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PART I. THE INHIBITION BY DIOXANE OF THE ALKYLATION OF PHENOL WITH TERTIARY-BUTYL CHLORIDE.

PART II. THE SOLUBILITY OF HYDROGEN CHLORIDE IN PHENOL-DIOXANE MIXTURES

Thesis for the Degree of M. S.
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John Junior Bordeaux
1949

This is to certify that the

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PART I. THE INHIBITION BY DIOXANE OF THE ALKYLATION OF PHENOL WITH TERTIARY-BUTYL CHLORIDE. PART II. THE SOLUBILITY OF HYDROGEN CHLORIDE IN PHENOL-DIOXANE MIXTURES

By

John Junior Bordeaux

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PART I

THE INHIBITION BY DIOXANE OF THE ALKYLATION OF PHENOL WITH *TERTIARY*-BUTYL CHLORIDE

INTRODUCTION

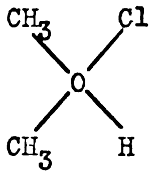
The uncatalyzed alkylation of phenol in the para position using tertiary-alkyl halides was first reported by van Alphen (1) with further work by Bennett and Reynolds (2) and later by Simons and Hart (3). The kinetics and mechanism of this reaction was recently studied by these latter investigators (4) whose work included a study of the effect of various diluents on the rate of alkylation. They observed that the alkylation was inhibited completely by 1,4-dioxane (hereinafter referred to as dioxane) when this diluent was used. When para-xylene was used in comparable amounts, the observed decrease was only that calculated for the diminution in phenol concentration. It was postulated that the inhibitory effect of dioxane was due to the formation of an oxonium compound between dioxane and phenol.

It was the purpose of this investigation to study the inhibitory property of dioxane in the alkylation of phenol with tertiary butyl chloride; to determine the stoichiometry and, if possible, the mechanism of the inhibition.

HISTORICAL

Since oxonium compounds probably play an important role in the mechanism of the inhibitory property of dioxane in the alkylation of phenol, it is well to briefly review the literature of such compounds.

The formation of addition compounds of simple ethers with hydrogen halides was discovered by Friedel in 1875 (5); these compounds and others similar to them were called oxonium salts. Two structures for these oxonium salts have been proposed (6),

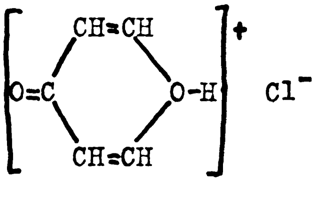


I

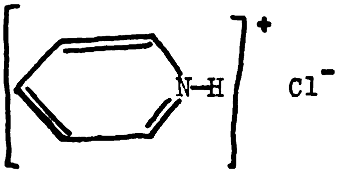
$[(CH_3)_2O\cdots\cdot H]^+\ Cl^-$

II

Structure I gives rise to a tetravalent oxygen atom; II shows the formation of a salt-like compound which is analogous to the ammonium salts. The anion is not attached by a covalent bond. The γpyrones were the first definitely established compounds which formed oxonium salts. They formed crystalline compounds with acids whose structures might be compared to those formed by such nitrogen containing compounds as the pyridines:

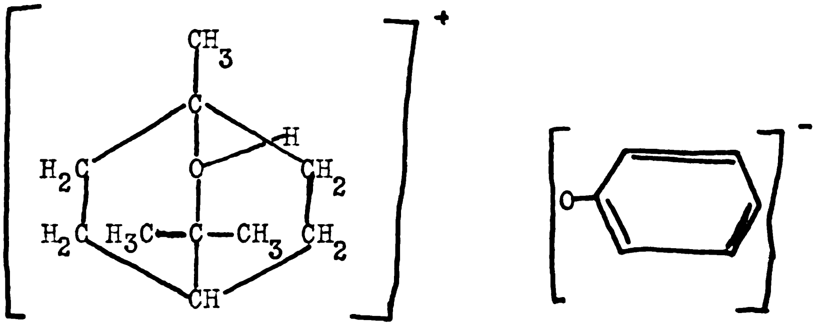


γ pyrone salt

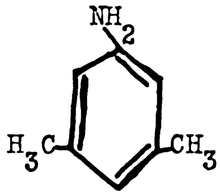


pyridine salt

Cineole has been reported to form similar addition compounds with acidic substances indicating the basic character of the oxygen atom in the ring. Bellucci and Grassi (7) show evidence of the formation of oxonium compounds of cineole with phenol, certain substituted phenols, α- and β-naphthols. Their data shows the formation of addition compounds containing one molecule of cineole to one molecule of phenol, indicating the following formula:

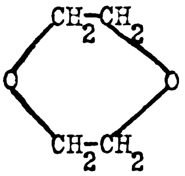


From the work of Morgan and Pettet (8), the analogies between oxonium and ammonium compounds are further strengthened. They confirm the work of Bellucci and Grassi and also show the formation of an addition compound of o-cresol with both m-5-xylidine and cineole.

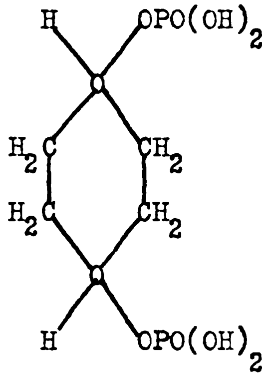


m-5-xylidine

The study of the formation of salts with dioxane has been of some interest and according to Whitmore (9), it will form oxonium compounds in a manner similar to those compounds previously discussed. Examination of the structure of dioxane leads one to believe that it might form a compound containing one molecule of dioxane to two molecules of the acid since it has two oxygens available for combination:

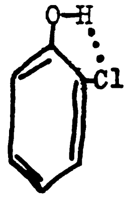


Faworski (10) and Smeets (11) have shown this to be true with sulfuric and perchloric acids respectively. Recently Baer (12) has prepared dioxane diphosphate:

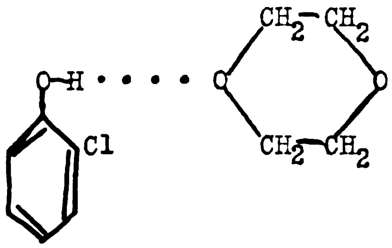


His discussion of the compound stated that it was soluble in certain organic solvents, indicating that the bonds formed by the addition of the acid were of a covalent nature.

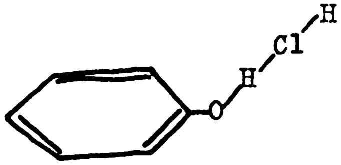
Intramolecular hydrogen bonding was studied by Batuev (13) using infra-red adsorption spectra, and in this connection, the effect of dioxane on the chelate ring formed in o-chlorophenol:



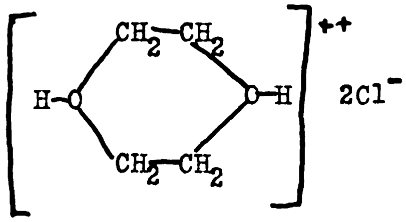
It is pointed out in this paper that the addition of an equivalent amount of dioxane to a solution of o-chlorophenol in carbon tetrachloride tends to disrupt the formation of the chelate ring, probably due to the attraction for the hydrogen of the phenol by the oxygen atoms of the dioxane:



Bartlett and Dauben (14) have evidence to support the formation of oxonium compounds between dioxane and phenol. They discussed the increase in the acid strength of hydrogen chloride in dioxane brought about by phenols and alcohols. The formation of a complex between the phenol and the hydrogen chloride in which there was a hydrogen-bond formed by the hydrogen of the hydroxyl group and the chlorine was postulated:



They pointed out that the basic strength of dioxane was sufficient to assure them the hydrogen chloride was entirely combined with the solvent, as dioxanonium chloride:



The formation of these two compounds offers an explanation of the greater dissociation of hydrogen chloride because it can be supposed that there is a pull on both of the atoms of the hydrogen chloride. The same basic characteristic of dioxane may cause it to be combined with phenol in mixtures of these compounds.

EXPERIMENTAL

I. Materials

The phenol was J. T. Baker Chemical Company material, which was distilled with benzene to remove the water. The fraction boiling from 177 to 184° was taken. This was in turn fractionated, retaining the sample from 180 to 182°. This was then stored under nitrogen until ready for use.

The tertiary butyl chloride was prepared from Eastman Kodak Company tertiary butyl alcohol by shaking portions of it with concentrated hydrochloric acid in a separatory funnel and separating the organic layer from the water layer (15). The tertiary butyl chloride thus prepared was distilled keeping the fraction boiling between 49 and 53.5°. This was further fractionated to obtain a sample which boiled at 51 to 52°, at atmospheric pressure.

The dioxane, an Eastman Kodak product, was purified by the method described by Fieser (16). 200 ml. of dioxane was refluxed with 2.7 ml. of concentrated hydrochloric acid and 20 ml. of water for twelve hours, the solution was cooled and saturated with potassium hydroxide pellets. The layers were separated, and the dioxane was treated with fresh potassium hydroxide pellets, decanted and refluxed with sodium for twelve hours. The dioxane was then distilled from the sodium and stored over fresh sodium. The entire purification was carried out under an atmosphere of nitrogen and the purified dioxane was stored in a nitrogen atmosphere.

II. Apparatus

The apparatus used is shown in figure 1. It consisted of a 125 ml. reaction flask, A, having a gas inlet tube, B, extending to the bottom. In the early work, the flask was sealed at C to a condenser, D, fitted at the top with a 14/35 male ground glass joint, E. Later the flask was fitted with a 24/40 female ground glass joint at C and the condenser with the same sized male joint. The condenser was attached to a tube, F, with a three-way stopcock, G, whose outlets were fitted with 14/35 male ground glass joints, H, to which sodium bicarbonate tubes, I, were connected. The sodium bicarbonate tubes were connected to trap vessels, J, which were kept in a dry ice-acetone bath. The system was stirred with a magnetic stirring device and a continuous stream of dried nitrogen gas was bubbled through the mixture at B. The reaction flask, A, was submerged in a constant temperature bath maintained at 50.0 ± 0.1° during the experiments.

III. Method of Measuring Rate

The rate of the reaction was followed by converting the evolved hydrogen chloride to sodium chloride and determining the amount of sodium chloride formed at definite time intervals.

Weighed amounts of dioxane and phenol were thoroughly mixed in the reaction flask. In the early stages of this work, the tertiary butyl chloride was added to the reaction mixture by pipetting it down through the condenser. It was later thought that this method of addition might not be satisfactory because of the possibility that tertiary butyl chloride might be lost by volatilization during the process of

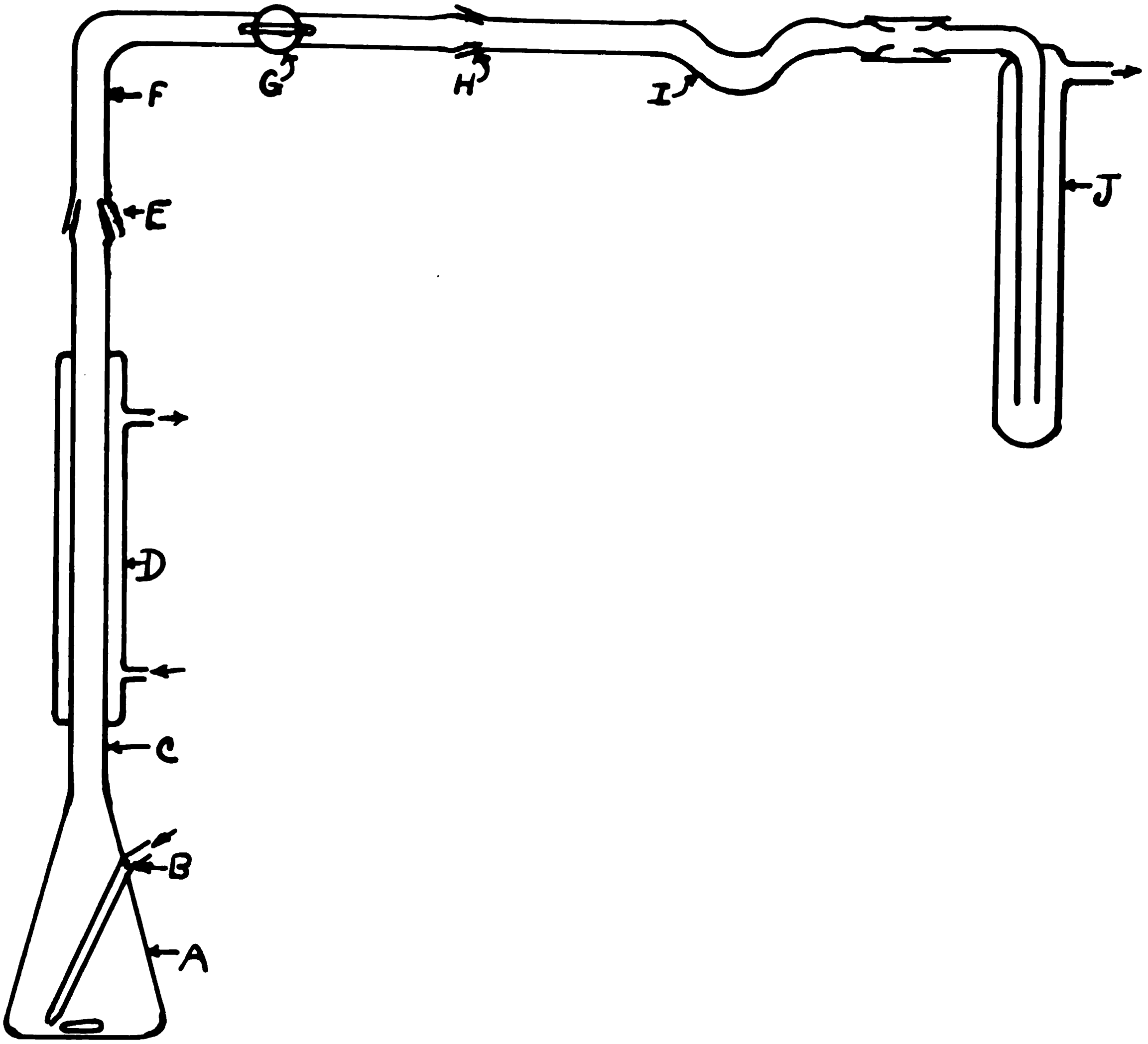


Fig. 1

The rate measuring apparatus

pipetting. This proved to be incorrect since the results were duplicated by a different method.

The other method of adding the tertiary butyl chloride was to seal a weighed amount in a thin walled ampoule and break it in the reaction flask with the system closed. This method proved highly successful since, by using a weighed amount of the tertiary butyl chloride, it was possible to calculate the exact number of moles that were added. In the first method of addition, it was necessary to assume that the total amount of the halide in the pipette was added to the solution.

The reaction was followed by the hydrogen chloride given off during the reaction. The hydrogen chloride, when passed through the sodium bicarbonate tube, reacted to form sodium chloride, water and carbon dioxide. The contents of the tube were then dissolved, made acid with nitric acid, and the amount of chloride determined by the Volhard method (17). Since it was believed that small amounts of tertiary butyl chloride might distil over during the reaction, a trap cooled by a dry ice-acetone bath was employed. The trap was rinsed with absolute alcohol several times; this solution was then diluted with water and acidified with nitric acid and the chloride determined as before. The total chloride carried over in any one experiment was always less than 10 per cent of the original tertiary butyl chloride used. The values in column 4 of Table I represent values which have been corrected for the small amount of tertiary butyl chloride carried out of the reaction flask by the nitrogen and evolved hydrogen chloride.

RESULTS

I. Data

A sample of the data taken during experiment number six is shown in Table I. Space prevents recording the detailed data for each run, but the essential data for all experiments is summarized in Table II. The experimentally determined first order rate constants (k) and the half-times ($t_{\frac{1}{2}}$) are given in columns (6) and (7) respectively.

II. Treatment of Data

The data obtained was in the form of moles of hydrogen chloride evolved (column (3), Table I). Since this was equivalent to the moles of tertiary butyl chloride that had reacted, it was subtracted from the number of moles added at the start of the reaction to give the number of moles of tertiary butyl chloride remaining (column (4), Table I). The volumes of the reactants were assumed to be additive and by dividing the number of moles of tertiary butyl chloride remaining by the total volume of solution the concentration at the end of each time interval was obtained (column (5), Table I). Since the reaction was determined to be first order with respect to the halide (4), the minus log of the concentration was plotted against the time (see figure 2). From this graph, the half-time of the reaction was determined (column (7), Table II). The rate constant, which is the slope of the line was calculated (column (6), Table II). The best line was drawn through the experimental points using the method of least squares (18).

Table I

Sample of Data from Experiment #6.

(1) Sample No.	(2) Time (min.)	(3) Moles of HCl Evolved per Time Interval	(4) Moles of t-Butyl Chloride Unreacted	(5) Concentration of t-Butyl Chloride in moles/liter
0	0	0.000000	0.011261	0.4941
1	20	0.000283	0.010978	0.4815
2	40	0.000561	0.010417	0.4569
3	60	0.000606	0.009811	0.4303
4	80	0.001145	0.008666	0.3801
5	110	0.000982	0.007684	0.3370
6	150	0.001425	0.006259	0.2745
7	200	0.001302	0.004955	0.2173
8	260	0.001124	0.003833	0.1681
9	320	0.000823	0.003010	0.1320
10	380	0.001022	0.001988	0.0872

Table II

Summary of Rate Data

(1) Exp	(2) t-Bu Cl Moles	(3) Phenol Moles	(4) Dioxane Moles	(5) Molarity of (a) Phenol	(6) k	(7) $t_{\frac{1}{2}}$ (min)
1	0.009872	0.2172	0.00000	10.61	0.011017	53.3
2	0.009189	0.2090	0.00000	10.58	0.010560	55.0
3	0.009745	0.2163	0.00615	10.25	0.005258	79.8 ✓
4	0.010034	0.2184	0.01174	10.00	0.003679	104.0
5	0.009983	0.2179	0.01190	9.99	0.004071	108.1 ✓
6	0.011261	0.2180	0.02315	9.56	0.001940	174.2
7	0.012144	0.2073	0.02362	9.40	0.002010	164.0 ✓
8	0.010823	0.2185	0.03476	9.15	0.000699	429.3
9	0.011748	0.2188	0.03538	9.09	0.000688	435.0 ✓
10	0.011149	0.2167	0.05774	8.40	0.000080	8663.5(b)

(a) These molarities were calculated on the basis of dioxane acting only as a diluent.

(b) This value was estimated using the rate constant k.

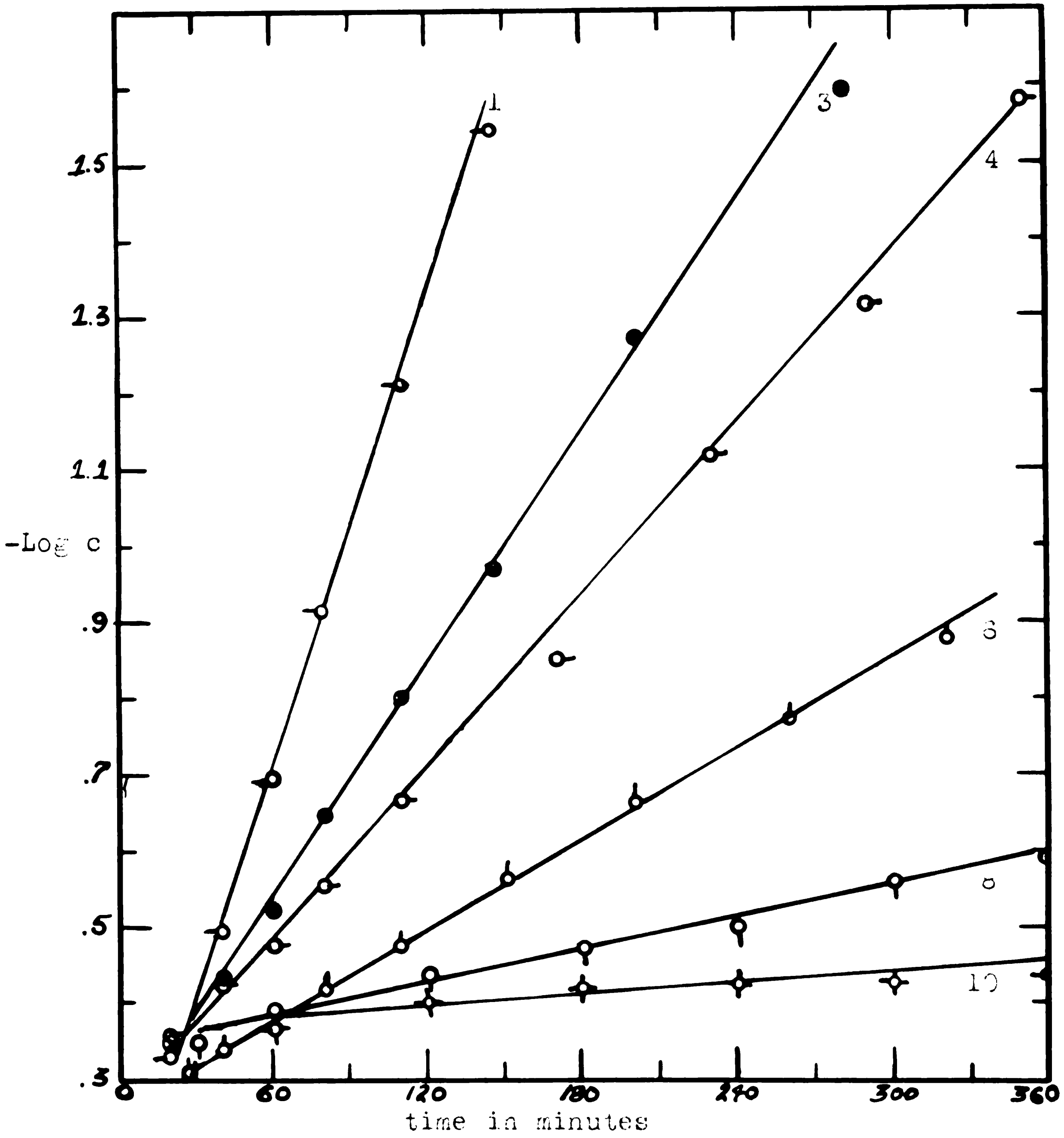


Fig. 2

Minus log c vs. time for experiments 1, 3, 4, 6, 8, and 10. (Table II)

The expression in which the time, t, necessary to complete any fraction of the reaction is proportional to n' the total order of the reaction is shown by the following equation (19):

$$t \propto 1/a^{n'-1}$$

where a is the initial concentration of reactants. Thus from any two different experiments it is seen that

$$t_1/t_2 = (a_2/a_1)^{n'-1}$$

Since the reaction is first order with respect to the halide, the half-time is independent of the tertiary halide concentration. Knowing that n' is the total order of the reaction, n'-1 may be taken as the order of the reaction with respect to phenol. n may be used to represent n'-1. Now using M, the molarities, to express the concentrations, a, the following equation is obtained:

$$t_{\frac{1}{2}}/t_{\frac{1}{2}}^{o} = (M^{o}/M)^{n} \qquad (1)$$

where $t_{\frac{1}{2}}^{o}$ is the half-time for the reaction with no dioxane present, $t_{\frac{1}{2}}$ is the half-time for the particular reaction, M^{o} is the molarity of the phenol in the no dioxane experiment, and M is the molarity being studied. The reference values are $t_{\frac{1}{2}}^{o} = 53.5$, and $M^{o} = 10.61$ at 50°. It is possible, using equation (1), to calculate the half-time $t_{\frac{1}{2}}$ which one would expect under varying assumptions concerning the effect of dioxane on the reaction. These values are given in Table III, and their significance is discussed below.

The values for $t_{\frac{1}{2}}^{a}$ (column (3), Table III) were calculated on the assumption that dioxane acts only to decrease the phenol concentration by diluting the solution. As an example, data from experiment eight is taken:

Table III

(1) Exp.	(2) $t_{\frac{1}{2}}$	(3) $t_{\frac{1}{2}}^{a}$	(4) $t_{\frac{1}{2}}^{b}$	(5) $t_{\frac{1}{2}}^{c}$	(6) Moles of Dioxane Per Mole of Phenol
1	53.3				
2	55.0				
3	79.8	65.6	78.1	92.9	0.02843
4	104.0	76.0	106.1	148.9	0.05394
5	108.1	81.9	108.0	153.7 ✓	0.05461
6	174.2	97.0	195.6	417.1	0.10601
7	164.0	110.2	227.6	518.3 ✓	0.11408
8	429.3	129.6	367.7	1286.7	0.15908
9	435.0	134.8	396.8	1403.4 ✓	0.16170
10	8663.5(a)	216.4	3089.4		0.26645

(a) See footnote (b) page 13.

$$\text{I} \quad \frac{t_{\frac{1}{2}}^{a}}{53.3} = \left(\frac{10.61}{9.15}\right)^{6} \quad , \quad t_{\frac{1}{2}}^{a} = 129.6 \text{ minutes}$$

The value of six was used for n because Hart and Simons (4) pointed out that the apparent order of the reaction with respect to phenol was fifth to sixth.

The values for $t_{\frac{1}{2}}^{b}$ (column (4), Table III) were calculated by assuming that one mole of dioxane would combined with one mole of phenol, and thus decrease the phenol concentration. Using the same experiment as before for the example, $t_{\frac{1}{2}}^{b}$ was found to be:

$$\text{II} \quad \frac{t_{\frac{1}{2}}^{b}}{53.3} = \left(\frac{10.61}{7.69}\right)^{6} \quad , \quad t_{\frac{1}{2}}^{b} = 367.7 \text{ minutes}$$

The $t_{\frac{1}{2}}^{c}$ values (column (5), Table III) were obtained in the same way by assuming that each mole of dioxane combined with two moles of phenol. Again experiment eight will be used as an example.

$$\text{III} \quad \frac{t_{\frac{1}{2}}^{c}}{53.3} = \left(\frac{10.61}{6.24}\right)^{6} \quad , \quad t_{\frac{1}{2}}^{c} = 1286.7 \text{ minutes}$$

A plot of these $t_{\frac{1}{2}}$ values against the moles of dioxane per mole of phenol is seen in figure 3. These curves may be compared with the curve for the experimental half-times (column (2), Table III).

The same type of calculations could be carried out using five as the n value. For comparison with the value of $t_{\frac{1}{2}}^{a}$ calculated in I, the same concentration will be used, but the order of the reaction will be taken as fifth order:

$$\text{IV} \quad \frac{t_{\frac{1}{2}}^{a}}{53.3} = \left(\frac{10.61}{9.15}\right)^{5} \quad , \quad t_{\frac{1}{2}}^{a} = 111.8 \text{ minutes}$$

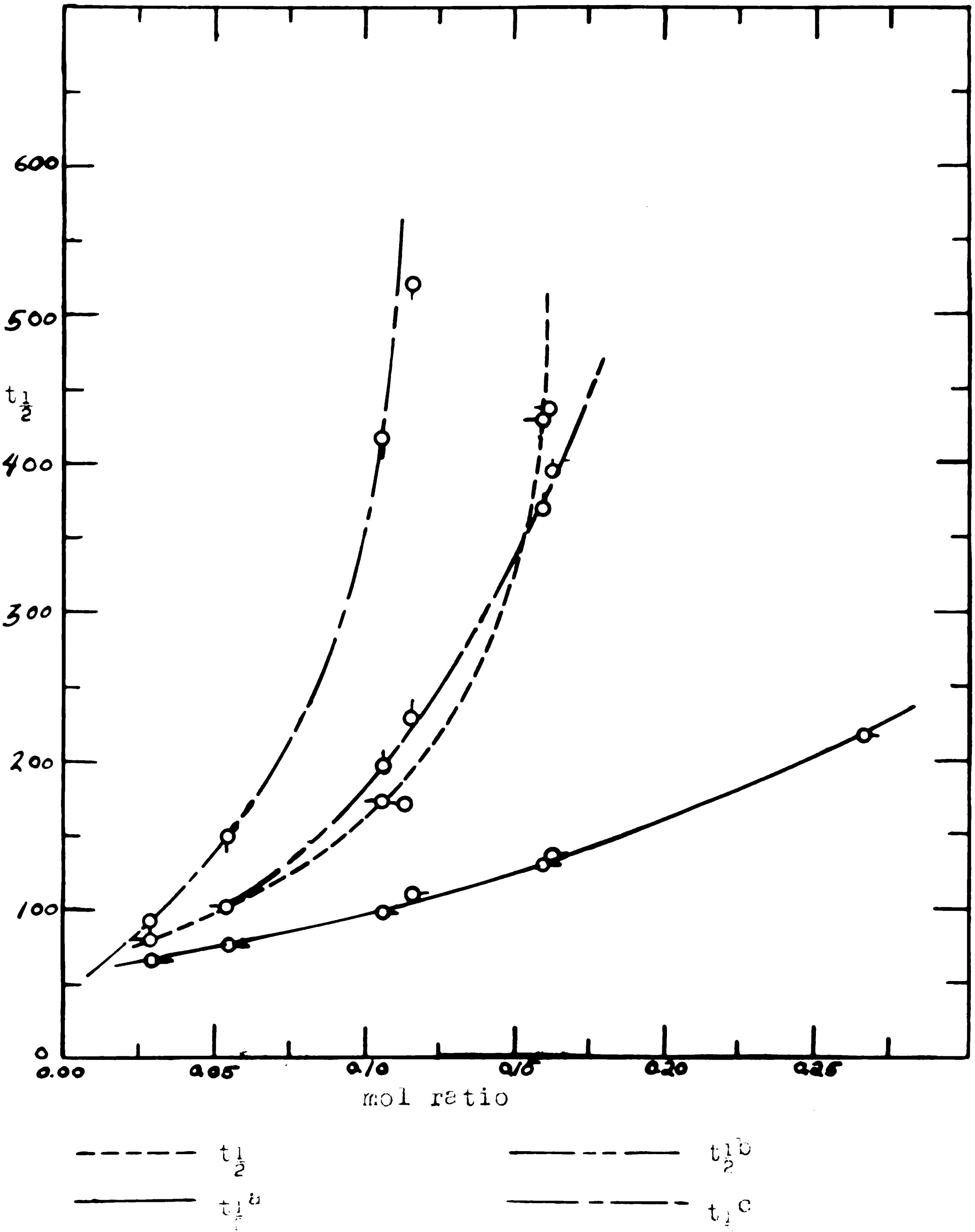


Fig. 3

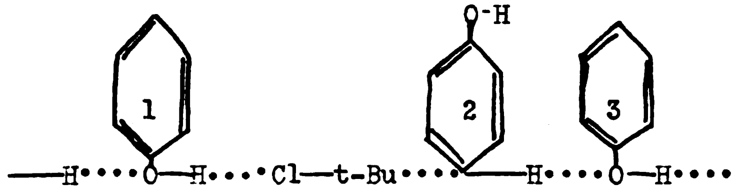
$t_{\frac{1}{2}}$ vs. mol ratio of dioxane to phenol. (Table III)

It is readily seen that this last value calculated is less than the corresponding value when n is taken as equal to six, thus magnifying the inhibitory effect. It is unlikely that n could be greater than six.

DISCUSSION

The kinetics and mechanism of the uncatalyzed alkylation of phenol with tertiary butyl chloride has been investigated by Hart and Simons (4). As a result of their studies, in which they found that tertiary butyl chloride could be used to alkylate phenol quantitatively at convenient temperatures and with a measurable rate, they proposed a mechanism for the reaction. This mechanism is shown schematically below:

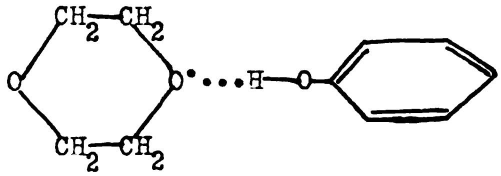
I



The solid lines are the bonds before the reaction takes place and the dotted lines show what occurs in the reaction and the new bonds formed. The reaction showed an apparent order with respect to phenol of about five or six. They pointed out that the remainder of the phenol molecules involved in the transition state may be attached to 1 and 3 in a linear fashion, or that several phenol molecules may be involved in a cluster, solvating both the halogen and the displaced hydrogen. It is important that the bonds be made and broken simultaneously. It is also necessary that phenol act both as an acid (molecule 1) and as a base (molecule 3). Thus, this mechanism has been said to involve the "amphoteric medium effect" (3). They also point out that the addition of dioxane in an amount of about 21.7 mol % inhibited the reaction almost completely.

In the present work it was the purpose to show to what extent dioxane affected the reaction and to draw some conclusions as to why it affected the reaction as it did. It was previously shown (see Historical) that dioxane was basic in nature and would form oxonium compounds with acidic substances such as phenol. It is believed that the formation of an oxonium compound is the factor causing the inhibition. As was pointed out by Hart and Simons (4), the ability of the reaction to proceed at a reasonable rate was dependent upon a large excess of phenol being present. Any decrease in the phenol concentration caused a large decrease in the rate. Therefore, the addition of dioxane would be expected to decrease the rate. The results show this to be correct, but the decrease is greater than would be expected if dioxane were acting only as a diluent. The experimentally determined half-time for experiment six was one hundred seventy-four minutes; the calculated half-time on the basis of dioxane acting as a diluent for the same experiment was ninety-seven minutes. By calculating the half-time of reaction based on the assumption that one mole of dioxane would combined with one mole of phenol, the half-time was found to be one hundred ninety-five minutes. Comparing this latter value with the experimentally determined half-time, it can be seen that they are of about the same order of magnitude. The results for experiments one through seven also coincide in the manner mentioned above. This is illustrated in Figure 3, where it is seen that the curve representing the experimentally determined half-times follows closely the curve calculated on the basis of a 1:1 oxonium complex between phenol and dioxane.

This leads one to the belief that a mechanism similar to the one shown in equation I prevails, but that the effective concentration of phenol is decreased by the formation of complexes such as:



The possibility that one mole of dioxane might be combining with two moles of phenol cannot be entirely discarded since the experimental results for experiments eight through ten show a decrease in the rate greater than that calculated for the combination of one mole of dioxane to one mole of phenol. This point is best seen by comparing the curves in figure 3. The experimental curve begins to approach the curve of the theoretical values calculated for the combination of one mole of dioxane with two moles of phenol.

It might be argued that the apparent inhibition shown on the addition of dioxane to the reaction might be due to the increased solubility of hydrogen chloride in dioxane-phenol mixtures rather than the formation of an oxonium compound between phenol and dioxane. This is improbable, however, since during the reaction, the volume of nitrogen passing through the system was at least eighty times as great as the volume of hydrogen chloride given off. To determine whether or not the rate of the nitrogen flowing through the system had any effect on the rate of reaction, experiments were run in which mol ratios of dioxane to phenol were about 0.15 and the amounts of nitrogen passed through for the same length of time were eighty and forty times as great as the amount of hydrogen chloride evolved. The rate constants for the two experiments checked with each other within the limits of experimental error. These rate constants were also of the same order of magnitude as the rate constants for experiments six and seven shown in Table II. Further evidence against the possibility that solubility of hydrogen chloride in the reaction mixture might be the governing factor was shown by Hart and Simons (4). Two experiments were run in which the mol ratio of dioxane to phenol was about 0.30; in the first experiment, the reaction was merely carried out with dioxane present in the reaction mixture. The results showed that no alkylation of the phenol was taking place. In case two, Hart and Simons first saturated the reactants with hydrogen chloride and then carried out the reaction as before. The results from this experiment were the same as those for case one, that is, there was complete inhibition of the reaction.

Since there was no evolution of hydrogen chloride in either experiment, it was concluded that the increased solubility of hydrogen chloride in the reaction mixture was not the cause for an apparent inhibition.

SUMMARY

The kinetics of the alkylation of phenol with tertiary butyl chloride in the presence of varying amounts of 1,4-dioxane has been studied at 50.0° C. The investigation has shown that dioxane inhibits the reaction to an extent greater than would be expected if it were merely acting as a diluent. Evidence has been presented to show that the mechanism of the inhibition may involve a 1:1 oxonium compound between dioxane and phenol.

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PART II

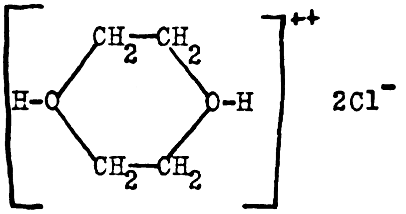
THE SOLUBILITY OF HYDROGEN CHLORIDE IN PHENOL-DIOXANE MIXTURES

INTRODUCTION

In the course of studying the inhibitory power of dioxane in the alkylation of phenol with tertiary butyl chloride, it was believed that the solubility of hydrogen chloride in mixtures of phenol and dioxane might be of considerable value in trying to show the mechanism of the reaction.

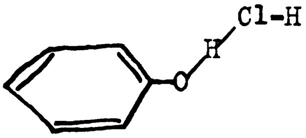
A search of the literature failed to yield any critical data on the solubility of hydrogen chloride in such a mixture. However, Bartlett and Dauben (1) present evidence to show the formation of a dihydrochloride of dioxane which they call dioxanonium chloride:

I



They further postulate that hydrogen chloride will form a complex with phenol which is due to the electrondonor property of the chloride portion of hydrogen chloride and the acceptor property of the hydroxyl hydrogen of the phenol.

II



EXPERIMENTAL

I. Materials

The dioxane was C. P. grade and was purified by refluxing over sodium for two hours and then distilling from sodium, collecting the portion coming over from 100 to 102°. The index of refraction for this roughly purified dioxane was ^{20}D 1.4228 as compared to ^{20}D 1.4224, the value found in the literature (2). The dioxane was stored over sodium until ready for use.

The phenol was Baker Chemical Company material, which was distilled with benzene to remove any water present. The portion boiling at 180 to 183° was collected and kept well covered under an atmosphere of nitrogen.

Anhydrous hydrogen chloride was prepared by dropping concentrated sulfuric acid on sodium chloride. The gas evolved was bubbled through concentrated sulfuric acid to dry it.

The apparatus consisted of a fifty milliliter erlenmeyer flask fitted with a 24/40 female ground glass connection. The stopper, a 24/40 male ground glass connection, was sealed to four inches of capillary tubing (3).

II. Measurement Procedure

In making the solubility measurements, the calculated amount of phenol for the particular mol fraction was placed in the previously weighed reaction flask and the weight of phenol determined. The calculated amount of dioxane was added and weighed. From these data the mol fractions of each constituent were calculated. The anhydrous hydrogen chloride was bubbled into the mixture for two hours at room temperature. A magnetic stirrer was placed in the flask, the stopper inserted, and the flask placed in a 50° constant temperature bath. It was noted that when the flask was first placed in the bath there was a rapid evolution of hydrogen chloride from the solution, showing it to be saturated. The capillary tubing was used on the top of the stopper to prevent a rapid escape from the flask of any gas given off and to prevent the back diffusion of air into the system, thus keeping the reaction under an atmosphere of hydrogen chloride. When the mixture had come to constant temperature (about thirty minutes) samples were removed by pipette and titrated to a phenolphthaline endpoint with standard sodium hydroxide. Thirty minutes after the first sample, a second sample was taken, this was repeated until constant values were obtained. The mixture was stirred constantly throughout the process.

RESULTS AND CONCLUSIONS

I. Data

Solubility at 50° C

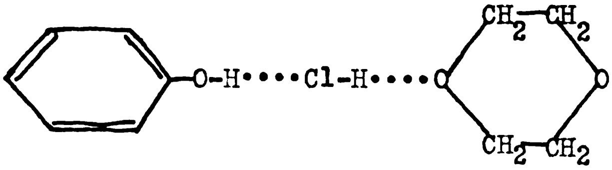
Mol fraction of Dioxane	g of HCl per 100g of Solvent
1.000	14.33
0.804	10.59
0.608	6.86
0.379	4.08
0.196	2.53
0.000	1.01[a]

a. This value was obtained from other data (4).

The solubility in grams of hydrogen chloride per hundred grams of solvent mixture was plotted against the mol fraction of dioxane in the solvent mixture (see figure 1).

II. Discussion of Results

The results show that dioxane is definitely a good base and that there is undoubtedly an oxonium compound formed between the dioxane and the hydrogen chloride as Bartlett and Dauben postulate (1). They show that there is an increase in acidity of hydrogen chloride-dioxane solutions on adding phenol. This might be attributed to the concerted pull on both the chlorine and the hydrogen by phenol and dioxane respectively. This is shown below:



The curve in figure 1 shows that as an oxygen base, dioxane is considerably stronger than phenol.

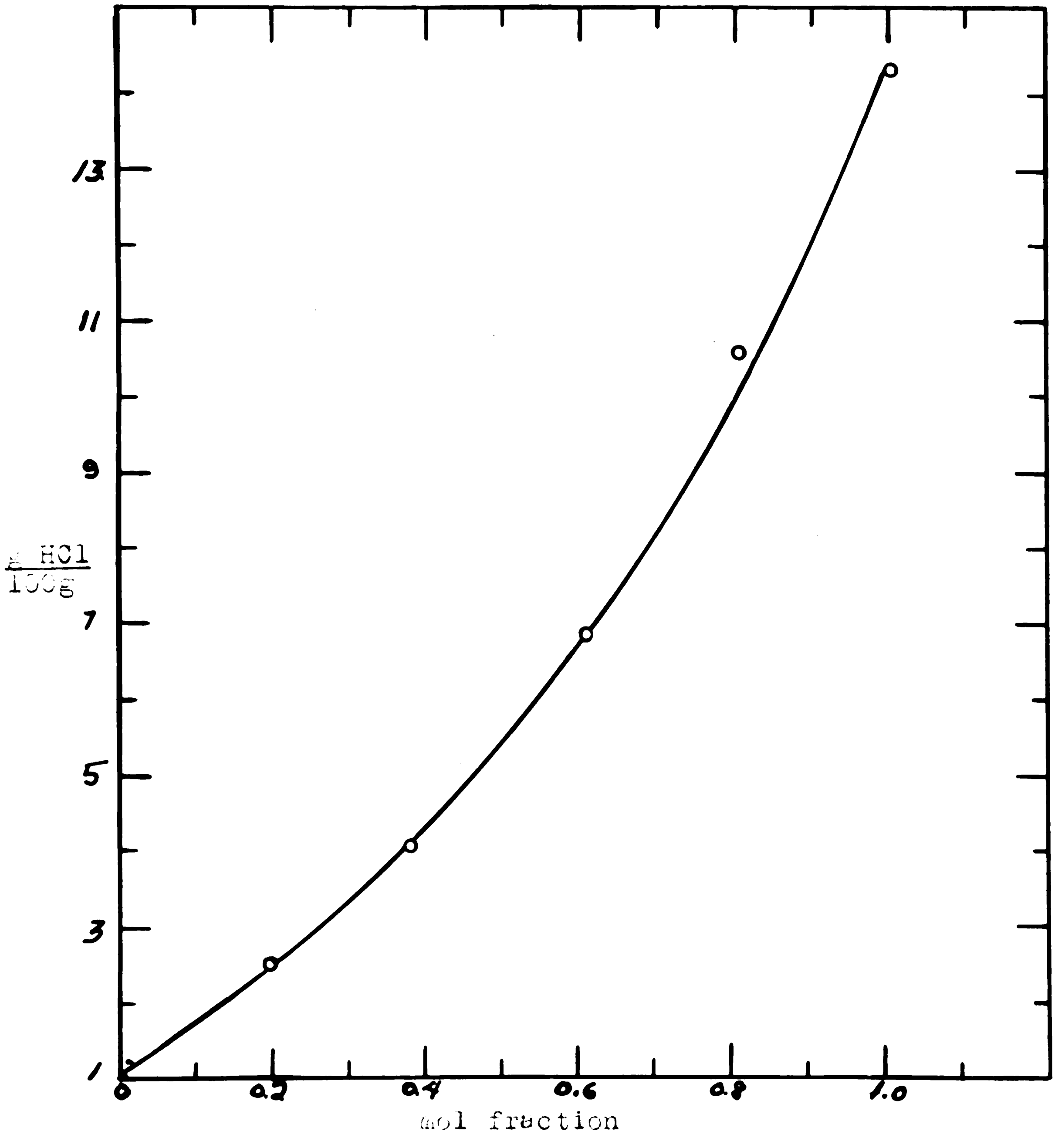


Fig. 1

g HCl per 100g of solvent vs. mol fraction of dioxane

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