the effect of added water is to steadily decrease the rate of reaction, with the percentage decrease per millimole of water being greater the smaller the water concentration. The ratio of (moles of water)/(moles of acid) is apparently of no particular significance.

TABLE IV

$$\underset{0.022\,M}{(C_6H_5)_2Hg} + \underset{0.022\,M}{HCl} \xrightarrow[H_2O]{\text{DMSO}} C_6H_5HgCl + C_6H_6$$

Mmoles H_2O	Mmoles HCl	$\frac{\text{Mmoles } H_2O}{\text{Mmoles HCl}}$	k, l. mole^{-1} sec.$^{-1}$
0.0	0.07	0.0	1.15×10^{-2}
1.39	.07	19.8	1.11×10^{-2}
5.56	.07	79.3	1.06×10^{-2}
27.8	.07	397	8.88×10^{-3}
55.6	.07	793	6.90×10^{-3}
111	.07	1590	4.76×10^{-3}

Since, in the present case, there is a marked change in reaction rate with little change in dielectric constant, it would seem that this effect must be due, as in the case of added dioxane, to a shift of the dissociation equilibria of the HCl in solution. That a small amount of water could significantly shift the equilibria toward dissociated HCl appears plausible in view of the work by Braude[11] indicating that small amounts of water in dioxane act like a strong base to the HCl molecules.

Effect of Added Salts.—The effect of added sodium chloride on the rate of cleavage of two of the organomercuries with HCl was determined by dissolving calculated amounts of the salt in the DMSO–dioxane reaction solvent. This was done with diethylmercury and diphenylmercury and the results are shown in Table V. It is evident that the addition of a small amount of sodium chloride has a marked effect on the reaction rate, with the increase in rate being roughly proportional to the amount of added sodium chloride. Because equivalent amounts of Na_2SO_4 *did not* change the reaction rate this effect is undoubtedly caused by chloride ion, and is in agreement with the increase in reaction rate with added chloride found by Kaufman and Corwin[12] for the cleavage of diphenylmercury with perchloric acid.

Since a small amount of added chloride affects the reaction rate considerably, the chloride ion could be acting in one of two ways—either by its powerful coördinating ability, in this case

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(11) E. H. Braude, *J. Chem. Soc.*, 1976 (1948).

(12) F. Kaufman and A. H. Corwin, THIS JOURNAL, **77**, 6280 (1955).

TABLE V

$$\mathrm{R_2Hg + HCl \xrightarrow[NaCl]{DMSO} RHgCl + RH}$$

R	Concn. NaCl, mole/liter	Concn. of HCl and organomercurial, mole/liter	Temp., °C.	k, l. mole^{-1} sec.$^{-1}$
Diphenyl	0.0	0.07	25	9.3×10^{-3}
	.01	.07	25	1.08×10^{-2}
	.02	.07	25	1.38×10^{-2}
Diethyl	.0	.07	65	5.3×10^{-3}
	.01	.07	65	$6.0 \times 10^{-}{}_{3}$

coördination with mercury, or by shifting the equilibrium between undissociated and ionized HCl toward undissociated acid. Of the two possibilities the former seems the more unlikely, as Strobel[13] has found that the slight solubility of mercury-substituted benzoic acids is not increased by the presence of a large excess of chloride, iodide or cyanide ion. It is concluded then that the chloride ion effect is mainly due to a shift in the HCl dissociation and, since the rate is increased by added chloride ion, this again indicates that an increase in the amount of undissociated HCl results in an accelerated reaction rate—pointing to undissociated HCl as an attacking species.[14]

The Effect of Added Sulfuric Acid on the Rate of Reaction.—The effect of added sulfuric acid on the rate of cleavage of organomercurials with HCl was determined by adding an equimolar amount of H_2SO_4 to a diphenylmercury–HCl reaction solution at 32°. Second-order kinetics were obtained using only the concentration of HCl and diphenylmercury employed and neglecting the concentration of added sulfuric acid. The calculated rate constant was found to be increased slightly from the corresponding reaction without added sulfuric acid—from 1.52×10^{-2} to 1.67×10^{-2}.

The fact that second-order kinetics were obtained using the concentration of HCl rather than the total acid concentration appears significant. This appears to substantiate the theory that the rate-determining step of the cleavage is not an attack of the proton of the acid, otherwise the reaction would have plotted second order using total acid concentration rather than the concentration of HCl alone. This result is not surprising, however, in view of the fact that it was found that sulfuric acid did not react noticeably with diphenylmercury when used alone. This is further indication that it is undissociated HCl that is the attacking agent in the cleavage reaction.

The fact that the reaction rate is increased by added sulfuric acid can be ascribed, as in the case of the chloride ion effect, to a shift in the equilibrium between undissociated and dissociated acid toward the undissociated acid. In this case the rate is increased less than for an equivalent concentration of chloride ion, but this is to be expected since the sulfuric acid is like HCl, a weak electrolyte in dimethyl sulfoxide, and therefore the resulting shift in the HCl equilibrium is considerably less.

Effect of Replacing HCl by DCl.—The rates of reaction of DCl with diphenylmercury at 32° and diethylmercury at 65° were determined at different concentrations of DCl using equal amounts of organomercury and DCl in each case. The results are shown in Table VI along with data on corresponding reactions with HCl in the same concentration range.

TABLE VI

$$\mathrm{R_2Hg} + \left\{\begin{matrix}\mathrm{HCl}\\ \mathrm{DCl}\end{matrix}\right. \xrightarrow{\mathrm{DMSO}} \left\{\begin{matrix}\mathrm{RH}\\ \mathrm{RD}\end{matrix}\right. + \mathrm{RHgCl}$$

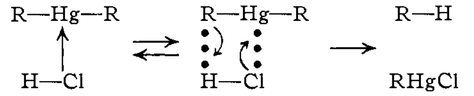
		DCl reactions		HCl reactions	
R	Temp., °C.	N_{DCl}	k, l. mole^{-1} sec.$^{-1}$	N_{HCl}	k, l. mole^{-1} sec.$^{-1}$
Diphenyl	32	0.068	1.22×10^{-2}	0.068	1.51×10^{-2}
	32	.068	1.26×10^{-2}	.068	1.53×10^{-2}
	32	.058	1.47×10^{-2}	.062	1.57×10^{-2}
	32	.047	1.69×10^{-2}	.034	1.62×10^{-2}
Diethyl	65	.068	4.56×10^{-3}	.068	5.26×10^{-3}
	65	.058	5.19×10^{-3}	.068	5.28×10^{-3}

It is apparent from the above results that it is difficult to cleanly determine the isotope effect from the comparative rates of reaction with DCl and HCl. This is because the rate constants calculated from the DCl runs, unlike those of the HCl runs, vary considerably depending on the concentration of DCl employed. This phenomenon is undoubtedly related to the fact that while the reactions with HCl proceed with approximately a linear increase in the resistance of the solution with time, the increase in resistance of the DCl reaction solutions is not strictly linear, but falls off. In other words, the DCl cleavage reactions do not follow as good second-order kinetics as do the HCl reactions, for some unknown reason.

From the above considerations it is difficult to draw any definite conclusions. Nevertheless, it does seem likely that what isotope effect there is must be small, with some decrease in the reaction rate caused by a substitution of deuterium in place of the hydrogen of the acid.

Further evidence as to the anomalous behavior of DCl comes from a determination of the conductances of solutions of DCl and HCl in DMSO–dioxane. In all cases studied, in the range of acid concentrations from 0.068 to 0.0068 *N*, the DCl solutions had a specific conductance some 10 to 15% higher than the HCl solutions. This leads to a possible explanation for the anomalous behavior of DCl– an increased strength of the DMSO–D$^+$ bond over DMSO–H$^+$. This, of course, is to be expected.

Mechanism.—From the experimental data it is clearly evident that under the experimental conditions employed in this investigation the cleavage of organomercury compounds is dependent upon a concerted attack by both the chloride ion and proton of the acid. This concerted attack can best be pictured by a four center or cyclic mechanism, thus



Whether the HCl is in the form of ion pairs or unionized molecules is immaterial. The important point is that nucleophilic attack on mercury is as

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[13] A. F. Strobel, Dissertation, John Hopkins University, 1943.

[14] Since this type of investigation is incapable of distinguishing between un-ionized HCl and ionized, but not dissociated HCl, *i.e.*, intimate ion pair, the term undissociated HCl will be used as an ambiguous term representing either or both.

important as electrophilic attack on carbon. This is in agreement with similar conclusions by Winstein based on the reaction of a bis-organomercury with mercuric chloride,[6] and also supports the supposition of Kaufman and Corwin[15] that un-ionized HCl might be an attacking species in the cleavage reaction.

The faster rates of reaction exhibited by the unsaturated groups attached to mercury arise either from an increased electropositivity of the mercury, due to the increased s-character of the attached carbon, or from the ability of these unsaturated groups to stabilize bonding to the incoming hydrogen atom *via* "onium" ion formation.

The lack of significant isotope effect indicates that in the transition state the H–Cl bond is only slightly weakened while the C–H and Hg–Cl bonds are in the process of formation.[16]

The present work would seem to rule out a mechanism in which the rate-determining step is an attack by the solvated proton, analogous to that proposed by Kaufman and Corwin[15] for the perchloric acid cleavage of diphenylmercury. Not only are the reactions over-all second order, regardless of added sulfuric acid or chloride ion, but activation energy calculations for the cleavage of diphenylmercury with HCl and HBr give a difference of over 5 kcal. for the two acids. The reaction of diphenylmercury with HCl in DMSO-dioxane gives the values $-E^*$, 12.2 kcal./mole; ΔS^*, -29 e.u. For diphenylmercury, HBr in DMSO–dioxane the values are $-E^*$, 17.4 kcal./mole; ΔS, -11 e.u.; such differences could not be expected to arise from an attack by the solvated proton alone.

The mechanism as outlined above is consistent with effect of change in structure of R; with the effect of added dioxane, added water, added salt, added sulfuric acid; with the large negative entropies of activation and the deuterium isotope effect, and with the over-all kinetic picture.

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[16] K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanism of Hypochlorite Decompositions. The Thermal Decomposition of L-(+)-2-Methyl-3-phenyl-2-butyl Hypochlorite

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Decomposition of L-(+)-2-methyl-3-phenyl-2-butyl hypochlorite of 53% optical purity in carbon tetrachloride at 80° affords acetone and α-phenylethyl chloride (1-chloroethylbenzene) of 0.71% optical purity (L-configuration) in high yield under conditions in which α-phenylethyl chloride has been shown to be optically stable. The optical results and the marked inhibitory effect of oxygen on rate of decomposition are interpreted in terms of a chain mechanism (equations 2–5) as the principal path of disappearance of hypochlorite.

The organic hypochlorites have received attention principally from the standpoint of synthesis and use as oxidants.[1] Recently a detailed report of the synthesis and isolation of a large number of primary, secondary and tertiary hypochlorites has appeared.[2] Primary and secondary hypochlorites undergo spontaneous decomposition at room temperature to carbonyl compounds and hydrogen chloride. The tertiary hypochlorites, of substantially greater stability, undergo decomposition to carbonyl compounds and alkyl chlorides, equation 1. Isolated examples in the literature, such as

$$R_3C\text{–}O\text{–}Cl \longrightarrow R_2CO + RCl \tag{1}$$

the conversion of 1-methylcyclopentyl hypochlorite to 6-chloro-2-hexanone,[3] are suggestive of considerable selectivity in the decomposition process. The nature of the decompositions[4] represented by equation 1 has received little attention, although the conversion of toluene to benzyl chloride by the action of *t*-butyl hypochlorite and the rapid decomposition of hypochlorites in sunlight are strong indications of the facility with which hypochlorites may enter into free radical reactions. The principal processes, *a priori*, for thermal decomposition of a *t*-hypochlorite in an inert solvent would appear to be unimolecular processes and chain decomposition processes (equations 2–5). Our interest was attracted to this area by the likelihood we attached to the chain process and by the potential use to which such a reaction might be placed in the investigation

$$R_3C\text{–}O\text{–}Cl \longrightarrow R_3C\text{–}O\cdot + Cl\cdot \tag{2}$$

$$R_3C\text{–}O\cdot \longrightarrow R_2CO + R\cdot \tag{3}$$

$$R\cdot + R_3C\text{–}O\text{–}Cl \longrightarrow R_3C\text{–}O\cdot + RCl \tag{4}$$

$$2R\cdot \longrightarrow R\text{–}R \tag{5}$$

of stereospecificity and selectivity in free radical chain reactions.[5] This paper presents evidence in support of a chain mechanism as the principal path for the thermal decomposition of the tertiary hypochlorite derived from 2-methyl-3-phenyl-2-butanol.

Results and Discussion

The processes on which information was sought were chain decomposition (equations 2–5) and unimolecular four-center decomposition of hypochlorite to alkyl chloride and ketone (equation 6).

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[2] R. Fort and L. Denivelle, *Bull. Soc. chim. France*, 1109 (1954); 534 (1955).

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