building up ionic atmospheres about the ions which decrease their net charges and their tendency to approach each other and react. Olson and Simonson[16] have studied the reaction of very small concentrations of bromopentamminecobaltic bromide with excess sodium hydroxide in water. A plot of log k_2 *vs.* $u^{1/2}$ is linear. Since sodium hydroxide is the major component determining ionic strength, the plot of log k_2 *vs.* $[HO^-]^{1/2}$ or $[Na^+]^{1/2}$ is also linear. Further, the authors have developed a three parameter equation which also reasonably fits the data.

$$k = k_a\left[\frac{1}{1 + K(X)} + k'\,\frac{K(X)}{1 + K(X)}\right] \qquad (37)$$

For (37) Olson and Simonson[16] define k as the second-order rate constant, k_a as the rate constant when hydroxide ion concentration is low, k' and K' as adjustable parameters and (X) as the concentration of hydroxide ions. Finally, it will be noted that (37) is very similar to (35) and (36), derived for the case where ion pairs might give product both directly and by reaction with one of the free ions.

It is possible, however, by working at constant ionic strength and by varying the concentrations of reagents and "inert" salts to assess the importance of ion pair formation. Such an analysis, for the reaction of diphenyliodonium and phenoxide ions, is reported in the following paper.[3]

BROOKLYN 1, N. Y.

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

Diaryliodonium Salts. III. Kinetics of the Reaction of Diphenyliodonium and Phenoxide Ions[1]

BY F. MARSHALL BERINGER AND E. MELVIN GINDLER[2]

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In continuation of studies on the synthesis[3] and reactions[4] of diphenyliodonium salts the reaction of diphenyliodonium and phenoxide ions to give diphenyl ether and iodobenzene has been found to be of second order in most dioxane–water mixtures, with the order decreasing at high dioxane concentration.[1] Second-order rate constants in 1:1 dioxane–water at 45–70° gave Arrhenius parameters log $PZ = 12.8$ and $E_a = 25.9$ kcal./mole. At 65.1° a plot of log k_2 *vs.* $u^{1/2}$ had a slope of -2.7, while with u constant, log k_2 varied linearly with $1/D$. At constant u, D and T variation of k_2 with reagent concentration allowed calculation of the association constant for formation of the diphenyliodonium phenoxide ion pairs and the rate constant for irreversible decomposition of the ion pairs to products under a variety of conditions.

Introduction

Previous papers have reported improved syntheses[3] of diphenyliodonium salts and have shown that under relatively mild conditions organic and inorganic bases effect nucleophilic displacement on the 1-carbons of diphenyliodonium ions to form new bonds with carbon, hydrogen, oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic, antimony and the halogens.[4] Thus iodonium salts show promise as general phenylating agents.

In the present work the reaction of diphenyliodonium and phenoxide ions to give diphenyl ether and iodobenzene[4] was examined cursorily in water and more intensively in dioxane–water mixtures.[5] Runs were made by preparing a thermostatted solution of diphenyliodonium chloride or nitrate and phenol in water or dioxane–water, adding a known amount of thermostated solution of sodium hydroxide in the same solvent and analyzing aliquots removed at intervals for unreacted base. Excess phenol repressed the hydrolysis of the phenoxide ion.

Solvents.—Exploratory runs showed that while the reaction in water had a convenient rate at 80°, the kinetics were complicated by the fact that the finely dispersed second phase of insoluble reaction products effected a considerable acceleration of the reaction. In a typical run a zeroth order plot is linear from about 3–70% reaction. The reaction caused by the second phase cannot be equally distributed throughout the second phase, for the bulk of this second phase increased at least 20-fold during this portion of the reaction. Possibly surface effects are operative, small drops being initially formed but coalescing to larger drops having a smaller surface–volume ratio.

It might be noted that in the copper-catalyzed reaction of diphenyliodonium chloride to give chlorobenzene and iodobenzene in water or water–dioxane the presence of a finely dispersed second phase of products has a similar accelerating effect.[6] (Copper salts do not catalyze the reaction between diphenyliodonium ions and phenoxide ions.)

To maintain homogeneity, dioxane–water mixtures were used in all subsequent runs.[7]

Arrhenius Parameters.—In 1:1 dioxane–water reactions were considerably faster than in water and

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(1) This paper is taken from a dissertation submitted by E. Melvin Gindler in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1956. The preceding paper developed the theory and equations for the kinetics of reactions of oppositely charged ions which occur by the formation and decomposition of ion pairs: F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3200 (1955). The symbols here used are as defined in the preceding paper, with specialization to the present reaction. Equations are numbered as one series through both papers.

(2) Du Pont Postgraduate Fellow, 1953–1955.

(3) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

(4) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

(5) (a) These results were presented at the American Chemical Society Meeting, New York City, September 13–18, 1954; see Abstracts of Papers, p. 11R. (b) Recently a note has appeared in which the present reaction in water was discussed: E. S. Lewis and C. A. Stout, THIS JOURNAL, **76**, 4619 (1954).

(6) F. M. Beringer, E. J. Geering and I. Kuntz, Abstract of Papers, American Chemical Society Meeting, New York City, September 13–18, 1954, p. 90-O.

(7) Failure to maintain homogeneity probably helped make the results given in reference 5b erratic and difficult to interpret.

were found to be of second order from 45–70°. A series of runs identical in concentration and ionic strength was made over this temperature range and gave a linear Arrhenius plot, with log PZ = 12.8 (in sec.$^{-1}$) and E_a = 25.9 kcal./mole. These data are summarized in Table I. The large value of log PZ is interpreted to mean that the opportunity for reaction is greatly increased by "sticky collisions" arising from ion pair formation.[1] The importance of the change of the dielectric constant with temperature is recognized, but no attempt has been made here to estimate the effect of this change on the Arrhenius parameters. A more detailed analysis of the variation of k_2 with temperature, in terms of ion pair formation and decomposition, is given later in this paper.

TABLE I

DEPENDENCE OF k_2 ON TEMPERATURE[a]

Run	Temp., °C.	k_2[a]	Run	Temp., °C.	k_2[a]
51	70.1	0.643	56	55.1	0.1142
49	65.1	.373	58	50.1	.0611
55	60.1	.202	61	45.1	.0329

[a] In 1:1 dioxane with sodium chloride as inert salt, with constant u_0 = 165, a_0 = 51.3 and b_0 = 13.4 mmoles/liter; k_2 in liters/mole-min.

Dependence of k_2 on Concentration of Reagents.—Six series of runs are summarized in Table II. In each series u, D, T and the initial stoichiometric concentration of phenoxide ion (b_0) were held constant (b_0 = 13.4 mmoles/liter) while the initial stoichiometric concentration of diphenyliodonium ion (a_0) varied from 17.90 to 101.6 mmoles/liter. In each series except F k_2, the experimental second-order rate constant, drifted lower as a_0 increased. Further, within each run the rate constant gradually increased as the run progressed more than would be predicted from the decreasing ionic strength, and this increase in the rate constant was greatest when m, the excess of a over b, was the least.[8]

These and other observations[9,10] suggested that the free ions were in mobile equilibrium with ion pairs[1] or complexes[10] which decomposed to products

$$\overset{+}{R_2I} + \overset{-}{RO} \overset{K}{\rightleftarrows} R_2\overset{+-}{IOR} \xrightarrow{k} ROR + RI$$
$$(R = \text{phenyl})$$

This kinetic system is included in the general case formulated with $\overset{+}{A}$ and $\overset{-}{B}$,[1] and thus $[R_2\overset{+}{I}]$ and $[R\overset{-}{O}]$ may be equated to A and B.

TABLE II

DEPENDENCE OF k_2 ON a

b_0 = 13.43, u_0 = 165 mmoles/liter

Series	Run	a_0, mmoles/l.	100 k_2, l./mole min. Obs.	Calcd.[e]
A (65.1°, 1:1,[a] NaCl)	89	21.24	38.8	38.4
	67	31.2	38.7	38.6
	69	31.2	39.0	38.6
	72	41.2	36.5	35.8
	49	51.3	37.3	34.8
	65	61.3	35.6	33.6
	68	71.4	32.5	32.6
	73	101.6	29.6	29.7
	74	131.7	28.5	27.4
B (65.1°, 1:1,[a] $NaNO_3$)	85	17.90	44.0	42.7
	87	21.24	41.7	41.6
	83	31.2	40.4	40.7
	82	51.3	37.5	37.7
	88	101.6	32.0	32.0
C (55.2°, 1:1,[a] $NaNO_3$)	94	17.90	13.2	12.8
	93	21.24	12.4	12.4
	92	31.2	12.0	12.1
	91	51.3	11.2	11.2
	90	101.6	9.47	9.52
	118[b]	12.8	12.9	13.4
	114[c]	51.3	10.8	11.1
D (45.1°, 1:1,[a] $NaNO_3$)	99	17.90	3.49	3.47
	98	21.24	3.39	3.38
	97	31.2	3.28	3.28
	100	51.3	3.08	3.07
	95	101.6	2.69	2.60
E (65.1°, 1:2,[a] $NaNO_3$)	105	17.90	9.77	10.0
	104	21.24	9.83	9.85
	101	31.3	9.20	9.35
	102	51.3	8.85	8.88
	103	101.6	8.32	7.89
F (65.1°, 1:5,[a] $NaNO_3$)	111	17.90	2.51	[d]
	110	21.24	2.44	[d]
	109	31.3	2.46	[d]
	107	51.3	2.41	[d]
	112	101.6	2.49	[d]

[a] Volume ratio dioxane:water. [b] b_0 = 8.03 mmoles/liter. [c] b_0 = 24.1 mmoles/liter. [d] It was not found possible to determine K for series F, and thus k_2 could not be calculated. [e] k_2 was calculated using eq. 18 and the values of K given in Table III.

Equation 19 and its analytical form (24) relate k_2, the experimental second-order rate constant, to K, the equilibrium constant for ion association (eq. 1), k, the rate constant for irreversible decomposition of the diphenyliodonium phenoxide ion pair to products, and the concentrations of reagents.

TABLE III

VARIATION OF K AND k WITH CONDITIONS

Series	Wt. % diox.	Temp., °C.	K, l./mole	100 k min.$^{-1}$	100 Kk,[b] l./mole min.
A	50.7	65.1	4.4	10.1	44.4
B	50.7	65.1	5.0	10.1	50.5
C	50.7	55.1	5.0	2.95	14.8
D	50.7	45.1	5.0	0.82	4.1
E	34.0	65.1	3.1	3.45	10.7
F	17.1	65.1	[c]	[c]	(2.46)[c]

[a] See Table II. [b] Kk represents the limiting value for k_2 as reagent concentrations approach zero. [c] No values of K and k were obtained as a systematic variation of k_2 with A could not be found: 100 k_2 = 2.46 ± 0.03 liters/mole min.

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[8] Slopes of the usual second order plots (eq. 16) were very nearly linear over the first 20% of reaction for which k_2 was determined.

[9] In work separately reported (ref. 6) it was observed that the uncatalyzed decomposition of diphenyliodonium chloride to chlorobenzene and iodobenzene was extremely slow and of second order in water, much faster and of first order in diethylene glycol and still faster and again of first order in dimethylformamide. It is suggested that the reaction proceeds through ion pairs, whose concentration and rate of decomposition increase as the dielectric constant and solvating power of medium decrease. For kinetic studies with trialkylsulfonium salts see R. F. Corran, *Trans. Faraday Soc.*, **23**, 607 (1927), and J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1571 (1933).

[10] That interactions other than coulombic may be involved in the diphenyliodonium phenoxide ion pair is indicated by the yellow color that appears immediately on mixing diphenyliodonium and phenoxide ions and disappears immediately on acidification of the solution. It is planned to study the yellow complex spectrophotometrically. Lewis and Stout (ref. 5b) have also reported this color.

These equations correlate the variations in k_2 noted above in this section and allow the quantitative determination of K and k.[10a]

The Determination of K and k.—For each of the six series (except F) summarized in Table II a plot of $1/k_2a$ against $1/m$ according to (25) gave rough values of K and k. The values of $1/A$ found with this K were plotted against $1/k_2a$ according to (24) to give improved values of K and k. A final cycle with (24) (Fig. 1) gave the values of K and k collected in Table IV.

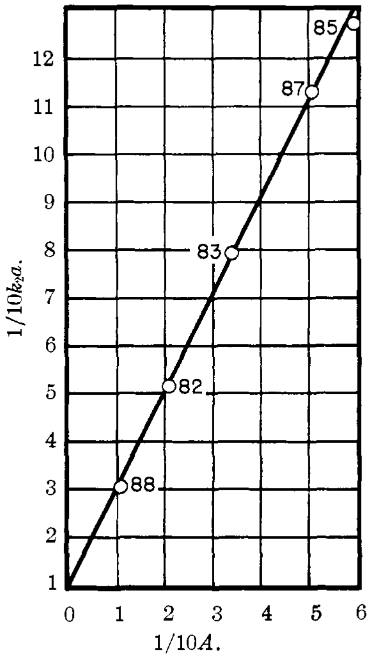

Fig. 1.—Determination of K and k for series B, Table II, using equation 24.

A Discussion of K and k.—Series A and B (Tables II and III) differ only in that in series A the "inert" anion used in making up the ionic strength is chloride ion while in series B the "inert" anion is nitrate ion. It is reassuring that k has the same value (0.101 min.$^{-1}$) in both series. It is assumed that the smaller value of K in series A (4.4 liters/mole) as compared to that in series B (5.0 liters/mole) arises from a parasitic equilibrium leading to ion pair formation between diphenyliodonium and chloride ions. The equilibrium constant for this ion association would have a value of about 1 liter/mole (or more if there is appreciable association between diphenyliodonium and nitrate ions).[11] To minimize the complications of parasitic equilibria, nitrate ion was used in all the later studies.

A more detailed analysis of series A and B using (33) indicates that the equilibrium constant for association of the sodium and phenoxide ions is zero, or very close to it, under these conditions.

A comparison of series B, C and D reveals that K is constant over a 20° range of temperature. An Eyring plot of the values of k in these series gives $\Delta H^{\ddagger} = 26.2$ kcal./mole and $\Delta S^{\ddagger} = 6$ e.u. This suggests that the geometry of the transition state is not very different from that of the ion pair, but that possibly some solvent molecules attached to the ion pair are bound less lightly in the transition state.

The data on series B and E indicate that as the solvent becomes more aqueous and acquires a higher solvating power for charged particles and a higher dielectric constant, both K and k decrease.[9] Finally, in series F with a largely aqueous solvent K has decreased to such a point that a systematic variation of k_2 with A could not be found: $100\ k_2 = 2.46 \pm 0.03$ liters/mole-min.[12] Here $k_2 = Kk$.

Dependence of k_2 on Dielectric Constant.[13]—In addition to the runs discussed in the preceding section there was a series in which u, T and reagent concentrations were held constant while the solvent varied from 1:5 to 7:5 dioxane–water.[14] From the slope of the plot of log k_2 against $1/D$ (123.3) (Fig. 2) it was calculated with equation 38 (see ref. 13) that r, the distance between charge centers in the activated complex, was about 1.7 Å.

$$r = (N\epsilon^2/RT)\mathrm{d}(1/D)/\mathrm{d}\ln k_2 \qquad (38)$$

Here N is Avogadro's number, ϵ is the electronic charge and R is the gas constant.

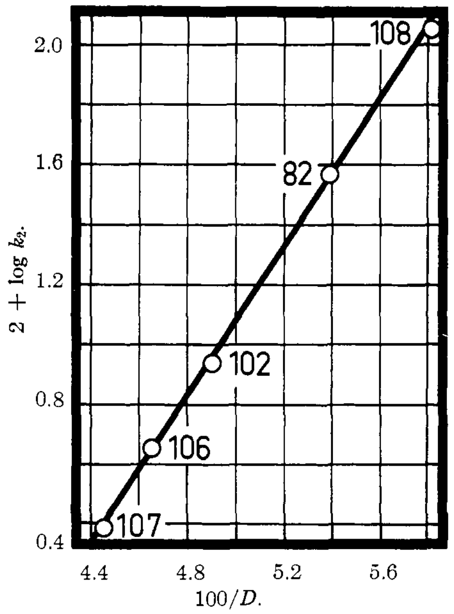

Fig. 2.—Dependence of k_2 on dielectric constant in dioxane-water mixtures of 65.1° with sodium nitrate as inert salt; $a_0 = 51.3$, $b_0 = 13.47$ and $u_0 = 165$ mmoles/liter.

The somewhat low value of r may be due to the fact that the actual dielectric constant about the

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[10a] NOTE ADDED IN PROOF.—This analysis may determine the concentration of diphenyliodonium phenoxide complexes but not their nature, *e.g.*, whether or not they are ion pairs.[10]

[11] The greater number of rotational states for nitrate ion than for chloride ion might lead to a smaller association constant: R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Cambridge, England, 1949, p. 377.

[12] In series E runs that solutions became turbid after 12–15% of reaction, with consequent acceleration. Therefore, k_2 was calculated from the first 12% of reaction. See previous discussion of the effect of a second phase under Solvents.

[13] For a discussion of the influence of dielectric constant on rates of ionic reactions see K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 127–130.

[14] The data of Åkerlöf and Short, THIS JOURNAL, **58**, 1241 (1936), were used to calculate the values of D, with no correction for the dissolved salts.

charge centers is almost certainly less than the bulk dielectric constants because of the three phenyl groups attached to the iodine and oxygen. Further, it should be noted that in the above calculations actual experimental values of k_2 were used rather than theoretically preferable[13] values at zero ionic strength to be obtained by extrapolation. In the present work this has not proved feasible. The dependence of k_2 on ionic strength is discussed in the next section.

Dependence of k_2 on Ionic Strength.—For runs at 55.6° in 1:1 dioxane–water with different concentrations of reagents and with sodium chloride as the "inert" salt a plot of k_2 against $u^{1/2}$ (eq. 30, $q = 0$) was linear with a slope of -2.7. The slope has the sign expected for the reactions of ions of opposite charge and a magnitude somewhat smaller than might be predicted by the Debye–Hückel limiting law.[15,16]

To see if this linearity still prevailed over a wider range of ionic strengths, a series of runs was made at 55.1° in 1:1 dioxane–water with constant small initial concentrations of reagents and various added amounts of sodium nitrate (Fig. 3). Not only is the slope here less than that predicted by the Debye–Hückel limiting law[15] but the slope decreases with increasing ionic strength. Factors possibly contributing to such behavior include finite ionic size and incomplete dissociation of sodium nitrate.

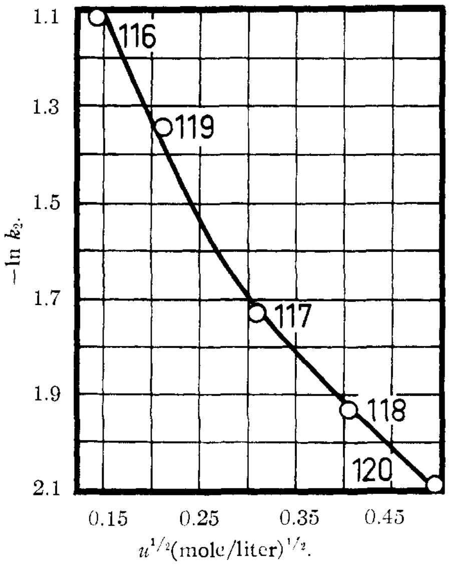

Fig. 3.—Dependence of k_2 on ionic strength in 1:1 dioxane-water at 55.1° with sodium nitrate as inert salt; $a_0 = 12.8$ and $b_0 = 8.03$ mmoles/liter.

The Reaction in 5 : 1 Dioxane–Water.—In the accompanying paper[1] it was suggested that K increased, the kinetic order of the reaction between oppositely charged ions would go below two and approach one in the limit. This is in accord with the observation that in 5:1 dioxane–water (where ion association should be favored) good linear 1.5-order plots (Fig. 4) were found up to 80% reaction for

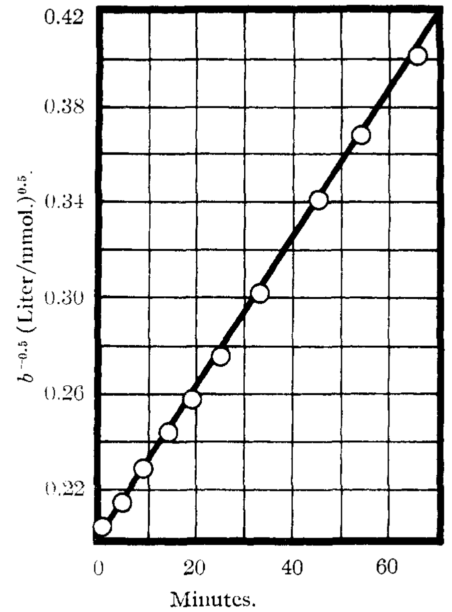

Fig. 4.—Reaction in 5:1 dioxane-water in the presence of sodium chloride; $a_0 = b_0 = 26.84$ mmoles/liter. Reaction is plotted as of 1.5 order.

systems with equal concentrations of diphenyliodonium and phenoxide ions. In Table IV some relevant data obtained over a range of temperatures are summarized. The Eyring parameters from this work are $\Delta H^{\ddagger} = 24.8$ kcal./mole, and $\Delta S^{\ddagger} = 6$ e.u. These data are comparable to those for k_2 (previous section, Arrhenius Parameters) and for k (previous section, A Discussion of K and k), and previous comments apply. The small decrease in $\Delta H^{\ddagger}$ is probably attributable to the fact that with decreasing dielectric constant and solvating power the collapse of ion pairs to products is facilitated by decreased stabilization of ion pairs.

Table IV

Dependence of $k_{1.5}$ on Temperature[a]

Run	Temp., °C.	100 $k_{1.5}$
12, 13	30.0	1.33, 1.33
10, 11	39.6	4.80, 4.87
15	45.1	9.71
9	55.5	35.3

[a] In 5:1 dioxane–water with sodium chloride as inert salt, with constant $u_0 = 53.7$, $a_0 = b_0 = 26.84$ mmoles/liter; $k_{1.5}$ in mole $^{1/2}$ liter$^{-1/2}$ min.$^{-1}$.

By adding an excess of one reagent ion it was found that the kinetics approached first order in the other ion (Table V). Four such graphs are shown in Fig. 5. The fact that k_1 was largest when the excess of one reagent was large is in accord with the general picture and more specifically with the relationships of equation 23.

It is interesting and possibly significant that the present authors have found that a 1.5-order graph, similar to Fig. 4, fits the data of Svirbely and Lander[17] for the transformation of ammonium cyanate to urea in partially aqueous solvents containing more than 50% dioxane. While an attempt in that paper to explain the results on the basis of ionic strength

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(15) See ref. 13, pp. 123-127.

(16) In a private communication Dr. Ernest Grunwald has suggested that this slope could be accommodated by the Debye–Hückel theory if the finite size of the ions were taken into consideration.

(17) W. J. Svirbely and J. Lander, This Journal, **61**, 3538 (1939).

TABLE V

UNEQUAL REAGENT CONCENTRATIONS IN 5:1 DIOXANE-WATER, MMOLES/L.

Run	Temp., °C.	a_0	b_0	u_0[b]	100 k_1[a]
14	30.0	26.84	13.42	40.3	4.75
18	30.0	26.84	20.13	47.0	4.18
16	30.0	20.13	13.42	33.6	4.31
19	30.0	13.42	20.13	33.6	4.49
24	39.6	33.55	5.37	38.9	19.8
27	39.6	26.84	5.37	32.2	19.6
22	39.6	26.84	13.42	40.3	18.7

[a] Calculated from a first-order plot of the ion present in smaller concentrations; in min.$^{-1}$. [b] Added sodium chloride present.

changes[18] was unsuccessful, an approach based on ion pair formation and decomposition holds some promise.

Experimental

Materials.—The water used in the kinetic runs was doubly distilled. Dioxane was distilled, refluxed with sodium until no further reaction occurred and redistilled. Phenol (Matheson, Coleman and Bell) was used as received. **Diphenyliodonium chloride** was prepared as previously described.[3] Diphenyliodonium nitrate was prepared as follows.

To a vigorously stirred mixture of 198 g. (1.00 mole) of anhydrous sodium iodate, 180 ml. of benzene and 200 ml. of acetic anhydride in a 3-liter 3-necked flask immersed in an ice-bath there was added a cold solution of 140 ml. of concd. sulfuric acid in 200 ml. of acetic anhydride slowly so that the temperature stayed below 5°. After four hours the ice-bath was removed, and the reaction mixture was stirred until a sample did not liberate iodine from aqueous potassium iodide (3–6 days). The ice-bath was replaced while 400 ml. of water was added. After two extractions each with ether and with ligroin, the volume of the reaction mixture was 830 ml. Treatment of a 400-ml. aliquot with 170 g. of sodium nitrate in 400 ml. of water gave, after cooling, 105 g. (0.306 mole, 63.5%) of **diphenyliodonium nitrate**, m.p. 149–151° (reported 149–150.5°,[2] 153–154°[19]). The diphenyliodonium nitrate was recrystallized from water (1 g./2 ml. water) with no change in m.p.[20]

Solutions.—Aqueous solutions regularly used included 0.322 *N* sodium hydroxide, 0.851 *N* phenol, 1.20 *N* sodium chloride and 0.60 *N* sodium nitrate. In addition various standard dioxane–water mixtures were prepared and stored. For titrations approximately 0.05 *N* nitric acid solutions were prepared and standardized before use.

Kinetic Runs.—To a weighed amount of diphenyliodonium chloride or nitrate (more soluble) were added 10 ml. of phenol solution and measured volumes of aqueous sodium chloride or nitrate and of a dioxane–water solution. The flask was placed in a water-bath controlled to ±0.03°. After 15 minutes the diphenyliodonium salt was dissolved by swirling, and a known volume of aqueous sodium hydroxide at the same temperature was added by an accurately standardized transfer pipet. The total volume of liquids added to the flask was always 120 ml., as was the final volume of the solution, within experimental error.

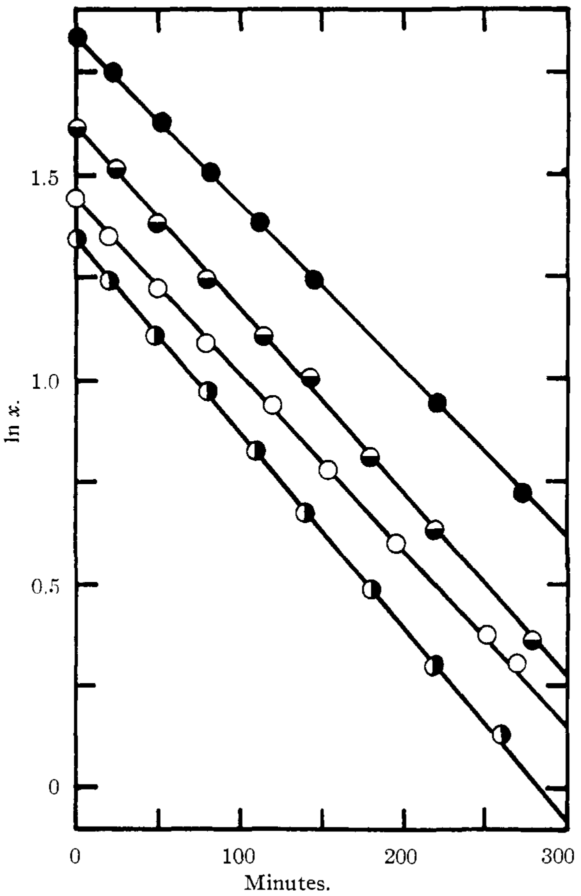

Fig. 5.—Reaction in 5:1 dioxane–water at 30.0° in the presence of sodium chloride (Table V). Runs: 14, ◑; 16, ◒; 18, ●; 19, ○. Variable x is proportional to the concentration of reagent present in lower concentration.

After the solutions had been mixed, an aliquot was withdrawn, this being taken as zero time. This sample and subsequent samples were added to 10 ml. of water and sufficient nitric acid, added from a 10-ml. buret, to neutralize 80–90% of the phenoxide ions. The titration was completed by adding more nitric acid, to a brom cresol green–methyl red end-point.[21]

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[18] E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, pp. 71–89.

[19] C. Hartmann and V. Meyer, *Ber.*, **27**, 1592 (1894).

[20] Caution should be exercised on heating diphenyliodonium nitrate in alcohol as vigorous reaction may result.

[21] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Ed., The Macmillan Co., New York, N. Y., 1943, p. 451.