[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Aromatic Substitution. The Cleavage of Diphenylmercury[1]

BY ALSOPH H. CORWIN AND MARCUS A. NAYLOR, JR.[2]

Introduction

The studies on aromatic substitution initiated by Vorländer[3] and carried on by Robinson,[4] Ingold[5] and others have made it abundantly clear that polar influences associated with substituents in the benzene ring play a decisive part in orientation effects. Many questions concerning the details of the substitution process which should be amenable to treatment by kinetic methods remain to be answered, however. This is partly due to the fact that it is only under special conditions that the usual substitution reactions can be made suitable for kinetic studies.[5c] The usual type of electrophilic substitution reaction is also unsuited for certain refinements because of the impossibility of confining the attack to a single position in the benzene ring unless all the others are blocked.

The aromatic mercurials furnish a rich storehouse for kinetic studies on aromatic substitution. The gradations in polarity obtainable are nicely shaded and a wide variety of suitable materials of known structure has been prepared, thanks mainly to the work of Kharasch.[6] These substances may be used for the study of attack by either electrophilic or nucleophilic reagents. Wide variations in the attacking power of the reagents may be secured so that it seems justifiable to predict that conditions can be found with nearly any compound which will permit kinetic studies. This paper constitutes an orienting study with diphenylmercury to determine the accuracy of these predictions of suitability.

In his studies on the cleavage of diarylmercury derivatives with acid, Kharasch has assumed that the step which determines the composition of the reaction products is an ionization of the type

$$\mathrm{R{:}Hg{:}R'} \longrightarrow \mathrm{R{:}Hg^+} + \mathrm{:R'^-}$$

This ionization is then followed by combination of the organic ions with the ions of the acid employed

$$\mathrm{R{:}Hg^+} + \mathrm{:R'^-} + \mathrm{H^+} + \mathrm{:X^-} \longrightarrow \mathrm{R{:}Hg{:}X} + \mathrm{R'{:}H}$$

Such a reaction should exhibit first order kinetics.

If this mechanism were valid, there would probably be little relation between the results obtained by studies on the acid cleavage of aromatic mercurials and other substitutions on the benzene ring. We were encouraged to hope for a correlation with other substitution reactions, however, by the observation that the electron-attracting or electron-repelling characteristics deduced by Kharasch from his studies on aromatic mercurials are in almost exactly the same sequence as those observed by the English investigators and those deduced by Hammett[7] from many sources in the literature, but that Kharasch's series is *in inverted order*. Such an inversion is to be expected in changing from an ionic dissociation mechanism to a direct attack on the diphenylmercury by acid. Our studies show that the cleavage of diphenylmercury is dependent on the concentrations of both reagents. The attack of acid on diphenylmercury can be assumed, therefore, to parallel the attack of other electrophilic agents on aromatic hydrocarbons, with the important exception that the position of the attack is uniquely determined by the presence of the carbon-mercury linkage.

Experimental

Methods and Materials

Kinetic Technique.—In an effort to determine the factors affecting the rate of this cleavage, kinetic studies were made with a tapless dilatometer[5c] on the reactions of diphenylmercury with acetic and formic acids.

The dilatometer contained about 16 ml. of solution and was equipped with a magnetic stirrer. It was read with a Gaertner M-301 Micrometer slide capable of being estimated to one micron. It was held in place in an 18-gallon water-bath by means of a removable frame. The temperature of the bath was controlled accurately to within 0.001° by employing a mercury switch activated by toluene contained in a copper coil immersed in the bath. A sensitive electronic relay was attached to control the intermittent heater. Efficient stirring of the bath was accomplished by the use of a low speed stirring motor and a four inch propeller.

Solvent.—The insolubility of the mercurials limited the choice of solvent. Dioxane was found to be the best solvent and it was discovered that the course of the reaction could be followed roughly by adding water to the cleavage mixture. This caused precipitation of the diphenylmercury but allowed the more soluble cleavage products to remain in solution.

Choice of Acids.—The original intention was to study the cleavage of diphenylmercury with hydrochloric acid. This reaction took place in about three minutes at room temperature, however, using 0.1 *M* acid and diphenylmer-

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[1] From the doctoral dissertation of Marcus A. Naylor, Jr., The Johns Hopkins University. Presented at the Chicago Meeting of the American Chemical Society, September, 1946.

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[3] Vorländer, *Ber.*, **52**, 263 (1919).

[4] Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Inst. of Chem. of Great Britain and Ireland, London, 1932.

[5] (a) Ingold and Smith, *J. Chem. Soc.*, 905 (1938); (b) Bird and Ingold, *ibid.*, 918; (c) Benford and Ingold, *ibid.*, 929 and earlier papers of this series. See also Ingold, *Ann. Reports Chem. Soc.*, **23**, 129–143 (1926).

[6] See, for example, Kharasch and Chalkley, THIS JOURNAL, **46**, 1211 (1924); Kharasch and Grafflin, *ibid.*, **47**, 1948 (1925); Kharasch and Marker, *ibid.*, **48**, 3130 (1926); Kharasch and Flenner, *ibid.*, **54**, 674 (1932); Kharasch, Pines and Levine, *J. Org. Chem.*, **3**, 347 (1938–1939); Kharasch and Swartz, *ibid.*, **3**, 405 (1938–1939); Kharasch, Legault and Sprowls, *ibid.*, **3**, 409 (1938–1939).

[7] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

TABLE I

Expt.	k (sec.$^{-1}$)	$C_6H_5HgC_6H_5$, g.	Approx. concn., m	Acid, cc., HAc	Dioxane, cc., unpurified	Temp., °C.
1	5.20×10^{-4}	0.700	0.0972	10.00	10.00	42.2
2	5.66	0.700	0.0972	10.00	10.00	42.2
3	5.72	0.700	0.0972	10.00	10.00	41.9
4	4.24	1.050	.1458	10.00	10.00	41.9
5	3.87	1.050	.1458	10.00	10.00	41.5
6	3.27	1.400	.1915	10.00	10.00	42.2
7	5.32	0.700	.0972	10.00	10.00	41.8
8	1.08×10^{-3}	0.700	.0972	7.50 90% HCOOH	12.50	30.2
9[a]	1.12	0.700	.0972	7.50 90% HCOOH	12.50	30.2
10	8.66×10^{-4}	1.050	.1458	7.50 90% HCOOH	12.50	30.1
12[b]	9.69	0.700	.0972	7.50 90% HCOOH	12.50 Purified	30.2
13	9.91	0.700	.0972	7.50 90% HCOOH	12.50	30.2
14[c]	9.36	0.700	.0972	7.50 90% HCOOH	12.50	30.2
15[d]		0.700	.0972	7.50 90% HCOOH	12.50	30.2
16[e]		0.700	.0972	0.1044 g. 90% HCOOH	20.00	42.0
17[f]	9.68	0.700	.0972	7.50 cc. 90% HCOOH	12.50	30.2
18[g]	1.10×10^{-3}	0.700	.0972	7.50 cc. 90% HCOOH	11.00	30.2
19	4.38×10^{-4}	0.700	.0972	6.00	14.00	30.2
23	2.69	0.700	.0972	5.00	15.00	30.2
24	1.14×10^{-3}	0.700	.0972	8.50	11.50	30.2
27	1.13	0.700	.0972	8.50	11.50	30.2

[a] Dioxane contained about 15% water. [b] In runs 12 through 27 the dioxane was purified by refluxing thirty-five minutes over metallic sodium and then distilling in an atmosphere of nitrogen. Titanium sulfate tests for peroxide were negative. [c] This run was made with diphenylmercury having a melting point of 121°. [d] Two drops of 30% hydrogen peroxide were added. The readings were too erratic to be of value. [e] This reaction was too slow to measure. [f] 0.028 g. of sodium chloride was added to the reaction mixture. [g] 1.50 cc. of water was added to the reaction mixture.

cury. The reaction could be slowed considerably by lowering the temperature to just above the freezing point of dioxane but even so it was deemed expedient to use a weaker acid to reduce the rate of the reaction.

It was found that 0.1 M acetic acid and diphenylmercury required more than three days to react completely while a 50% (by volume) solution of glacial acetic acid and dioxane cleaved 0.1 M diphenylmercury in about three hours at room temperature. The same molar concentration of formic acid caused complete cleavage in a little more than an hour. A solution of 0.1 M oxalic acid in dioxane caused the precipitation of a white solid after standing forty-six hours. The melting point of this compound was 245° (uncor.).

These rough experiments are evidence in favor of a second order mechanism since they indicate that the concentration and the strength of the acid strongly influence the rate of the cleavage.

Starting Materials and Products.—Glacial acetic and 90% formic acids were used in the cleavage experiments. The diphenylmercury used had a melting point reversible at 125° and the uniformity of the plots of the data is an indication of the purity of the reagents and of the absence of interfering reactions.

The product of the cleavage with acetic acid was isolated by adding a large excess of water to the solution at the end of run 6. After cooling and standing for some time, crystals of phenylmercuric acetate formed; m. p. found 148–149°; m. p. reported 148–149°.

Phenylmercuric formate is quite soluble in aqueous dioxane. The product of the cleavage with formic acid was isolated indirectly by adding a solution of sodium chloride to the residues from the formic acid runs; m. p. of phenylmercuric chloride found, 252°; reported, 252°.

Procedure.—In a typical run, the diphenylmercury was weighed out to the nearest milligram, placed in a 50 ml. Erlenmeyer flask and the calculated quantity of dioxane was added. The calculated quantity of acid was introduced from a buret and the time was noted as the start of the reaction.

The well mixed solution was drawn into the dilatometer by vacuum and the dilatometer was placed in the thermostat. The operation from the time of mixing to the first reading required from four to six minutes. The magnetic stirrer hastened temperature equilibration. The use of such a sensitive reading device revealed, however, that the movement of the stirring rod caused the dilatometer bulb to expand and about three minutes was required for equilibration of the dilatometer after the use of the stirrer. Readings reproducible to about 10 microns were obtained by using the stirrer for ten seconds and allowing three minutes for equilibration before each reading was taken.

The total change in length of the dilatometer column, Δl, which was read in a given reaction was of the order of 0.15 cm. A considerable portion of the total volume change took place before the first readings could be taken. It was found essential to allow several minutes for temperature equilibrium to be established since there is a pronounced heat of mixing encountered when formic acid is mixed with dioxane. The difficulties in controlling conditions for such a small volume change made the use of a smaller capillary ineffective. The reproducibility of the method is indicated by the results given in Table I. The absolute value of the rate constants may be slightly in error due to the difficulty encountered in measuring such small volume changes. For this reason we have drawn only those conclusions which can be based on the relative values of the constants.

Calculation of Results.—No reaction in solution has been studied in which there is no volume change during the course of the reaction. The reactions studied here were accompanied by a slight expansion. It may be seen that if l_∞ designates the length of the liquid column in the capillary of the dilatometer when the reaction is finished and l_t the length of the column at time t after the reaction has started, then $(l_\infty - l_t)$ is a measure of the extent of the incompleted portion of the reaction at time t. Thus a plot of $(l_\infty - l_t)$ *vs.* t gives the same form of curve as a plot of the concentration of diphenylmercury *vs.* t.

Since in all cases the concentration of the acid was from 60 to 100 times as great as that of the mercurial and remained essentially constant throughout the course of the reaction, only the variation in concentration of diphenylmercury was considered in the rate calculation. A plot of $(l_\infty - l_t)$ *vs.* t gave an exponential curve and a plot of log $(l_\infty - l_t)$ *vs.* t gave a straight line. This behavior is characteristic of a first order reaction and therefore it was concluded that under the conditions employed the cleavage was pseudo first order.

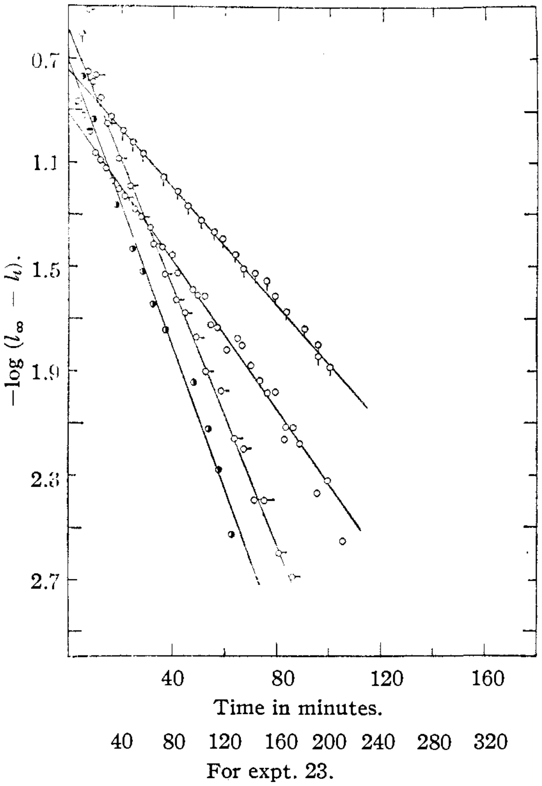

Fig. 1.—Pseudo first order rate curves for the cleavage of diphenylmercury by varying strengths of formic acid in dioxane: o-, expt. 17; ♀, expt. 19; O, expt. 23; ◑, expt. 27.

The rate constants for the reactions were obtained by multiplying the slopes of the curves from the plots of log $(l_\infty - l_t)$ *vs.* t by 2.303. Sample log plots are shown in Fig. 1.

Table I gives the experimentally determined rate constants and the conditions under which they were measured.

Results and Discussion

The following effects were tested for their influence on the rate of cleavage

(1) change in the type of acid (acid strength)
(2) change in the concentration of the diphenylmercury
(3) presence of peroxide in the dioxane
(4) presence of chloride ions in the mixture
(5) presence of water in the dioxane
(6) change in the concentration of acid

Effects of Acid Strength.—A comparison of experiments 1–3 and 7 with 8 and 9 shows the effect of acid strength on the rate constant. Although the runs with formic acid were made at a temperature 12° below that of the corresponding runs with acetic acid, the rate constants with formic acid are still roughly twice as large as those obtained with acetic acid. The fact that hydrochloric acid in low concentration cleaves diphenylmercury much more rapidly than either acetic or formic acid is also evidence of the strong dependence of rate of cleavage upon acid strength.

Assuming acid attack on the mercurial, a dependence of this nature would be expected since stronger acids, by virtue of their greater proton donating power, should attack more vigorously. Assuming preliminary ionization on the other hand, the rate of cleavage should be almost independent of the strength of the acid employed so long as it is a reasonably strong acid.

Effects of the Concentration of Diphenylmercury.—A comparison of experiments 1–3 and 7 with 4–6 and experiments 8 and 9 with 10 illustrates this effect. If we assign the value of unity to the concentration and average velocity constant of the first group, we obtain the comparative constants shown in Table II.

TABLE II

RELATION BETWEEN CONCENTRATION OF DIPHENYLMERCURY AND VELOCITY CONSTANT

Expts.	Comparative concn. of diphenylmercury	Comparative rate constant	
1, 2, 3, 7	1.0	1.00	In dioxane–acetic acid
4, 5	1.5	0.74	
6	2.0	.60	
8, 9	1.0	1.00	In dioxane–formic acid
10	1.5	0.79	

These results indicate that as the concentration of the mercurial is decreased the rate constant increases, in spite of the fact that within a given run the reaction is apparently purely first order. Moelwyn-Hughes[8] has made the statement that in the majority of cases rate constants of reactions in solution increase with the dilution but no explanation of this phenomenon is given for non-ionic reactions.

The results in dioxane–acetic acid may be expressed in the form:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -k_1 \frac{c}{c_0{}^x}$$

Solving for k_1 and x we obtain:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -9.78 \times 10^{-5} \frac{c}{c_0{}^{0.737}}$$

One possible explanation of this concentration dependence would be based upon association of the solute, decreasing in extent with dilution. To test this hypothesis, molecular weight determinations were made upon diphenylmercury in pure dioxane. These indicated that no significant amount of association takes place over a much wider range of concentrations of diphenylmercury than was used in the cleavage experiments. This does not necessarily disprove the association hypothesis because association would probably be greater in the acid–dioxane mixture used in the cleavages than in pure dioxane. This seems probable since the mercurial is less soluble in the cleavage mixture than in pure dioxane. If association of the diphenylmercury alone were the cause of this effect, an individual run would show an increased rate constant as the reaction progressed and the plot of log $(l_\infty - l_t)$ *vs.* t would be concave downward. Such a deviation from a straight line was not encountered. We must conclude that phenylmercuric acetate associates with diphenylmercury, if this explanation is to be accepted.

Results analogous to ours were encountered by Kapanna[9] during his investigation of the decomposition of trichloroacetic acid in water but we feel that as yet no satisfactory explanation for this phenomenon has been developed.

Effect of Peroxide.—Since dioxane tends to form peroxides on standing, it was felt advisable to determine whether they influence the cleavage. Experiment 9 was made with dioxane containing about 15% water and enough peroxide to give a strong test with potassium iodide. The peroxide had formed spontaneously. Since the constant for 9 (containing water and peroxide) agrees with the constant from 18 (containing water but no peroxide) it seems safe to say that peroxides have little or no effect upon the rate of this reaction. The small difference between the rate constants for experiments 12 and 13 (made with dry, peroxide-free dioxane) and those for 9 and 18 may possibly be accounted for on the basis of the difference in water content.

Experiments 1–10 were made with dioxane containing varying quantities of peroxides (formed spontaneously) but the reproducibility of the curves is evidence that this had little effect.

An attempt was made to add a specific quantity of hydrogen peroxide to experiment 15 but the decomposition of the hydrogen peroxide itself caused the readings to be too erratic to be of value. The fact that the decomposition of hydrogen peroxide is catalyzed by the salts of heavy metals and by glass makes this result logical and does not alter the conclusion that the organic peroxides which have formed spontaneously in dioxane have little or no effect upon the rate of the acid cleavage.

Effect of Chloride Ion.—The possibility that the negative ions present might strongly influence the rate of cleavage was tested in the following manner. As a rough qualitative experiment, some 60% aqueous dioxane was saturated with sodium chloride and diphenylmercury was added. After standing for half a day, excess water was added but the melting point of the precipitate which formed was 124° indicating that little if any cleavage had taken place (m. p. of diphenylmercury is 124–125°).

Experiment 17 contained 0.028 g. of sodium chloride per 25 g. of solution (saturated solution) but the rate constant was the same within experimental error as that obtained in 12 and 13, made under the same conditions but without the salt present. It may be concluded that chloride ion at the saturation value for sodium chloride is without effect on the rate of the reaction in the concentration employed.

Effect of Water.—A comparison of experiment 18 made with dioxane containing 11.6% water with experiments 12 and 13 illustrates the effect of water upon the rate constant of the cleavage. While the presence of water appears to cause an increase in the rate constant, the effect is so small that it may be charged to experimental error. This indicates that a moderate change in dielectric constant has little if any influence upon the rate constant.

Effects of Acid Concentration.—It was found that the rate constants were strongly influenced by the concentration of the acid even though it was always from 50 to 100 times as great as that of the mercurial. A consideration of experiments 12, 13, 14, 17, 19, 23, 24 and 27 shows that a small increase in acid concentration causes proportionately a much larger increase in the rate constant. If we again assign the value unity to the concentration and average velocity constant of the first group, we obtain the comparative constants shown in Table III.

These results may be expressed in the form

$$\mathrm{d}c/\mathrm{d}t = -k\ [\mathrm{Acid}]^y c$$

Solving for y we obtain

$$\mathrm{d}c/\mathrm{d}t = -k\ [\mathrm{Acid}]^{2.85} c$$

This effect is opposite in direction to the effect of

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[8] Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford Univ. Press, New York, N. Y., 1933, pp. 99–104.

[9] Kapanna, *Z. physik. Chem.*, **158A**, 355 (1931–1932).

TABLE III

RELATION BETWEEN CONCENTRATION OF FORMIC ACID AND VELOCITY CONSTANTS

Expts.	Comparative concn. of formic acid	Comparative rate constant
23	1.0	1.00
19	1.2	1.63
12, 13	1.5	3.64
24, 27	1.7	4.22

changing the concentration of mercurial, as well as opposite to that usually observed.[8]

It might be argued that the agent causing the cleavage is the solvated proton, whose concentration would increase rapidly with the increase in dielectric constant caused by the increasing proportion of formic acid. This explanation is rendered improbable by the observation, recorded above, that water, with a much higher dielectric constant than formic acid, causes little, if any, increase in the rate constant. For this reason, we must seek an explanation based upon the assumption of molecular formic acid as the active species.

A dependence of this nature might mean that several molecules of acid are involved in the reaction according to the mechanism

$$R_2Hg + nHA \longrightarrow R_2HgH^+ + A(HA)^-_{n-1} \longrightarrow RHgA + RH + (n-1)HA$$

The value of 2.85 obtained for n suggests the possibility that a trimer of formic acid may be the active species in dioxane solutions.

Another explanation for the dependence of the rate constants upon acid concentration involves an equilibrium between the acid and the dioxane. Dioxane exerts a strong levelling effect upon acids and spectral measurements by Gordy and Stanford[10] have shown that it possesses a pronounced ability to form hydrogen bonds. A reaction between dioxane and acids as strong as acetic or formic would be expected to take place in the form of extensive hydrogen bridging. This reaction between acid and solvent may be represented by the equilibrium $HA + S \leftrightarrows HAS$.

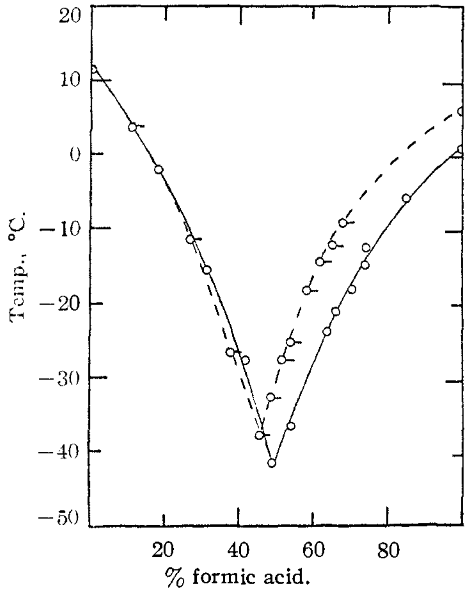

Fig. 2.—Freezing point of formic acid–dioxane mixtures: – – – o-, 99% formic acid; —— o, 90% formic acid.

An attempt was made to detect the presence of the complex HAS by plotting the freezing point curve of formic acid and dioxane but no irregularities indicating compound formation were found. Two such plots are shown in Fig. 2.

Since it is known that some association takes place between dioxane and the acid, calculations may be set up using this equilibrium which will give the observed rate constants for the cleavage reaction. Thus, if it is assumed that the acid associated with the solvent is not as strong an attacking agent as the free acid, then the free acid present in the solution and not the total acid concentration is the important factor in determining the reaction rate. If we denote initial concentration with the subscript 0 and equilibrium concentrations with the subscript eq, this equilibrium concentration of free acid may be determined as follows

$$K_{eq} = \frac{[HAS]}{[HA]_{eq}\,[S]_{eq}}$$

$$[HA]_{eq} = [HA]_0 - [HAS]$$

$$[S]_{eq} = [S]_0 - [HAS] = [S]_0 - ([HA]_0 - [HA]_{eq})$$

or

$$K_{eq} = \frac{[HA]_0 - [HA]_{eq}}{[HA]_{eq}\,([S]_0 - [HA]_0 + [HA]_{eq})}$$

If an equilibrium constant of 2 is assumed, $[HA]_{eq}$ calculated at the various concentrations may be used to calculate the rate constants at these concentrations. Using k from run 12 as the standard and the acid concentrations calculated from the above expression, the following results were obtained.

Expts.	k, obs.	k, calcd.
12	9.69×10^{-4}	
19	4.38	4.49×10^{-4}
23	2.69	2.61
24	1.14×10^{-3}	1.47×10^{-3}

It is thus evident that a solvation equilibrium constant in the neighborhood of 2 can account for observed variation of the rate constant with changing acid concentration.

Proof of the existence of molecular association of the acid in dioxane or proof of the presence of a fairly large quantity of a complex formed from dioxane and acid is necessary to warrant the acceptance of either of the above explanations for the dependence of the rate constants upon acid concentration under the conditions employed. As yet the experimental evidence necessary for a decision between these hypotheses is not available.

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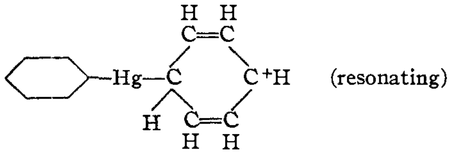
[10] Gordy, *J. Chem. Phys.*, **7**, 93 (1939); Gordy and Stanford, *ibid.*, **8**, 170 (1940); *ibid.*, **9**, 204 (1941); Gordy, *ibid.*, **9**, 215 (1941).

Conclusions

It is evident from our studies that the mechanism of cleavage of diphenylmercury by formic and acetic acids involves an attack of the acid upon the mercurial. Our results are consistent with the formulation of the first intermediate in the reaction as follows[11]



It thus becomes possible to utilize the large variety of known aromatic mercurials for the purpose of studying the mechanism of aromatic substitution.

In spite of the general applicability of this mechanism, the kinetics of the cleavage reaction are not second order when followed through changes in concentration of each reagent. Further study will be necessary to determine whether or not molecular association constitutes the reason for the variation of the rate constant with changes in concentration.

One of us (M.A.N.) wishes to acknowledge a grant-in-aid from Hynson, Westcott and Dunning Research Fund.

Summary

1. The cleavage of diphenylmercury in dioxane with formic and acetic acids has been followed dilatometrically.

2. The velocity constants are independent of the concentration of peroxide or of chloride ion at the saturation value in the reaction mixture.

3. The addition of water has little effect on the rate of cleavage.

4. The rate constant is increased by increasing acid strength.

5. The rate of the reaction is dependent upon the concentration of diphenylmercury. Within a single experiment, the rate constant does not drift with exhaustion of the reagent. In spite of this, the rate constant is dependent upon the initial concentration of diphenylmercury, decreasing concentration causing an increase in the rate constant.

6. The relation between the preceding observation and the possibility of molecular association of the diphenylmercury is discussed.

7. The rate of the reaction is dependent upon the concentration of the acid employed. The rate constant varies with the concentration of the acid, increasing with increasing concentration.

8. Two hypotheses are advanced to account for the variation of rate constant with acid concentration. The first assumes the formation of a polymolecular acid complex. The second assumes association between acid and solvent.

9. It is concluded that aromatic mercurials may be utilized to study the mechanism of aromatic substitution.

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[11] See Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, 1941, p. 473.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Arylsulfenyl Chlorides. I. Addition to Unsaturated Compounds[1]

BY ROBERT A. TURNER[2] AND RALPH CONNOR[3]

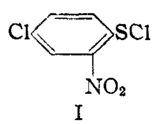
The arylsulfenyl halides, ArSX, discovered by Zincke,[4] were reinvestigated by Lecher and his collaborators.[5] Lecher and Stöcklin[6] demonstrated that an arylsulfenyl chloride would react with ethylene

$$ArSCl + CH_2{=}CH_2 \longrightarrow ArSCH_2CH_2Cl \quad (A)$$

(Ar represents C_6H_5–, 4-$CH_3C_6H_4$–, or 4-$NO_2C_6H_4$–)

The yields of aryl β-chloroethyl sulfides varied from 60 to 80%. The investigations to be described here were undertaken in order to examine the generality of the addition of arylsulfenyl chlorides to unsaturated compounds.[7]

The arylsulfenyl chlorides chosen for use were 2-nitro-4-chlorophenylsulfenyl chloride (I) and 4-nitrophenylsulfenyl chloride (II). Of these, I



I

II

is the more stable and may be stored indefinitely. On the other hand, II can be stored only a few

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[1] This paper is abstracted from the dissertation of Robert A. Turner presented to the Graduate School of the University of Pennsylvania in June, 1943, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] Present address: Rohm and Haas Co., Philadelphia, Pennsylvania.

[4] Zincke, *Ann.*, **391**, 55; 57 (1912).

[5] The literature of arylsulfenyl chlorides is reviewed in a recent article by Kharasch, Potempa and Wehrmeister, *Chem. Rev.*, **39**, 269-332 (1946).

[6] Lecher and Stöcklin, *Ber.*, **58**, 414 (1925).

[7] The work reported in this paper was completed in the spring of 1943, but war-time conditions have prevented earlier publication. Recently, Fuson, *et al.* [Fuson, Price, Bauman, Bullitt, Hatchard and Maynert, *J. Org. Chem.*, **11**, 469 (1946); Fuson, Price and Burness, *ibid.*, **11**, 475 (1946)] have reported the results of their work on the Levinstein process (for the synthesis of mustard gas) which includes a study of the addition of 2-chloroethylsulfenyl chloride to olefins.