removal of solvents *in vacuo* below 70° the residual oil was treated with anhydrous ether at 0°. The crystals were collected, washed with cold anhydrous ether and dried to give 8.8 g. (20.8 mmoles, 92%) of **4-methoxydiphenyliodonium trifluoroacetate**, m.p. 166–169° (dec.) after two further crystallizations from benzene.

Anal. Calcd. for $C_{15}H_{12}F_3IO_3$: C, 42.47; H, 2.85. Found: C, 42.63; H, 2.95.

Reaction D-5 (Oxidation of an Iodo Compound Followed by Condensation).—No reactions of this type have been previously reported by this group; *cf.* Sandin and co-workers.[24] Reported below are the oxidation and condensation of a nitroiodobenzene and iodobenzoic acid to nitro- and carboxydiphenyliodonium salts.

2-Nitrodiphenyliodonium Iodide.—To a solution of 5.0 g. (20 mmoles) of 2-nitroiodosobenzene in 100 ml. of concd. sulfuric acid there was added with stirring at 20–25° 6.0 g. (22 mmoles) of potassium persulfate and then 25 ml. of benzene. After further stirring for 1.5 hours, the reaction mixture was poured onto ice, the solid was removed by filtration, unreacted benzene was separated, and the solution was clarified by several treatments with activated carbon. Addition of aqueous potassium iodide gave an orange precipitate which on washing and drying gave 7.2 g. (17.4 mmoles, 79%) of **2-nitrodiphenyliodonium iodide**, m.p. 102°; see Table V for salt of m.p. 106–107°.

4-Carboxydiphenyliodonium Iodide.—To a solution of 10.0 g. (40 mmoles) of 4-iodobenzoic acid in 100 ml. of concd. sulfuric acid there was added with stirring 21.6 g. (80 mmoles) of potassium persulfate at −10° and then, after 15 minutes, 50 ml. of benzene at −20°. The mixture was stirred at −10° for 1 hour and at 0° for 3 hours and then was processed as in the preceding experiment to give 13 g. (28 mmoles, 69%) of crude **4-carboxydiphenyliodonium iodide**. After crystallization from methanol the product softened at 155–160° but finally melted at 265°; 4-iodobenzoic acid melts at 265°.

Anal. Calcd. for $C_{13}H_{10}I_2O_2$: C, 34.45; H, 2.21. Found: C, 34.37; H, 2.35.

Metathesis. Diphenyliodonium Fluoroborate.—To a solution of 44 g. (139 mmoles) of diphenyliodonium chloride in 800 ml. of water there was added at 60° 150 mmoles of silver fluoroborate (61.3 g. of Baker and Adamson solution: 47.75% $AgBF_4$, 3.58% HBF_4, 0.71% H_3PO_3). The precipitate of silver chloride was removed, and the filtrate was cooled and seeded. Alternate crystallization and concentration of mother liquors at 50 mm. pressure yielded 43.8 g. (120 mmoles, 86%) of **diphenyliodonium fluoroborate**, m.p. 134–136°. Recrystallization of 40 g. of this material from 125 ml. of water raised the m.p. to 136°, reported[30] m.p. 136°.

Diphenyliodonium Benzenesulfonate.—To a solution of 81 g. (260 mmoles) of diphenyliodonium chloride and 53 g. (300 mmoles) of benzenesulfonic acid monohydrate in 450 ml. of methanol boiling under reflux there was added in small portions 34.1 g. (130 mmoles) of lead carbonate. The reaction mixture was stirred at reflux for two hours and then for four hours at room temperature. After the removal of lead chloride from the chilled solution, the solution was concentrated to one-half the original volume, and one-half pound of ether was added with stirring. The first and second crops of crystals (96 g.) obtained from the cold solution were combined and recrystallized from a liter of isopropyl alcohol to give 76 g. (177 mmoles, 68%) of **diphenyliodonium benzenesulfonate**, m.p. 175–184°. This material was neutral to litmus paper and gave negative tests for lead and chloride ions. Two more crystallizations raised the m.p. to 178–182°.

Anal. Calcd. for $C_{18}H_{15}IO_3S$: C, 49.33; H, 3.45; I, 28.94; S, 7.32. Found: C, 49.51; H, 3.69; I, 28.93; S, 7.32.

Diphenyliodonium Tosylate.—In a similar manner there was obtained from 107.5 g. of diphenyliodonium chloride, 76 g. of *p*-toluenesulfonic acid monohydrate and 45.3 g. of lead carbonate in methanol 133 g. of crude product. This was crystallized from isopropyl alcohol to give 105.6 g. (69%) of **diphenyliodonium tosylate**, m.p. 176–184°, neutral to litmus and free of lead and chloride ions. Two further crystallizations raised the m.p. to 178–181°.

Anal. Calcd. for $C_{19}H_{17}IO_3S$: C, 50.45; H, 3.79; I, 28.06; S, 7.09. Found: C, 50.70; H, 4.03; I, 28.00; S, 7.40.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. X. Catalysts and Inhibitors in the Reactions of Diphenyliodonium Ions with Anions and Hydroxylic Solvents[1]

BY F. MARSHALL BERINGER, E. MELVIN GINDLER, MORRIS RAPOPORT AND ROY J. TAYLOR

RECEIVED JUNE 20, 1958

The retardation of the hydrolysis of the diphenyliodonium ion by acid and by chloride ion and the retardation of the reaction with chloride ion by acid have suggested: (a) that these reactions proceed by the reversible formation from the diphenyliodonium ion of an intermediate, (b) that the intermediates may be reconverted to diphenyliodonium ion by acid, and (c) that the intermediate may be hydrolyzed by water or react with chloride ion and water. Equations derived on the basis of these assumptions have been used to analyze the data. Oxygen was found to have little effect on the initial rates of these reactions but to affect the shapes of the curves; these effects have been discussed but cannot now be explained. The results of the hydrolyses of diphenyliodonium salts catalyzed by added cupric sulfate and run under oxygen, nitrogen and hydrogen do not fully distinguish between various mechanistic possibilities, including: (a) reversible formation and irreversible hydrolysis of a copper-containing intermediate and (b) reaction of the diphenyliodonium ion with copper(I) hydroxide. Indeed, our evidence allows both copper(I) and copper(II) species as catalysts but suggests that the copper(I) catalyst is more reactive. Some peroxide-catalyzed reactions of iodonium salts with ethers and alcohols also are discussed.

Introduction

About ten years after the discovery of the iodonium salts Büchner reported a preliminary study[2] of the decomposition of diphenyliodonium chloride and iodide to halogenobenzenes with heat and light. An earlier paper[3] of the present series reported on

$$C_6H_5I^+C_6H_5\ X^- \longrightarrow C_6H_5X + C_6H_5I \qquad (A)$$

further work in this field and commented on Büchner's findings.[4] In the present study the

---

(1) This paper is taken largely from the master's thesis of Morris Rapoport and in smaller part from the doctoral dissertations of E. Melvin Gindler and Roy J. Taylor; see also Acknowledgments. Attention is directed to the recent substantial contribution to this field by M. C. Caserio, D. L. Glusker and J. D. Roberts (ref. 8).

(2) E. H. Büchner, *Koninklijke Akad. v. Wettenschappen te Amsterdam, Proc. Sec. Sci.*, **5**, 646 (1903) (in English).

(3) F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(4) Ref. 2: "Very small quantities of acid retard the reaction (with chloride ion) to a remarkable extent or bring it to a standstill; the presence of traces of iodine causes a regular fall in the reaction coefficient; a little of the free base (diphenyliodonium hydroxide) accelerates, on the other hand, the decomposition to a strong degree. The halogenobenzenes formed during the reaction appear to be inert."

reactions of diphenyliodonium chloride have been re-examined, in part to resolve various discrepancies in the literature.[4] Further, to aid in understanding the hydrolysis of the cation, the reactions

$$C_6H_5I^+C_6H_5 + 2H_2O \longrightarrow C_6H_5OH + C_6H_5I + H_3O^+ \quad (B)$$

of diphenyliodonium benzenesulfonate[5] and *p*-toluenesulfonate[5] have been studied. These salts were chosen because of their solubilities and the inertness and low nucleophilicities of the anions. Special attention has been given to the effects of the atmosphere (air, oxygen, nitrogen or hydrogen) copper salts, acid and iodine,[4] which may be a trace product.

Some less intensive studies of reactions in partially aqueous or non-aqueous systems are reported later in the paper. They include reactions with various alcohols, glycols and glycol ethers[6] and with hydroxide ion in dioxane–water.[7]

At the start of this work it was believed that the hydrolysis of the diphenyliodonium ion obeyed first-order kinetics (eq. i), while the reaction with chloride ion obeyed second-order kinetics (eq. ii).[3] These two equations together give eq. iii. Indeed plots according to eq. ii and iii were roughly linear.[3]

$$d[H_3O^+] = k_S[(C_6H_5)_2I^+]dt \quad (i)$$

$$-d[Cl^-] = k_2[(C_6H_5)_2I^+][Cl^-]dt \quad (ii)$$

$$-d\ln[Cl^-] = (k_2/k_S)d[H_3O^+] \quad (iii)$$

Preliminary hydrolyses of diphenyliodonium benzenesulfonate showed that while the kinetic order might be roughly first, rate constants were not reproducible. To determine whether atmospheric oxygen was exerting an effect, runs were made under nitrogen. Linear first-order plots no longer were obtained; the experimental first-order rate constants decreased with time (Fig. 1). This prompted a study of the effects of atmosphere and added acid on both reactions.

Uncatalyzed Reactions of Diphenyliodonium Ions

Hydrolysis.—The hydrolysis of the diphenyliodonium ion was studied by following the formation of acid (reaction B) in aqueous solutions of diphenyliodonium chloride, benzenesulfonate and *p*-toluenesulfonate at constant temperature near 100°. For the main observations see Fig. 1.

(a) Hydrolysis was in all cases repressed by small amounts of added sulfuric acid; 0.006 *N* acid made the initial rate of hydrolysis negligible. (This inhibition was weakened progressively with increasing time.)

Because of the effect of added acid, the observed decrease of the empirical first-order rate constant for the hydrolysis of diphenyliodonium benzenesulfonate or *p*-toluenesulfonate during a run under nitrogen or hydrogen has been attributed to the inhibitory effect of the acid formed. The fact that a similar run under oxygen showed no decrease in the first-order rate constant with acid formed is still unexplained.

(b) Hydrolysis appears to have been slower in the presence of chloride ion than in the presence of benzenesulfonate ion (Table I). Under nitrogen, hydrolysis occurred about five times as rapidly in the absence of chloride ion as in its presence (about 0.06 *N* initially), while under oxygen the corresponding factor was about two. It is considered possible, though unlikely, that the differences observed in the presence and absence of chloride ion were due to different amounts of adventitious catalyst or inhibitors in the two salts, in spite of precautions to obviate contamination.

TABLE I

INITIAL RATES OF HYDROLYSIS OF DIPHENYLIODONIUM SALTS IN WATER AT 98.8°

Anion	Atm.	Millimoles/kilogram $[C_6H_5I^+C_6H_5]_0$	Millimoles/kilogram $[H_3O^+]_{100}$[a]	$\frac{10^3[H_3O^+]_{100}}{[C_6H_5I^+C_6H_5]_0}$[b]
$C_6H_5SO_3^-$	N_2	66.2	4.0	60[c]
	H_2	49.2	2.8	57
	O_2	43.0	2.0	47
Cl^-	N_2	56.9	0.4	7
		56.6	0.8	14
	O_2	50.5	0.9	18
		67.1	2.0	30

[a] Acid formed in 100 hr.; no acid initially present. [b] This ratio approximates 10^5 times the initial first-order rate constant for hydrolysis, in hr.$^{-1}$. [c] Average for six runs, of initial concentration 39–66 mmoles/kg., was 59 ± 6.

(c) Phenol in comparatively large amounts (168 mole %) slowed acid formation somewhat less than iodine in small amounts (2.4 mole %). The addition of hydroquinone caused the rapid formation of one equivalent of acid. These effects have not been investigated further.

The main conclusion to be drawn from these observations is that hydrolysis in neutral or acid solution cannot be a one-step nucleophilic attack of water on the diphenyliodonium cation; such a mechanism does not account for repression of hydrolysis by acid and by chloride ion.

Reaction with Chloride Ion.—The reactions of aqueous solutions of diphenyliodonium chloride held at constant temperature near 100° were studied by following the disappearance of chloride ion (reaction A) and the formation of acid (reaction B). The main observations of the present work, which supplement those previously reported,[3] are given: (a) The disappearance of chloride ion was repressed by acid initially present for runs under nitrogen or oxygen. In both atmospheres, however, the repression decreased with increasing time (Fig. 2). (b) Runs under oxygen with no added acid gave linear second-order plots as previously reported[3] (Fig. 2). Plots of similar runs under nitrogen curved upward; *i.e.*, the apparent second-order rate constant increased with time (Fig. 2). (c) Runs with no added acid had about the same ini-

---

Ref. 3: "Thus in the present work there has been no evaluation of the effect of light, base or iodine on the rate of the reaction between diphenyliodonium and chloride ions in water. Büchner reported no solvolytic reaction, while one was found in the present work. The acid formed in the solvolytic reaction did not appear to inhibit the main reaction, as acid (in higher concentration) was reported to do by Büchner. Finally, while Büchner reported the product halogenobenzenes inert, the present workers found that they accelerated the decomposition of diphenyliodonium chloride, especially in the runs catalyzed by cupric chloride."

(5) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, THIS JOURNAL, **81,** 342 (1959).

(6) I. Kuntz, doctoral dissertation, Polytechnic Institute of Brooklyn, 1955.

(7) E. M. Gindler, doctoral dissertation, Polytechnic Institute of Brooklyn, 1957.

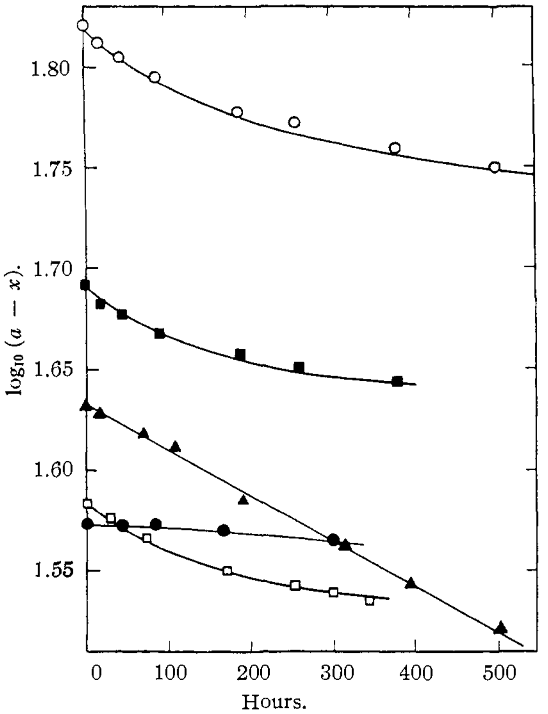


Fig. 1.—First-order plots of the hydrolysis of diphenyliodonium benzenesulfonate at 98.8°: symbol, atm., *a* and *h* in mmoles kg.$^{-1}$: ○, N_2, 66.2, none; ■, H_2, 49.2, none; ▲, O_2, 43.0, none; □, N_2, 38.3, 2.9; ●, N_2, 37.4, 6.7.

tial rates under nitrogen or oxygen. (d) The addition of a small amount (0.1 mole %) of iodine increased the initial rate of a run in air almost threefold and gave a linear second-order plot. The same slope was reached by a run under nitrogen with no added iodine (or acid) in about 250 hours.

The two main conclusions from these observations are that oxygen has little effect on the initial rate and that chloride ion does not disappear by a one-step reaction with the diphenyliodonium ion; such a mechanism does not account for repression by acid.

A Kinetic Scheme Involving an Intermediate.—One possible reaction pattern would seem to be: (a) a base might convert the diphenyliodonium cation to a reactive intermediate; (b) the concentration of this intermediate might be repressed by oxonium and by chloride ions; (c) this intermediate might give phenol by decomposing or reacting with water; and (d) this intermediate might give chlorobenzene by reacting with chloride ion and water.

A generalized kinetic scheme for reactions of the diphenyliodonium cation in water is

$$\mathrm{C_6H_5I^+C_6H_5} + n\mathrm{H_2O} \underset{\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftarrows}} \mathrm{C_{12}H_9I\cdot(H_2O)}_n \qquad (C)$$

$$\mathrm{C_{12}H_9I\cdot(H_2O)}_n + (1-n)\mathrm{H_2O} \longrightarrow \mathrm{C_6H_5OH} + \mathrm{C_6H_5I} \qquad (D)$$

$$\mathrm{C_{12}H_9I\cdot(H_2O)}_n + \mathrm{X^-} + \mathrm{H_2O} \longrightarrow \mathrm{C_6H_5X} + \mathrm{C_6H_5I} + \mathrm{HO^-} + n\mathrm{H_2O} \qquad (E)$$

$$\mathrm{C_{12}H_9I\cdot(H_2O)}_n + \mathrm{BH} \longrightarrow \mathrm{C_6H_5B} + \mathrm{C_6H_5I} + n\mathrm{H_2O} \qquad (F)$$

Reaction with the neutral base BH (*e.g.*, an alcohol, a mercaptan or an amine) is included only for completeness and is considered explicitly in the kinetic analyses only where BH is water.

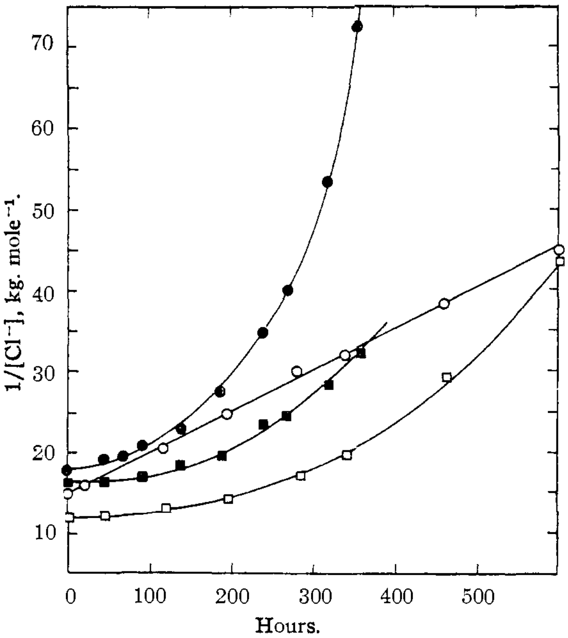


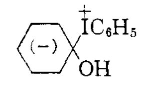
Fig. 2.—Second-order plots of the disappearance of chloride ion in aqueous diphenyliodonium chloride at 98.8°: symbol, atm., *a* and *h* in mmoles kg.$^{-1}$: ●, N_2, 56.9, none; ○, O_2, 67.1, none; ■, O_2, 60.0, 12.0; □, N_2, 82.4, 6.1.

The Composition of the Intermediate.—Kinetics of reactions in water cannot tell the degree of hydration of the intermediate, *i.e.*, the value of *n*. The two cases which seem most promising are those where $n = 1$ and $n = 0$.

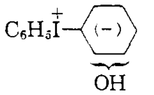
When $n = 1$, the intermediate has the composition of diphenyliodonium hydroxide, $C_{12}H_{10}IOH$. Three types of structures to be considered are: I (attachment of the hydroxyl group to iodine), II (attachment of the hydroxyl group to the 1-carbon) and III (attachment of the hydroxyl group to the 2-, 3- or 4-carbons).

$(C_6H_5)_2IOH$

I



II

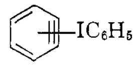


III

While I and II can be visualized as intermediates in the formation of phenol, III is not so amenable. And indeed it seems improbable that any of these intermediates would be more susceptible than the initial diphenyliodonium cation to attack by chloride ion.

If, on the other hand, we consider that the intermediate is the conjugate base, $C_{12}H_9I$, of the diphenyliodonium ion, $C_{12}H_{10}I^+$, there is a structural problem. At this time it seems that the only structures worthy of serious consideration are those formed on loss of an *ortho*- or 2-hydrogen as a proton. Structures IV and V are excluded by the recent reported observation of Caserio, Glusker

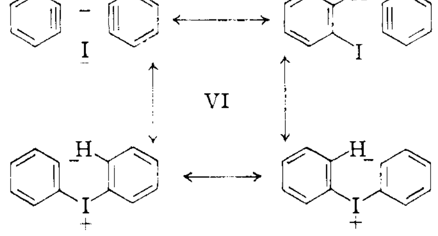
IV



V

and Roberts[8] that hydrolysis of the 4-nitro-4′-methoxydiphenyliodonium cation gave only 4-nitrophenol and 4-methoxyphenol. The absence of isomers means that symmetrical structures IV and V cannot represent the intermediate.

A final structure (VI) is that in which the 2-anion is stabilized by hydrogen bonding with a


VI

2′-hydrogen and by other interactions with the aromatic rings. Such stabilization might allow the compound to be a discrete intermediate and have a finite existence. While this bridged structure seems to be an interesting possibility and some results in this paper are discussed in terms of structure VI, it is realized explicitly that this is only a working hypothesis which needs substantiation. This includes testing the hypothesis by investigating possible deuterium exchange in heavy water; such work is planned.

$$C_{12}H_{10}I^+ + D_2O \longrightarrow C_{12}H_9I + D_2{}^+OH \qquad (C)$$

$$C_{12}H_9I + D_3O^+ \longrightarrow C_{12}H_9DI^+ + D_2O \qquad (D)$$

Kinetics of Reactions Proceeding Through the Conjugate Base, $C_{12}H_9I$.—For the sake of concreteness the kinetic scheme proposed in a preceding section may now be specialized for the formation of phenol and iodobenzene from the conjugate base in water.

$$C_6H_5I^+C_6H_5 + H_2O \underset{2}{\overset{1}{\rightleftarrows}} C_{12}H_9I + H_3O^+ \qquad (E)$$

$$C_6H_5I^+C_6H_5 + HO^- \underset{4}{\overset{3}{\rightleftarrows}} C_{12}H_9I + H_2O \qquad (F)$$

$$C_{12}H_9I + H_2O \xrightarrow{5} C_6H_5OH + C_6H_5I \qquad (G)$$

$$C_{12}H_9I + HO^- + H_2O \xrightarrow{6} C_6H_5OH + C_6H_5I + HO^- \qquad (H)$$

$$C_{12}H_9I + Cl^- + H_2O \xrightarrow{7} C_6H_5Cl + C_6H_5I + HO^- \qquad (I)$$

On the basis of arguments already advanced, it seems probable that if the conjugate base $C_{12}H_9I$ is the reaction intermediate, its concentration, *m*, would be sufficiently low to permit application of steady-state conditions (which do not apply to t_0), namely: $dm/dt = 0$. The resulting eq. 1 is the basis for the kinetics in this paper.

$$m = \frac{(k_1 + k_3[HO^-])[C_6H_5I^+C_6H_5)]}{k_4 + k_5 + k_2[H_3O^+] + k_6[HO^-] + k_7[Cl^-]} \qquad (1)$$

It should be emphasized that eq. 1 and others derived from it apply equally to systems proceeding through intermediates $C_{12}H_9I{\cdot}(H_2O)_n$, including $C_{12}H_9I$ and $(C_2H_5)_2IOH$.

Various experimental results will now be discussed in terms of eq. 1 and reactions E-I.

Hydrolysis in the Presence of Strong Base.—The general eq. 2 for the rate of hydrolysis, as measured

$$\frac{d[H_3O^+]}{dt} = \frac{-d[HO^-]}{dt} = (k_5 + k_6[HO^-])m \qquad (2)$$

by the appearance of acid or the disappearance of base, reduces to the simple second-order form of eq. 3 when the concentration of base is high, in

$$-d[HO^-]/dt = k_3[C_6H_5I^+C_6H_5][HO^-] \qquad (3)$$

accord with the results of Lewis and Stout.[9] An alternate explanation for the results of these workers is that the strongly nucleophilic hydroxide ion does indeed react with the diphenyliodonium cation by direct nucleophilic attack and displacement and not by any of the intermediates proposed here.

Hydrolysis in Neutral or Acidic Solution.—With reactions in solutions initially neutral or acidic eq. 2 resolves to eq. 4, whose form is in apparent

$$\frac{d[H_3O^+]}{dt} = \frac{k_1k_5[C_6H_5I^+C_6H_5]}{k_4 + k_5 + k_2[H_3O^+] + k_7[Cl^-]} \qquad (4)$$

accord with the experimental results that the hydrolysis was repressed by acid and by chloride ion. For hydrolyses in the absence of chloride ion or initial acid, the rates seemed roughly to obey eq. 5. In other words, the rates fell off with increasing acid concentration but not with a simple proportionality.

$$\frac{d[H_3O^+]}{dt} = \frac{k_3k_5[C_6H_5I^+C_6H_5]}{k_4 + k_5 + k_2[H_3O^+]} = \frac{p[C_6H_5I^+C_6H_5]}{q + [H_3O^+]} \qquad (5)$$

Some symbols are now defined

$[H_3O^+]_0 = h$ $\qquad$ $[H_3O^+] = h + x$

$[C_6H_5I^+C_6H_5]_0 = a$ $\qquad$ $[Cl^-]_0 = b$

$[C_6H_5I^+C_6H_5] = a - x$ (when $b = 0$)

When $b = 0$, eq. 4 may be recast as 6, 7 and 8.

$$\frac{dx}{dt} = \frac{k_1k_5(a - x)}{k_4 + k_5 + k_2h + k_2x} \qquad (6)$$

$$-[(1/k_2)(k_4 + k_5) + h + a]d\ln(a - x) + d(a - x) = (k_1k_5/k_2)dt \qquad (7)$$

$$-[(1/k_2)(k_4 + k_5) + h + a]\ln\left(1 - \frac{x}{a}\right) - x = (k_1k_5/k_2)t \qquad (8)$$

An approximation which casts 8 into a form more convenient for plotting involves dropping the first term in brackets, to give eq. 9.

$$-[h + a]\ln\left(1 - \frac{x}{a}\right) - x = (k_1k_5/k_2)t \qquad (9)$$

Values of k_1k_5/k_2 for various runs (Fig. 3, Table II) are in fair agreement; the causes of the scatter are not known, but they may arise in part from the approximation used.

Reaction with Chloride Ion in the Presence of Base.—In the general case the rate of disappearance of chloride ion (reaction A) is given by eq. 10; for *m* see eq. 1.

$$-d[Cl^-]/dt = k_7m[Cl^-] \qquad (10)$$

---

[8] M. C. Caserio, D. L. Glusker and J. D. Roberts, This Journal, **81**, 336 (1959).

[9] E. S. Lewis and C. A. Stout, *ibid.*, **76**, 4619 (1954); see also F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3203 (1955).

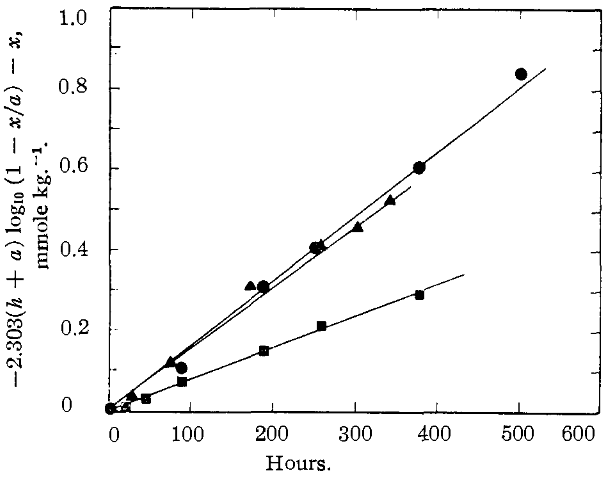


Fig. 3.—Hydrolysis of diphenyliodonium benzenesulfonate at 98.8° plotted according to eq. 9: symbol, atm., *a* and *h* in mmoles kg.$^{-1}$: ●, N_2, 66.2, none; ▲, N_2, 38.3, 2.9; ■, H_2, 49.2, none.

Results are available under three sets of conditions. Büchner reported that the reaction was accelerated by base but retarded by acid. For the first of these conditions eq. 10 may be further transformed to 11, and, if the concentration of

$$\frac{-\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}t} = \frac{k_7(k_1 + k_3[\mathrm{OH}^-])[(\mathrm{C_6H_5})_2\mathrm{I}^+][\mathrm{Cl}^-]}{k_4 + k_5 + k_6[\mathrm{OH}^-] + k_7[\mathrm{Cl}^-]} \quad (11)$$

base is relatively high, to 12.

$$-\mathrm{d}[\mathrm{Cl}^-]/\mathrm{d}t = (k_3k_7/k_6)[(\mathrm{C_6H_5})_2\mathrm{I}^+][\mathrm{Cl}^-] \quad (12)$$

TABLE II

RATE CONSTANTS FOR HYDROLYSIS OF DIPHENYLIODONIUM BENZENESULFONATE IN WATER UNDER INERT ATMOSPHERES AT 98.8° (EQ. 9)

Atm.	Millimoles/kilogram $[\mathrm{C_6H_5I^+C_6H_5}]_0$	$[\mathrm{H_3O^+}]_0$	Mmoles/kg. hr. k_1k_5/k_2
H_2	49.2		8
N_2	47.6		11
	52.8		11
	66.2		17
	38.3	2.9	16
	42.6	10.0	19

While the effect of hydroxide ion has not been investigated in these laboratories, it has been observed[10] that the rate of disappearance of chloride ion was approximately proportional to the concentration of added pyridine (over the range 0.025 to 0.2 molar). This is understandable if we consider that the formation of the intermediate $C_{12}H_9I$ is subject to general basic catalysis.

$$\mathrm{C_{12}H_{10}I^+ + C_5H_5N \underset{9}{\overset{8}{\rightleftarrows}} C_{12}H_9I + C_5H_5N^+H} \quad (j)$$

$$m = \frac{(k_1 + k_3[\mathrm{HO}^-] + k_8[\mathrm{C_5H_5N}])[\mathrm{C_6H_5I^+C_6H_5}]}{k_4 + k_5 + k_2[\mathrm{H_3O^+}] + k_6[\mathrm{HO}^-] + k_7[\mathrm{Cl}^-] + k_9[\mathrm{C_5H_5N^+H}]} \quad (13)$$

Substituting eq. 13 into eq. 10 and dropping the terms containing k_1, k_2, k_3 and k_6, one obtains eq. 14.

$$\frac{-\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}t} = \frac{k_7k_8[\mathrm{C_5H_5N}][\mathrm{C_6H_5I^+C_6H_5}][\mathrm{Cl}^-]}{k_4 + k_5 + k_7[\mathrm{Cl}^-] + k_9[\mathrm{C_5H_5N^+H}]} \quad (14)$$

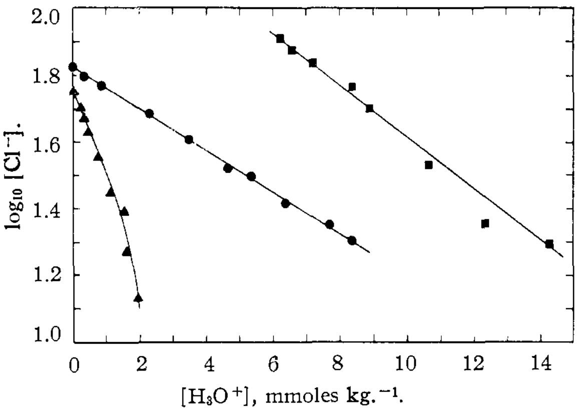


Fig. 4.—Competitive reactions of diphenyliodonium chloride in water at 98.8° plotted according to eq. iii and eq. 17: symbol, atm., *a* and *h* in mmoles kg.$^{-1}$: ■, N_2, 82.4, 6.1; ●, O_2, 67.1, none; ▲, N_2, 56.9, none.

If for reactions run 30–40% to completion the change in $(k_7[\mathrm{Cl}^-] + k_9[\mathrm{C_5H_5N^+H}])$] is smaller than $(k_4 + k_5)$, the apparent third order of the reaction in the presence of pyridine can be accommodated into the general picture.

$$\frac{-\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}t} = \frac{k_7k_8}{k_4 + k_5}[\mathrm{C_5H_5N}][\mathrm{C_6H_5I^+C_6H_5}][\mathrm{Cl}^-] \quad (15)$$

Reaction with Chloride Ion in the Presence of Acid.—The disappearance of chloride ion (reaction A) in the presence of acid has been further investigated since the last report.[3,4,8]

If the reaction scheme developed above is correct and complete, then this rate is given by eq. 16,

$$\frac{-\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}t} = k_7m[\mathrm{Cl}^-] = \frac{k_1k_7[\mathrm{C_6H_5I^+C_6H_5}][\mathrm{Cl}^-]}{k_4 + k_5 + k_2[\mathrm{H_3O^+}] + k_7[\mathrm{Cl}^-]} \quad (16)$$

and the competition of chloride disappearance with acid production is given by eq. 17. An attempt

$$\frac{-\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}[\mathrm{H_3O^+}]} = \frac{k_7[\mathrm{Cl}^-]}{k_5}; \frac{-\mathrm{d}\ln[\mathrm{Cl}^-]}{\mathrm{d}[\mathrm{H_3O^+}]} = \frac{k_7}{k_5} \quad (17)$$

will now be made to use these equations in the interpretation of the experimental results summarized earlier in this paper.

The most striking observation is: that disappearance of chloride ion is initially strongly inhibited by small amounts of acid added at the beginning of the reaction (as would be predicted by eq. 16). It might be noted that if the reaction of chloride ion with the intermediate were acid catalyzed, in the presence of added acid the reaction would be almost independent of acid concentration (eq. 18); this was not observed.

$$\mathrm{C_{12}H_9I + Cl^- + H_3O^+ \xrightarrow{10} C_6H_5Cl + C_6H_5I + H_2O} \quad (K)$$

$$\frac{-\mathrm{d}[\mathrm{Cl}^-]}{\mathrm{d}t} = \frac{k_1k_{10}[\mathrm{C_6H_5I^+C_6H_5}][\mathrm{Cl}^-][\mathrm{H_3O^+}]}{k_2[\mathrm{H_3O^+}] + k_{10}[\mathrm{Cl}^-][\mathrm{H_3O^+}]} = \frac{k_1k_{10}[\mathrm{C_6H_5I^+C_6H_5}][\mathrm{Cl}^-]}{k_2 + k_{10}[\mathrm{Cl}^-]} \quad (18)$$

When the above conclusion, that reaction of chloride ion is not acid catalyzed, is coupled with the fact that in air or oxygen plots according to eq. 17 of ln $[\mathrm{Cl}^-]$ *vs.* $[\mathrm{H_3O^+}]$ are roughly linear (Fig. 4), it is seen that the hydrolysis of the intermediate

---

(10) A. L. Brierley, M.S. Thesis, Polytechnic Institute of Brooklyn, 1953.

cannot be acid catalyzed. The hydrolysis could be effected by one or more water molecules or by a hydroxide ion and an oxonium ion together.

There are, however, some observations not accounted for by reactions considered to this point. One of these, copper catalysis, is so important and interesting that it is dealt with later in a separate section.

Another catalyst, also incompletely understood, is iodine. While Büchner[2] reported that iodine slowed reaction with chloride ion,[4] in these laboratories it has been observed that 3.1 mole % of iodine (based on diphenyliodonium chloride) increased the initial rate of a run in air about threefold. On the other hand, 2.4 mole % of iodine slowed hydrolysis of diphenyliodonium benzenesulfonate under nitrogen by about one-half. A reason for considering the effect of iodine is that it may be involved in reactions in the absence of oxygen.

In the presence of oxygen (and, possibly, in the absence of iodine) the hydrolysis of diphenyliodonium benzenesulfonate shows first-order behavior (Fig. 1); it apparently is not inhibited by acid formed. Also, in the presence of oxygen the disappearance of chloride ion apparently is second order (Fig. 2). Finally, in the presence of oxygen the plots of ln $[Cl^-]$ *vs.* $[H_3O^+]$ are linear (Fig. 4).

On the other hand, in the absence of oxygen (and, possibly, in the presence of iodine), the first-order plots of diphenyliodonium benzenesulfonate are concave upward (Fig. 1). The apparent slowing might be partly the effect of acid and partly that of iodine. In the absence of oxygen the second-order plots of disappearance of chloride ion are strongly concave upward. The acceleration is in opposition to the effect of the acid formed and may be due to catalysis by iodine. Finally, when plots of ln $[Cl^-]$ *vs.* $[H_3O^+]$ are made for runs in the absence of oxygen and initial acid, it is found that the slope is initially constant (although about three times larger than runs under oxygen with no initial acid, or under nitrogen with initial acid), but changes to show relative acceleration of chloride disappearance and slowing of acid formation (Fig. 4). These changes would fit the picture of formation of iodine or related compounds during these long runs (300–700 hours).

If iodine, iodine monochloride or a related compound is formed, it would presumably be by deiodination of iodobenzene by oxonium ion and either chloride ion or water. (Iodide ion is probably in too low a concentration to be effective.) The iodine monochloride formed might react with phenol, to give iodide ion, or with chloride ion to give the $ClICl^-$ ion. It might well be this ion which is reactive toward the intermediate ($C_{12}H_9I$), thus increasing the rate of disappearance of chloride ion. Oxygen might repress the concentration of inorganic iodine compounds and ions by using the iodine for the iodination of phenol.

It is obvious, however, that work to date is inadequate to pin down a reaction scheme of this complexity, which is advanced only as a method of summarizing results and as a working hypothesis.

One completely puzzling result is that obtained with diphenyliodonium chloride in the presence of oxygen and added acid (about 12 mmolar, see Fig. 2). *No* acid was formed, even after 350 hours. At first, chloride ion disappearance was extremely slow, but it became more rapid as the run progressed. There is at present no reaction scheme advanced to explain this result.

Reaction with Hydroxide Ion in Dioxane–Water.—When dioxane freshly distilled from sodium in an inert atmosphere was used, the reaction in 1:3 dioxane–water of diphenyliodonium and hydroxide ion was found to be of second order over-all (Table III).[7] Eyring activation parameters for the diphenyliodonium hydroxide reaction are: $\Delta H^\ddagger$ 29 kcal./mole, $\Delta S^\ddagger$ 20 e.u. These values may be compared to those for the diphenyliodonium phenoxide reaction[7,11] under comparable conditions ($\Delta H^\ddagger$ 25 kcal./mole, $\Delta S^\ddagger$ 1 e.u.) and with those for the first-order diphenyliodonium iodide reaction[3] in dimethylformamide ($\Delta H^\ddagger$ 29 kcal./mole, $\Delta S^\ddagger$ 3 e.u.).

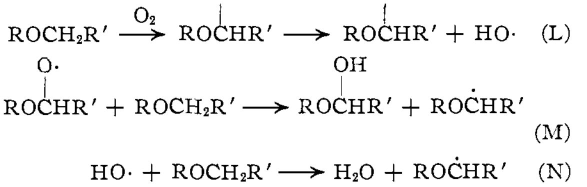
Table III

Second-order Rate Constants for the Reaction of Diphenyliodonium and Hydroxide Ions in 1:3 Dioxane–Water[a]

T, °C.	$[C_6H_5I^+C_6H_5]_0$	$[HO^-]_0/$ $[C_6H_5I^+C_6H_5]_2$	$100k^b$
55.1	26.9	1:2	2.37
	13.4	1:1	2.41
	13.4	2:1	2.43
65.1	13.4	1:1	8.57
	13.4	2:1	8.64
75.1	26.9	1:2	31.9
	13.4	1:1	31.3
	13.4	1:1	31.5
	13.4	2:1	32.0
80.1	13.4	3:5	56.8
	8.06	1:1	59.2
	13.4	5:3	60.0

[a] Concentrations are in mmoles/liter; initial ionic strength was set at 128 ± 2 mmoles/liter with sodium nitrate; k is in liters/mole-min. [b] k is a second-order rate constant obtained graphically from plots of initial 10–12% of reaction.

When, however, with the same solvent composition the dioxane was not freshly distilled and contained peroxides, the rates of the reaction were greater and not reproducible. In some runs it was noted that the rate of the reaction might initially be of the same order of magnitude as in the absence of peroxide but might subsequently increase to a much higher value. While a full explanation cannot be given at this time, it is possible to write a sequence of steps which are in accord with the observations; let $ROCH_2R'$ represent dioxane.



$$ROCH_2R' \xrightarrow{O_2} RO\overset{OOH}{\overset{|}{C}}HR' \longrightarrow RO\overset{O\cdot}{\overset{|}{C}}HR' + HO\cdot \qquad (L)$$

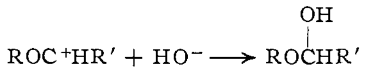
$$RO\overset{O\cdot}{\overset{|}{C}}HR' + ROCH_2R' \longrightarrow RO\overset{OH}{\overset{|}{C}}HR' + RO\dot{C}HR' \qquad (M)$$

$$HO\cdot + ROCH_2R' \longrightarrow H_2O + RO\dot{C}HR' \qquad (N)$$

---

[11] F. M. Beringer and E. M. Gindler, This Journal, **77**, 3203 (1955).

$$\mathrm{RO\dot{C}HR' + C_6H_5I^+C_6H_5 \longrightarrow ROC^+HR' + C_6H_5\dot{I}C_6H_5} \quad \text{(O)}$$

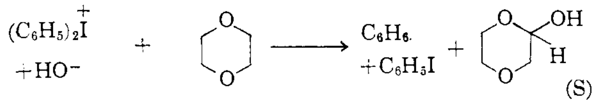


$$\mathrm{ROC^+HR' + HO^- \longrightarrow RO\overset{\displaystyle OH}{\overset{|}{C}}HR'} \quad \text{(P)}$$

$$\mathrm{C_6H_5\dot{I}C_6H_5 \longrightarrow C_6H_5I + C_6H_5\cdot} \quad \text{(Q)}$$

$$\mathrm{C_6H_5\cdot + ROCH_2R' \longrightarrow C_6H_5H + RO\dot{C}HR'} \quad \text{(R)}$$

In this sequence steps L, M and N may be considered as initiating steps forming the active intermediate (the free radical from dioxane), steps O and P describe the use of this radical to remove hydroxide ion and steps Q and R describe the re-formation of the active radical intermediate.[12] Over-all this amounts to the reduction of the diphenyliodonium ion and the oxidation of dioxane, initiated by a peroxide.



(S)

That hydroxide ion was not necessary for the reduction of diphenyliodonium ion by ethers is indicated by the fact that reaction of diphenyliodonium tosylate with various glycol ethers, measured by formation of acid (possibly reaction T), was accelerated by peroxides and by oxygen but was slowed by hydroquinone.

$$\begin{array}{ll} \mathrm{(C_6H_5)_2I^+ + 2H_2O \longrightarrow} & \mathrm{C_6H_6 + C_6H_5I + H_3O^+} \quad \text{(T)} \\ \mathrm{+\ O(CH_2CH_2OH)_2} & \mathrm{HOCH_2CH_2OH + HOCH_2CHO} \end{array}$$

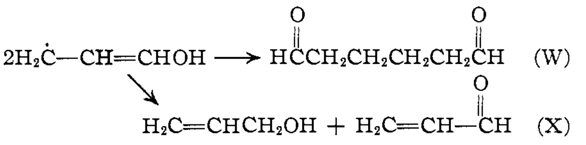
When the solvent was changed to 1:1 dioxane–water, even the use of dioxane freshly distilled from sodium in an inert atmosphere failed to prevent a rapid, non-reproducible reaction consuming hydroxide ion, presumably reaction S. It is suggested that under these conditions there may be an initiation process not involving peroxides, such as reaction U.

$$\mathrm{(C_6H_5)_2I^+\ HO^- \rightleftarrows (C_6H_5)_2IOH \longrightarrow C_6H_5I + C_6H_5\cdot + HO\cdot} \quad \text{(U)}$$

Two pieces of evidence support the existence of this reaction. First, Sandin and Brown[13] showed that treatment of pyridine with aqueous diphenyliodonium chloride and sodium hydroxide gave mixed phenylpyridines (a result confirmed in this Laboratory); this is most easily rationalized as an attack of the phenyl free radical on pyridine. More recently in this Laboratory it has been found that benzene may be isolated from reaction of aqueous diphenyliodonium chloride with sodium hydroxide ion in the presence of dioxane or triethylene glycol dimethyl ether (triglyme) in the absence of peroxides.

It appeared that addition of small amounts of allyl alcohol to the 1:1 dioxane–water mixture slowed down consumption of hydroxide ion. This effect may arise from reaction of a radical R· with allyl alcohol.

$$\mathrm{R\cdot + H_2C{=}CHCH_2OH \longrightarrow RH + H_2\dot{C}{-}CH{=}CHOH} \quad \text{(V)}$$



$$\mathrm{2H_2\dot{C}{-}CH{=}CHOH \longrightarrow H\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}H} \quad \text{(W)}$$

$$\searrow \quad \mathrm{H_2C{=}CHCH_2OH + H_2C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}H} \quad \text{(X)}$$

Reactions W and X end two radical chains. A competitive reaction might be the oxidation of the allyl radical by diphenyliodonium ion, which

$$\begin{array}{ll} \mathrm{C_6H_5I^+C_6H_5 + HO^- \longrightarrow} & \mathrm{C_6H_5\overset{\cdot -}{I}C_6H_5 + H_2O} \quad \text{(Y)} \\ \mathrm{H_2\dot{C}{-}CH{=}CHOH} & \mathrm{H_2C{=}CH{-}CHO} \end{array}$$

consumes hydroxide ion but does not end a radical chain.

In summary, it seems that under conditions where free radicals are formed, ethers may reduce the diphenyliodonium ion, with concomitant production of acid or consumption of base.

Reactions of Diphenyliodonium Ions Catalyzed by Copper Salts

Previous Work.—An earlier report[3] from this Laboratory surveyed the copper-catalyzed reaction of the diphenyliodonium ion with chloride ion in non-aqueous media and the competitive reactions with chloride ion and with water in water. The main conclusions may be summarized briefly. (1) In diethylene glycol the effective catalyst was a copper(I) species, probably the dichlorocuprate-(I) ion ($\mathrm{CuCl_2^-}$). (2) In water under air added cupric salts were catalysts for both hydrolysis and the reaction with chloride ion. Plots of ln [$\mathrm{Cl^-}$] *vs.* [$\mathrm{H_3O^+}$] were linear. The rate increased with concentration of added cupric salt, but apparently more slowly than in a linear fashion. The effective catalyst in aqueous solution was not identified.

In the present work attention has been focused on the copper catalysis of hydrolysis of the diphenyliodonium ion in the presence of the weakly nucleophilic anions benzenesulfonate and *p*-toluenesulfonate (tosylate).

Hydrolysis Catalyzed by Copper Salts. Observations.—The main observations on the hydrolysis of diphenyliodonium benzenesulfonate and tosylate in the presence of added cupric sulfate follow. (1) First-order plots were concave upward (Fig. 5); *i.e.*, the apparent first-order rate constant decreased with the progress of a run. Second-order plots (Fig. 6) were more nearly linear, but also showed no induction period. (2) The initial rate of hydrolysis was decreased by added acid but more weakly than in the uncatalyzed runs (*cf.* Fig. 1 and 5). (3) First-order rate constants taken early in a run at comparable, low acid concentrations showed that the initial first-order rate constants were roughly proportional to the concentrations of added cupric salt over a 500-fold range of catalyst concentration and independent of the presence of chloride or tosylate ions. (4) In the absence of added acid, hydrolysis was fastest under hydrogen, intermediate under nitrogen and slowest under oxygen (Figs. 5–8).

---

[12] The formation of diphenyliodine by the polarographic and chemical reduction of the diphenyliodonium ion and some subsequent reactions of diphenyliodine have been discussed previously: H. E. Bachofner, F. M. Beringer and L. Meites, THIS JOURNAL, **80**, 4269 (1958). Mechanisms for reactions of diphenyliodonium ions catalyzed by copper(I) species are also presented.

[13] R. B. Sandin and R. K. Brown, THIS JOURNAL, **69**, 2253 (1947).

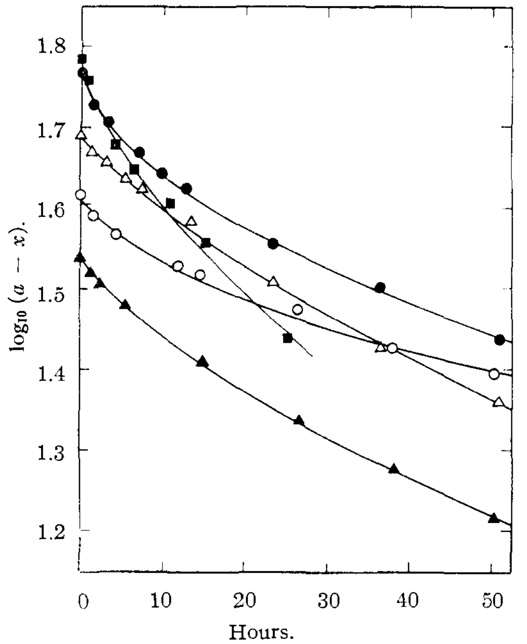


Fig. 5.—First-order plots of the copper-catalyzed hydrolysis of diphenyliodonium benzenesulfonate at 98.8° with cupric sulfate at 0.062 mmoles kg.$^{-1}$: symbol, atm., *a* and *h* in mmoles kg.$^{-1}$: ●, N_2, 58.5, none; ■, N_2, 60.9, none; △, N_2, 49.2, 10.1; ○, O_2, 41.3, none; ▲, O_2, 34.6, 11.7. The data are plotted in other ways in Figs. 6–8.

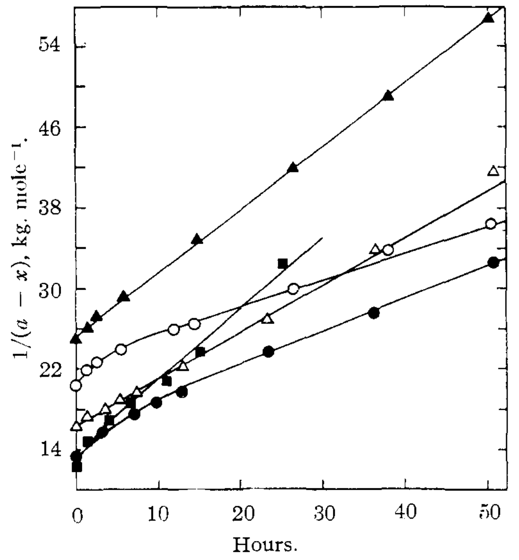


Fig. 6.—Second-order plots of the copper-catalyzed hydrolysis of diphenyliodonium benzenesulfonate. Conditions and symbols are those of Fig. 5.

Three possible reaction paths are discussed in the succeeding sections: (a) a copper-catalyzed hydrolysis of the same intermediate as in the uncatalyzed reaction, (b) formation and hydrolysis of copper complexes and (c) catalysis by a copper(I) species.[12]

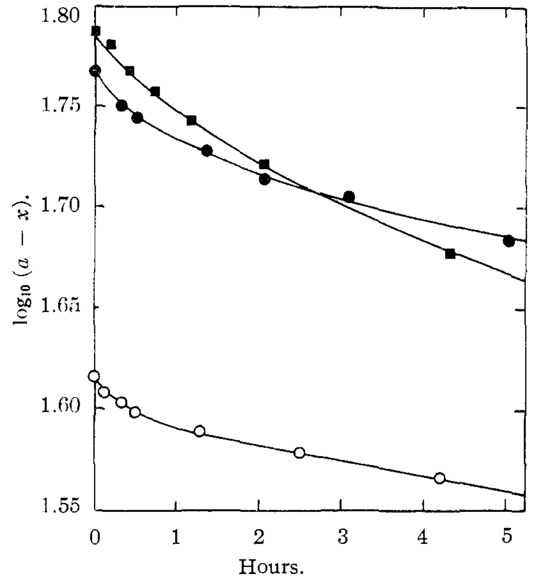


Fig. 7.—First-order plots of the initial points in the copper-catalyzed hydrolysis of diphenyliodonium benzenesulfonate under different atmospheres without added acid. Conditions and symbols are those of Fig. 5.

Reaction Path A: Copper-catalyzed Hydrolysis of $C_{12}H_9I$.—One possibility to be considered is that the same intermediate (perhaps $C_{12}H_9I$) is formed in the catalyzed as in the uncatalyzed reaction but that its hydrolysis is accelerated by some copper species, say Cu^{++}.

$$C_{12}H_9I + H_2O + Cu^{++} \xrightarrow{5a} C_6H_5OH + C_6H_5I + Cu^{++} \quad (Z)$$

$$d[H_3O^+]/dt = (k_5 + k_{5a}[Cu^{++}])m \quad (19)$$

If the solution is neutral or acid

$$m = \frac{k_1[C_6H_5I^+C_6H_5]}{k_4 + k_5 + k_2[H_3O^+] + k_{5a}[Cu^{++}]} \quad (20)$$

$$\frac{d[H_3O^+]}{dt} = \frac{k_1(k_5 + k_{5a})[Cu^{++}])[C_6H_5I^+C_6H_5]}{k_4 + k_5 + k_2[H_3O^+] + k_{5a}[Cu^{++}]} \quad (21)$$

$$\cong \frac{k_1k_{5a}[Cu^{++}][C_6H_5I^+C_6H_5]}{k_4 + k_5 + k_2[H_3O^+] + k_{5a}[Cu^{++}]} \quad (22)$$

When $[Cu^{++}]$ is large

$$d[H_3O^+]/dt = k_1[C_6H_5I^+C_6H_5] \quad (23)$$

According to eq. 23, as $[Cu^{++}]$ is increased, the kinetics of the hydrolysis should become of simple first order while the rate constant should tend to a value independent of $[Cu^{++}]$. On the other hand, the data reported in Table IV show no drop in

TABLE IV

DEPENDENCE OF FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF DIPHENYLIODONIUM SALTS ON THE CONCENTRATION OF CUPRIC SALTS

		Millimoles/kilogram			
Anion	*T*, °C.	*a*	$[Cu^{++}]^a$	*k*, hr.$^{-1b}$	$k/[Cu^{++}]$
Cl^-	98.3	104	0.096	0.0102	0.11
		75	.097	.0128	.13
		75	.159	.0189	.12
TsO^-	95	50	5.0	.75	.15
		50	10.0	1.5	.15
		25	10.0	1.5	.15
		50	50.0	6.0	.12

[a] In the runs with chloride ion,[3] $CuCl_2$ was used, while with the tosylate, $CuSO_4$ was used. [b] In the presence of chloride ion the first-order rate constants for hydrolysis were determined using eq. 2 and 3 (ref. 3). In the presence of tosylate ion the rate constants were obtained from the initial slopes of first-order plots.

specific catalyst efficiency with concentration and thus seem to exclude path A.

Reaction Path B: Formation and Hydrolysis of a Copper Complex from a Diphenyliodonium Cation.—If copper is involved in the step producing the intermediate, then the rate of the catalyzed reaction should be proportional to its concentration.

$$C_{12}H_{10}I^{+} + Cu^{++} + H_2O \underset{\mathrm{II}}{\overset{\mathrm{I}}{\rightleftarrows}} C_{12}H_9CuI^{++} + H_3O^{+} \qquad \text{(AA)}$$

$$C_{12}H_9CuI^{++} + H_2O \xrightarrow{\mathrm{V}} C_6H_5OH + C_6H_5I + Cu^{++} \qquad \text{(BB)}$$

$$\frac{d[H_3O^+]}{dt} = \frac{k_{\mathrm{I}}k_{\mathrm{V}}[Cu^{++}][C_6H_5I^+C_6H_5]}{k_{\mathrm{V}} + k_{\mathrm{II}}[H_3O^+]} = \frac{P[Cu^{++}][C_6H_5I^+C_6H_5]}{Q + [H_3O^+]} \qquad (24)$$

The form of rate repression by acid in eq. 24 is the same as that in eq. 5 for the uncatalyzed reaction.

With the symbols defined before, eq. 24 can be put into algebraic form (eq. 25).

$$-[k_{\mathrm{V}}/k_{\mathrm{II}} + h + a] \ln\left(1 - \frac{x}{a}\right) - x = (k_{\mathrm{I}}k_{\mathrm{V}}/k_{\mathrm{II}})[Cu^{++}]t \qquad (25)$$

If one assumes that $(k_{\mathrm{V}}/k_{\mathrm{II}}) << (a + h)$ one obtains the related eq. 26 (*cf.* eq. 9); see plots according to this equation in Fig. 8.

$$-[h + a] \ln\left(1 - \frac{x}{a}\right) - x = [k_{\mathrm{I}}k_{\mathrm{V}}/k_{\mathrm{II}})[Cu^{++}]t \qquad (26)$$

Values of $k_{\mathrm{I}}k_{\mathrm{V}}/k_{\mathrm{II}}$ collected from various runs are summarized in Table V.

TABLE V

RATE CONSTANTS FOR HYDROLYSIS OF DIPHENYLIODONIUM BENZENESULFONATE AND TOSYLATE AT 98.8°, CALCULATED BY EQ. 26

Atmos.	Millimoles/kg. a	Millimoles/kg. h	μmoles/kg. $[CuSO_4]$	$k_{\mathrm{I}}k_{\mathrm{V}}/k_{\mathrm{II}}$
O_2	41.3[a]		62.7	1.3
	74.8[b]		61.5	4.2
	34.6[a]	11.7	62.4	5.2
N_2	58.5[a]		62.6	3.9
	49.2[a]	10.1	61.5	5.9
	42.9[b]		62.5	6.1
H_2	60.9[a]		62.0	7.3

[a] Benzenesulfonate. [b] Tosylate.

The plots of the copper-catalyzed hydrolysis shown in Fig. 8 are in three of the four cases close to linear, and the behavior therefore approximates that described by eq. 26. In all these cases, however, the apparent rate constant increases with the progress of the reaction, this trend being most noticeable in the run under hydrogen. It should be remembered in this connection that eq. 26 was obtained from 25 by dropping, for convenience, the term $-[k_{\mathrm{V}}/k_{\mathrm{II}}]\ln(1-(x/a))$. As the ratio of rate constants $(k_{\mathrm{V}}/k_{\mathrm{II}})$ is not known, the "error" so introduced cannot be evaluated easily.

The plots in Fig. 8 and the data in Table V show that the rate constant $(k_{\mathrm{I}}k_{\mathrm{V}}/k_{\mathrm{II}})$ is least under oxygen (3.6 ± 1.5), intermediate under nitrogen (5.3 ± 1.0) and greatest under hydrogen (7.3). This suggests that a copper(I) species is a more effective catalyst for hydrolysis than the copper(II) species.[12]

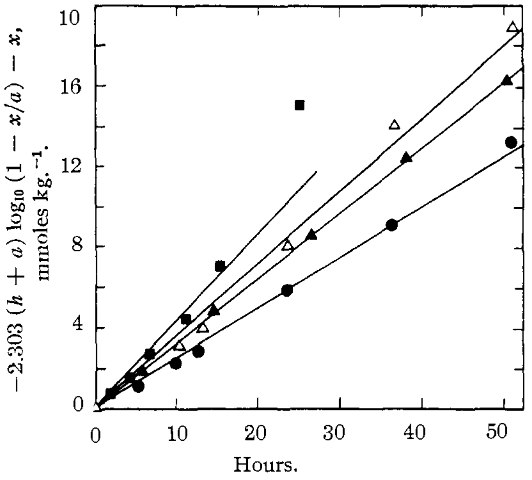


Fig. 8.—Plots of the copper-catalyzed hydrolysis of diphenyliodonium benzenesulfonate according to eq. 26. Conditions and symbols are those of Fig. 5.

A similar analysis has been made for the kinetic scheme in which a second diphenyliodonium ion is involved in the copper complex.

$$2C_{12}H_{10}I^{+} + Cu^{++} + H_2O \underset{\mathrm{ii}}{\overset{\mathrm{i}}{\rightleftarrows}} (C_{12}H_9I)_2HCu^{+++} + H_3O^{+} \qquad \text{(BB)}$$

$$(C_{12}H_9I)_2HCu^{+++} + H_2O \xrightarrow{\mathrm{v}} C_6H_5OH + C_6H_5I + C_{12}H_{10}I^{+} + Cu^{++} \qquad \text{(CC)}$$

Graphs made according to the equation which results from application of the steady-state hypothesis to this mechanism are strongly curved, while those according to eq. 26 are nearly linear. Thus this latter scheme does not seem attractive.

Reaction Path C: Catalysis by a Copper(I) Species.—It might be wondered whether the reaction could proceed in water through the same general steps as in diethylene glycol and similarly involve a copper(I) species.[3,12] Such a scheme is

$$Cu^{++} + \text{reductant} \underset{\mathrm{b}}{\overset{\mathrm{a}}{\rightleftarrows}} Cu^{+} + \text{oxidant} \qquad \text{(DD)}$$

$$Cu^{+} + 2H_2O \underset{\mathrm{d}}{\overset{\mathrm{c}}{\rightleftarrows}} CuOH + H_3O^{+} \qquad \text{(EE)}$$

$$C_6H_5I^{+}C_6H_5 + CuOH \xrightarrow{\mathrm{e}} C_6H_5OH + C_6H_5I + Cu^{+} \qquad \text{(FF)}$$

$$d[H_3O^+]/dt = k_e[CuOH][C_6H_5I^+C_6H_5] = \left(\frac{k_ck_e}{k_d}\right)\frac{[Cu^+][C_6H_5I^+C_6H_5]}{H_3O^+} \qquad (27)$$

Some results seem to be in accord with this formulation. This includes the fact that rates are repressed by acid and are slowest in the presence of oxygen (which should repress the formation of cuprous ion), intermediate with nitrogen and highest in the presence of hydrogen (which can help form cuprous ion); see Fig. 7.

$$2Cu^{++} + H_2 + 2H_2O \longrightarrow 2Cu^{+} + 2H_3O^{+} \qquad \text{(GG)}$$

This formulation leaves unexplained, however, the fact that there is no induction period. If, indeed, copper(I) species were the only effective catalysts then the copper(II)–copper(I) conversion must have proceeded appreciably in the first ten minutes after mixing. At the start of the reaction there is no obvious reductant; after some hydrolysis has occurred, phenol might take this role.

Finally, if a copper(I) species were the only effective species it would be hard to rationalize the data of Table IV, which show that for runs in air the specific catalytic effectiveness of added cupric sulfate did not depend on concentration (over a 500-fold range) or the anion present.

Our evidence to date allows both copper(I) and copper(II) species as catalysts but suggests that the copper(I) catalyst is more reactive.[12]

Acknowledgments.—It is a pleasure to acknowledge the work of Irving Kuntz on reactions of diphenyliodonium tosylate in diethylene glycol (ref. 6), of Arthur Brierley on the effect of pyridine on the diphenyliodonium chloride reaction (ref. 10) and of Anthony V. Maresco on isolation of benzene from diphenyliodonium hydroxide reactions in the presence of ethers. Support of this research by the Alfred P. Sloan Foundation, Inc., is gratefully acknowledged.

Experimental

Materials for Kinetic Runs.—Diphenyliodonium chloride[8] was converted by means of the appropriate lead salts to diphenyliodonium benzenesulfonate[6] and tosylate.[6] Diphenyliodonium nitrate was prepared as previously described.[7,9] Before use the salts were recrystallized three times and dried in a vacuum desiccator. Solvents were of Certified Purity grade and were redistilled. Dioxane was distilled, refluxed twice over sodium and redistilled into a chilled flask minutes before use. Distilled water was passed through an ion exchange mixed-bed resin (Amberlite MB-1, Rohm and Haas Co.) to remove traces of heavy metals. Solutions of sulfuric acid and cupric sulfate in deionized water were made from A.C.S. grade reagents. A.C.S. grade phenol was redistilled before use, while phenyl *p*-toluenesulfonate, sodium *p*-toluenesulfonate and sodium benzenesulfonate were crystallized three times from methanol. Resublimed A.C.S. grade iodine was used directly. Prepurified nitrogen was passed through Fieser solution, while oxygen and hydrogen were passed through concentrated sulfuric acid.

Reactions in Water. Apparatus.—Since many runs lasted 600 hours or more, the kinetic vessels were constructed so as to minimize contamination, with all standard taper joints inverted. Each sampling pipet and each condenser was fitted with a glass cover. The flow of gas through the bubble-counter and into the solution was controlled by a screw-clamp and was held to between two and four bubbles per minute. The gas then passed through a glass wool plug and into the gas inlet tube attached to the kinetic vessel. When hydrogen was used, the gas was led from the top of the condenser to a window.

The bath temperatures were controlled by an electronic relay to ±0.1° and were determined by total immersion thermometers calibrated in tenths of a degree.

Apparatus used for kinetic experiments was carefully cleaned in a potassium dichromate–sulfuric acid solution and then thoroughly rinsed with tap water and with deionized water.

Starting a Run.—The correct amount of water (usually 150 ml.) was pipetted into the kinetic vessel through the top of the condenser and allowed to equilibrate with respect to both temperature and atmosphere. Several hours was allowed for this. A weighed amount of iodonium salt was then poured from glazed paper into the top of the condenser. Immediately afterward the condenser was washed down and rinsed with water which had been drawn into the sampling pipet. Simultaneously the vessel was manually shaken to hasten solution and ensure homogeneity. Zero time was taken from when the sample was washed down the condenser.

Determination of Acid.—Aliquots of the kinetic solutions were delivered into tared 125-ml. erlenmeyer flasks chilled in an ice–water-bath, which served to quench the reaction. After a few minutes the flasks were wiped dry and allowed to come to room temperature. They were then weighed to the nearest milligram. The concentration units used in the treatment of the kinetic data were moles or millimoles per kilogram of solution; these units are not temperature dependent. The weighed aliquot then was diluted with 25 ml. of 3:1 methanol–water and titrated with 0.01 *N* sodium hydroxide using five drops of a 0.1% ethanolic solution of brom cresol green indicator (*p*H range 3.8–5.4). This indicator was used in order to prevent titration of the phenol which was also present.

Determination of Chloride Ion.—In the experiments with diphenyliodonium chloride the same sample which had been titrated for acid then was used for the mercurimetric determination of chloride ion.[3,13a] The titrations were carried out with 0.02 *N* mercuric nitrate with three drops of 10% sodium nitroprusside as an indicator. The end-point was the appearance of the first permanent white turbidity. To make the end-point more easily visible, all chloride titrations were performed inside a "dark box" with a small light source directed on the scrupulously clean flask. Agitation was provided by a magnetic stirrer.

Blanks were determined by titrating solutions of varying concentrations of mercuric chloride under the same experimental conditions, and a correction curve was plotted. The blanks were of the order of 0.10–0.70 ml. and were deducted from the volume of standardized reagents used. The stock solution of mercuric nitrate was made up with one liter of concentrated nitric acid to 15 liters of solution. This prevented hydrolysis of the mercuric ion and subsequent clogging of the buret.

Product Analyses.—The products of the aqueous decomposition of diphenyliodonium chloride already have been shown to be those of reactions A and B.[3,14] For this reason it was expected that the decomposition of diphenyliodonium benzenesulfonate or tosylate should also yield as major products iodobenzene, phenol and corresponding sulfonic acid (reaction B). However, since the uncatalyzed reactions were often of a duration of 600 hours or more, two other possible reactions conceivably could have led to an increase in acid formation: (a) the desulfonation of the anion

$$\mathrm{ArSO_3^- + H_3O^+ \longrightarrow ArH + H_2SO_4} \qquad \mathrm{(HH)}$$

(b) ester formation with subsequent hydrolysis

$$\mathrm{(C_6H_5)_2I^+ + ArSO_3^- \longrightarrow ArSO_3C_6H_5 + C_6H_5I} \qquad \mathrm{(II)}$$

$$\mathrm{ArSO_3C_6H_5 + H_2O \longrightarrow ArSO_3H + C_6H_5OH} \qquad \mathrm{(JJ)}$$

In Table VI are listed the results of runs attempting the hydrolysis of sodium benzenesulfonate, sodium *p*-toluenesulfonate and phenyl *p*-toluenesulfonate. No reaction occurred to a significant extent. The absence of sulfate ion was also shown by the test of aliquots with aqueous barium nitrate.

TABLE VI

ATTEMPTED HYDROLYSIS OF SODIUM BENZENESULFONATE, SODIUM *p*-TOLUENESULFONATE AND PHENYL *p*-TOLUENESULFONATE AT 98.8°

Starting material	Mmoles/kg. concn.	Hours	Acidity, mmoles/kg. Initial	Increase
$C_6H_5SO_3Na$	53.6	600	9.9	0.0
$C_7H_7SO_3Na$	59.4	700	6.3	.0
$C_7H_7SO_3C_6H_5$	42.9	700	6.3	.2

The depositions for the product analyses were run in a special double-jacketed vessel with steam as the heat transfer medium, under atmospheric pressure. The reaction mixture were removed and a small portion was tested with aqueous lead nitrate and starch–peroxide to determine iodide ion; none was detected. The reaction mixture then was titrated with 0.5 *N* sodium hydroxide to determine the extent of re-

---

[13a] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, pp. 479, 575.

[14] Marvin Mausner, Doctoral Dissertation, Polytechnic Institute of Brooklyn, 1956.

action. Sodium hydroxide pellets were added to raise the *p*H past 10 in order to convert all phenol present to the sodium salt. Extraction with ether followed, to recover the iodobenzene, and the residual solution was divided into two portions. To one portion aqueous sodium iodide was added to recover unreacted diphenyliodonium ion as the insoluble diphenyliodonium iodide. To the other portion bromine water was added to precipitate the phenol formed as the tribromo derivative. The crude solids were recrystallized and identified by melting point. The crude iodobenzene was redistilled and identified by boiling point and refractive index.

The results of the analyses are listed in Table VII. The amounts of phenol and diphenyliodonium ion indicated are corrected for aliquot size. The small amount of diphenyliodonium ion unaccounted for was lost partly through the finite solubility of diphenyliodonium iodide and partly in handling.

TABLE VII

PRODUCT ANALYSES FOR THE AQUEOUS DECOMPOSITION OF DIPHENYLIODONIUM SALTS[a]

			Starting material			Products		
Anion	$CuSO_4$	Hours	Initial	Recov.	Reacted	C_6H_5I	H_3O^+	C_6H_5-OH
$C_6H_5SO_3^-$	None	1392	40.1	26.7	13.4	12.7	12.3	9.1
$C_7H_7SO_3^-$	0.048	120	43.0	1.6	41.4	41.0	40.4	28.0

[a] All amounts in millimoles.

Reactions in Organic Solvents. Kinetic Runs in Dioxane–Water.—To a weighed amount of diphenyliodonium nitrate there were added measured volumes of water, dioxane, aqueous sodium nitrate and, sometimes, allyl alcohol. After the flask had been in the constant-temperature bath for 15 minutes, the salt was dissolved by swirling, and a known volume of aqueous sodium hydroxide was added from a transfer pipet. The total volume of liquids added was 120 ml.

After the solutions had been mixed, an aliquot was withdrawn, the time being taken as zero time. This sample, usually 10 ml., and subsequent samples were added to 10 ml. of water and sufficient nitric acid, added from a buret, to neutralize 80–90% of the base. The titration was completed with nitric acid to a brom cresol green–methyl red end-point.

Benzene from Diphenyliodonium Chloride and Potassium Hydroxide in Water–Ether Solutions.—A mixture of 330 g. of diglyme (freshly distilled from sodium), 500 ml. of distilled water, 113 g. of 85% potassium hydroxide in 68 ml. of water and 50 g. of diphenyliodonium chloride was boiled for two hours. Distillation gave a forerun, approximately 1 ml., of b.p. 71°. This halogen-free material gave with mixed acids *m*-dinitrobenzene, m.p. 89.5°, undepressed by admixture with an authentic sample.

TABLE VIII

ACID PRODUCTION BY DIPHENYLIODONIUM TOSYLATE IN ORGANIC HYDROXYLIC SOLVENTS, REPORTED AS APPROXIMATE FIRST-ORDER CONSTANTS

T, °C.	Mmoles/liter *a*	Solvents	Hr.$^{-1}$ 10^4k
~25	100	Methanol	0.3
		4:1 Methanol–water	0.2
		4:1 Acetone–water	0.5
		DEG[a]	1
		9:1 DEG–water[a]	2
	20	DEG[a]	4
51	100	Methanol	0–0.8
		Diethylene glycol	25
		9:1 DEG[a]–water	26
92	50	Diethylene glycol	470
		DEG[a] + hydroquinone[b]	0–50
		Ethylene glycol	0–20
		Propylene glycol	650
		Methyl Cellosolve (peroxide)[c]	7600
		Methyl Cellosolve (no peroxide)	0–300
		Methyl Cellosolve + hydroquinone[b]	0–20
98[d]	100	Diethylene glycol	1000
	50	Diethylene glycol	2000
	20	Diethylene glycol	5000

[a] Diethylene glycol. [b] 0.01 molar hydroquinone. [c] Solvent gave a positive test for peroxides. [d] Obtained by interpolation from data of Irving Kuntz, ref. 6.

Diphenyliodonium Tosylate in Organic Hydroxylic Solvents.—Diphenyliodonium tosylate in various organic hydroxylic solvents produced acids, by solvolysis or oxidation–reduction or both. Some exploratory runs were made under the following conditions: room temperature, 20–30° (68 days); 51° (40 hours); 92° (2.5 hours). Acid production was treated as a first-order process, giving the rough values for *k* shown in Table VIII.

BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Azobenzene- and Stilbene–Dilithium Adducts with Some Chlorosilanes

BY M. V. GEORGE, DIETMAR WITTENBERG AND HENRY GILMAN

RECEIVED JULY 25, 1958

Dichlorodiphenylsilane and dichloromethylphenylsilane on treatment with azobenzene–dilithium adduct gave octaphenyl-1,2,4,5-tetraza-3,6-disilacyclohexane and 1,2,3,4,5,6-hexaphenyl-3,6-dimethyl-1,2,4,5-tetraza-3,6-disilacyclohexane, respectively. The stilbene–dilithium adduct in tetrahydrofuran reacts with chlorotriphenylsilane to give hexaphenyldisilane and stilbene. Reactions of the stilbene–dilithium adduct with dichlorodiphenylsilane, dichlorodimethylsilane and dichloromethylsilane were attempted.

A systematic, elegant study of the addition of the alkali metals lithium, sodium and potassium to azobenzene was made by Reesor and Wright,[1] who observed that nearly quantitative yields of the dimetal adducts could be obtained by shaking excess of the alkali metal with azobenzene in ethylene glycol dimethyl ether. This addition reaction was, however, reported to be slow in a solvent like diethyl ether giving an unidentified product,[2] but tetrahydrofuran has been found to be effective as a medium for this reaction.[3] The same dilithium adduct of azobenzene was prepared by Wittig[4] from hydrazobenzene and methyllithium.

Reesor and Wright[1] have studied a number of reactions of azobenzene–dimetal adducts. Normal

---

[1] J. W. B. Reesor and G. F Wright, *J. Org. Chem.*, **22**, 375 (1957).

[2] W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

[3] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, THIS JOURNAL, **80**, 4532 (1958).

[4] G. Wittig, *Angew. Chem.*, **53**, 241 (1940).