1-Methyl-2-pyridone.—This compound was prepared by the action of potassium ferricyanide on 1-methylpyridinium hydroxide according to the directions given in "Organic Syntheses"[4]; b. p. 250° (740 mm.).

2-Pyridyldiphenylcarbinol.—2-Pyridylmagnesium bromide, prepared by the method of Overhoff and Proost,[5] was added to an ether solution of benzophenone. The carbinol which resulted was recrystallized from alcohol; m. p. 103–104°.[6]

1-Methyl-2-pyridone-diphenylmethide.—2-Pyridyldiphenylmethane was prepared by the method of Tschitschibabin and Benewolenskaja.[7] It was recrystallized from a mixture of alcohol and water; m. p. 63°.

2-Pyridyldiphenylmethane was heated with methyl iodide in a sealed tube and the product was recrystallized from hot water; m. p. 222–224°. This methiodide upon treatment with concentrated potassium hydroxide solution gave 1-methyl-2-pyridone-diphenylmethide which crystallized from alcohol in long, dark red-violet needles; m. p. 147°.

3-Pyridyldiphenylcarbinol.—In order to prepare 3-pyridylmagnesium bromide, the procedure of Overhoff and Proost for the preparation of the 2-isomer had to be modified somewhat. A few drops of ethyl bromide were added to 8 g. of magnesium under 20 cc. of absolute ether. When the reaction had started, a mixture of 20 g. of redistilled Eastman 3-bromopyridine and 10 g. of ethyl bromide in 100 cc. of ether was added drop by drop with heating and constant stirring, a reddish brown precipitate being formed. The solution was boiled for two hours.

To obtain 3-pyridyldiphenylcarbinol, 36 g. of benzophenone in ether was added to the 3-pyridylmagnesium bromide solution and after some time the addition compound was decomposed with an ice-cold solution of ammonium chloride. The ether layer was extracted with dilute hydrochloric acid and the carbinol precipitated with ammonia. On recrystallization from ethyl acetate, the carbinol melted at 115–116°.

Anal. Calcd. for $C_{18}H_{15}ON$: N, 5.36. Found: N, 5.32.

The picrate of 3-pyridyldiphenylcarbinol was formed by adding a hot alcoholic solution of picric acid to a hot alcoholic solution of the carbinol; m. p. 195°.

Anal. Calcd. for $C_{18}H_{15}ON \cdot C_6H_3O_7N_3$: N, 11.42. Found: N, 11.46.

4-Pyridyldiphenylcarbinol.—A mixture of 2- and 4-benzylpyridines was obtained by the action of benzyl chloride and pyridine according to the directions of LaForge.[8] Following the procedure of Tschitschibabin[9] this mixture was oxidized with permanganate to the 2- and 4-benzoylpyridines. For the preparation of 4-pyridyldiphenylcarbinol, previous investigators[7] used pure 4-benzoylpyridine. However, this requires a tedious separation of the mixture of 2- and 4-benzoylpyridines by means of the picrate. Therefore, in this work, the mixture of benzoylpyridines was added directly to phenylmagnesium bromide forming a mixture of 2- and 4-pyridyldiphenylcarbinols. The 2-pyridyldiphenylcarbinol dissolved readily in ether and the 4-isomer which is insoluble in ether was filtered off. After two recrystallizations from ethyl acetate, the melting point was 234–235°.

1-Methyl-4-pyridonediphenylmethide.—4-Pyridyldiphenylmethane was prepared by the method of Tschitschibabin and Benewolenskaja using gaseous hydrogen iodide to reduce 4-pyridyldiphenylcarbinol; m. p. 125°. To obtain the methiodide, 4-pyridyldiphenylmethane was heated with methyl iodide in a sealed tube and the product recrystallized from alcohol; m. p. 159–161°. The methiodide was treated with concentrated potassium hydroxide and 1-methyl-4-pyridonediphenylmethide was formed; recrystallization from alcohol gave yellow needles, m. p. 113°.

1-Methyl-2- and 4-Pyridonephenylmethides.—Each of these compounds was prepared according to the directions of Decker[10] by the addition of a concentrated solution of potassium hydroxide to the methiodides of 2- and 4-benzylpyridines.

Summary

1. Quantitative absorption spectral data indicate that 2-methylpyridine possesses only a pyridine structure in ether solution.
2. The absorption spectrum curve for 1-methyl-4-pyridonediphenylmethide in ether solution is very similar to the curve for diphenylquinomethane.
3. Curves for 2-, 3- and 4-pyridyldiphenylcarbinols show the presence of a pyridine structure only.

ANN ARBOR, MICHIGAN. RECEIVED JULY 26, 1948

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[4] Prill and McElvain, "Organic Syntheses," Vol. XV, John Wiley and Sons, New York, N. Y., 1935, p. 41.

[5] Overhoff and Proost, *Rec. trav. chim.*, **57**, 184 (1938).

[6] Proost and Wibaut, *ibid.*, **59**, 971 (1940).

[7] Tschitschibabin and Benewolenskaja, *Ber.*, **61B**, 551 (1928).

[8] LaForge, THIS JOURNAL, **50**, 2484 (1928).

[9] Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, **33**, 300 (1901).

[10] Decker, *Ber.*, **38**, 2494 (1905).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE DEPARTMENT OF CHEMISTRY OF THE MICHIGAN STATE COLLEGE]

The Kinetics and Mechanism of the Uncatalyzed Alkylation of Phenol

BY HAROLD HART AND J. H. SIMONS

Although the alkylation of the aromatic nucleus has long been an important reaction to the organic chemist, there have been relatively few kinetic studies of the mechanism of this reaction. Ionic intermediates for this reaction have been postulated,[1,2] but some recent kinetic studies[3] on the hydrogen fluoride catalyzed alkylation of toluene with *t*-butyl chloride present strong evidence against any high energy intermediate for that reaction. These conclusions were based on the fact that various oxygen-containing (basic) promoters affected the rate only as a function of their concentration, and independent of the structure of the particular promoter, upon the retardation effect of hydrogen chloride, and upon the energy requirements for the reaction.

Following the discovery that phenols could be alkylated in the para-position with tertiary alkyl halides in the absence of any added catalysts[4,5]

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

[2] C. C. Price, *Chem. Rev.*, **29**, 44–51 (1941).

[3] (a) W. H. Pearlson and J. H. Simons, THIS JOURNAL, **67**, 352 (1945); (b) J. W. Sprauer and J. H. Simons, *ibid.*, **64**, 648 (1942).

[4] J. H. Simons and H. Hart, *ibid.*, **66**, 1309 (1944).

[5] (a) G. M. Bennett and F. M. Reynolds, *J. Chem. Soc.*, 131 (1935); (b) J. van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).

we believed that it would be of interest to study the kinetics and mechanism of this reaction. A detailed study of the reaction has revealed several interesting facts which were not anticipated at the outset of the work.

It was found that the alkylation of phenol with *t*-butyl chloride is a homogeneous, quantitative reaction which proceeds at a measurable rate at convenient temperatures. The reaction could be readily followed by means of the increase in pressure due to the evolution of hydrogen chloride. Tertiary butyl chloride, *t*-amyl chloride, dimethylisopropylcarbinyl chloride and benzyl chloride were the halides used, and phenol and *p*-cresol were the phenols. The reactions were studied at several different temperatures in order to determine the activation energies. The effect of hydrogen chloride pressure, and of the diluents *p*-xylene, 1,4-dichlorobutane, ethylene dichloride, nitrobenzene and 1,4-dioxane was studied.

It is believed that the experimental results (a very high order rate dependency upon phenol concentration, low energies of activation, the lack of reactivity of anisole, and the very striking inhibitory power of dioxane) indicate the improbability of a simple ionic mechanism for this reaction, and a mechanism involving what has been termed the "amphoteric medium effect"[4] has been proposed which satisfactorily accounts for the experimental observations.

Experimental

Preparation of Materials.—The phenol was Eastman Kodak Company material, which was fractionated at a pressure of approximately 100 mm. in a column packed with multi-turn glass helices, with approximately 20 theoretical plates. The phenol was further purified and samples prepared in the apparatus which is described below (see Fig. 1).

The *t*-butyl chloride was prepared from *t*-butyl alcohol and concentrated hydrochloric acid in the usual manner.[6] It was dried over anhydrous potassium carbonate and fractionated through a glass-helices packed column with approximately 30 theoretical plates. The middle cuts which boiled constantly at 52° and had a constant refractive index n^{20}D 1.3850 were used in the sampling apparatus.

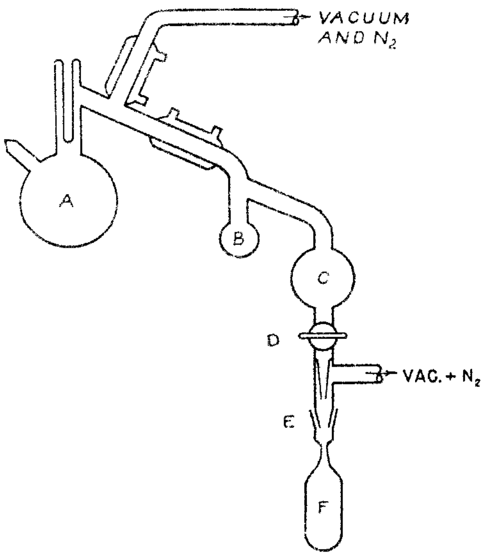

Fig. 1.—Diagram of the phenol sampling apparatus.

The *p*-cresol was Reilly Tar and Chemical Company's best grade of material. It was carefully fractionated in a manner similar to that used for the phenol. The *t*-amyl chloride was prepared and purified in a manner similar to that described above for *t*-butyl chloride. We are indebted to Dr. N. C. Cook for the dimethylisopropylcarbinyl chloride, which had been fractionated under reduced pressure in an efficient column.

Anhydrous hydrogen chloride was prepared by dropping concentrated hydrochloric acid on concentrated sulfuric acid, passing the gas through a concentrated sulfuric acid bubbler and a phosphorus pentoxide tube, and collecting the gas in a liquid air trap. The hydrogen chloride was degassed by alternate freezing, evacuation and thawing, and was then allowed to evaporate through (H) into bulb (B) in Fig. 2. It was stored there until used in the rate measurements as described below.

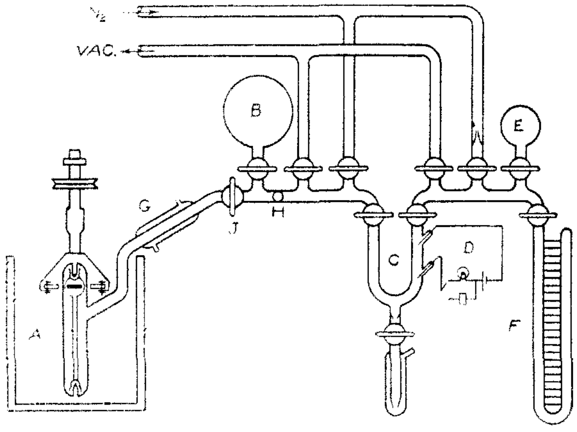

Fig. 2.—The rate measuring apparatus.

Aluminum triphenolate was prepared by dropping pieces of aluminum metal into hot phenol, which was contained in a round-bottomed flask equipped with a reflux condenser.[7] Once the reaction started, it was self-sustaining and the flame was removed. When a slight excess of the theoretical amount of aluminum was added, heat was again applied until the reaction was completed (no more evolution of hydrogen). The product was poured on Pyrex watch glasses and allowed to cool. It solidified almost immediately to a gray vitreous solid, which was readily pulverized to a grayish-white powder. This material was dried in an oven at 110° for eight hours before use.

The 1,4-dichlorobutane, ethylene dichloride, benzyl chloride, nitrobenzene, benzene, *p*-xylene and *p*-dioxane were all carefully fractionated (the last three over sodium) in packed columns. The samples were prepared in evacuated ampoules as described below. (The 1,4-dichlorobutane was kindly donated by the Electrochemical Division of E. I. du Pont de Nemours and Co.)

The Quantitative Nature of the Reaction.—The reaction between *t*-butyl chloride and phenol was demonstrated to be essentially quantitative. In Expt. 27 (see Table I) a determination of the quantitative nature of the reaction was made. After the reaction (carried out in *p*-xylene as a solvent) had reached essential completion (ninety hours at 40°), the volatile contents of the rate-determining apparatus were removed by evacuation with a Cenco Hy-

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(6) "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 144.

(7) H. Funk and E. Rogler, *Z. anorg. allgem. Chem.*, **252**, 323–328 (1944).

TABLE I

SUMMARY OF RATE DATE FOR THE ALKYLATION OF PHENOL WITH TERTIARY ALKYL HALIDES

(1) Expt.	(2) *t*-RCl, mole	(3) Phenol, mole	(4) Diluent, mole	(5) Molarity of phenol	(6) Initial HCl pressure, mm.	(7) *T*, °C.	(8) P_0, mm.	(9) P_f, mm.	(10) *a*	(11) *b*	(12) *C*	(13) $t_{1/2}$ (min.)	(14) *n*
1	0.01178B	0.236		10.54		45	78.7	372.5	0.00854		107.7	81.1	
2	.01109B	.263		10.52		45	62.1	344.4	.00914		103.7	75.8	
3	.01168B	.257		10.59		45	68.1	285.4	.00907	0.1148	68.8	84.1	
4	.00597B	.218		10.83		45	31.9	204.7	.00812		41.7	85.3	
5	.00572B	.224		10.87	392.2	45	415.9	562.6	.00812		21.5	85.4	
6	.00592B	.238		10.87	345.4	45	367.1	522.0	.00800		26.8	86.6	
7	.00544B	.221		10.86	195.9	45	217.2	366.1	.00767		17.4	90.4	
8	.00673B	.236		10.82	101.7	45	130.4	314.0	.00832		50.9	83.3	
9	.01288B	.118		9.83		45	127.1	442.7	.00558		101.4	124.2	6.72
10	.01485B	.110		9.56		45	142.1	547.1	.00616	.1271	139.9	121.9	5.43
11	.01124B	.234		10.51		50	78.2	361.7	.01107		103.6	62.5	
12	.01150B	.229		10.50		50	74.8	380.8	.01379	.1049	102.6	52.2	
13	.01182B	.225		10.42		55	89.5	397.0	.02053	.1764	88.4	35.2	
14	.01180B	.214C				45	46.7	310.2	.00192		−360.1	361.9	
15	.01094B	.229	0.0134DB	9.87		45	43.7	354.0	.00727	.0334	109.9	97.4	5.01
16	.01267B	.187	.0264DB	8.85		45	83.0	420.0	.00536	.0621	103.7	136.2	4.15
17	.01256B	.164	.0467DB	7.65		45	79.8	391.9	.00218		−178.2	318.7	4.77
18	.01028B	.115	.0883DB	5.35		45	59.4	328.4	.000454	.000172	−4631.0	1529.0	4.59
19	.01410B	.178	.0494E	7.87		45	137.8	460.7	.00388	.0442	48.8	188.4	3.66
20	.01422B	.177	.0291N	8.65		45	68.1	467.6	.00791	.0739	142.5	90.7	2.18
21	.01278B	.168	.0529N	7.65		45	64.7	399.6	.00674		120.8	102.9	1.81
22	.01399B	.120	.0962N	5.38		45	81.6	425.5	.00257		−47.5	269.5	2.26
23	.00937B	.166	.0497N	7.97		35	47.0	275.2	.00352	−0.0280	−52.2	187.4	
24	.01260B	.188	.0276X	8.66		45	59.9	395.8	.00296		−24.7	210.5	5.46
25	.01261B	.164	.0431X	7.62		45	84.0	396.8	.00127		−727.7	551.7	6.13
26	.00917B	.161	.0343X			40	67.3	255.0	.00157		−774.7	440.3	
27	.01885B	.205	.0334X			40	106.4	544.5	.00118		−561.7	588.3	
28	.01690B	.217	.0316X		156.4	40	203.9	622.8	.00183		−144.5	378.3	
29	.01151A	.247				45	14.0	330.2	.00555		101.2	125.0	
30	.01138A	.228				45	9.3	332.0	.00636	0.0626	108.2	113.9	
31	.00942A	.231				50	13.3	295.0	.01094	.1635	97.9	68.6	
32	.00958A	.230				50	15.0	298.1	.01003	.0968	100.6	72.7	
33	.01088A	.237				55	28.8	354.2	.01122	.0792	113.5	63.8	
34	.01058H	.214				45	9.2	320.0	.00204	.0887	−302.4	425.7	
35	.01769H	.229				50	4.1	420.1	.00305	.2192	15.8	304.2	
36	.01198H	.238				55	10.2	355.0	.00436	.0939	78.8	174.6	
37	.01406B	.174	0.0682D			45						[a]	
38	.01085B	.176	.0518D		91.4	45						[b]	

The capital letters in columns (2), (3) and (4) have the following meanings: A = *t*-amyl chloride; B = *t*-butyl chloride; C = *p*-cresol; DB = 1,4-dichlorobutane; E = ethylene dichloride; H = dimethylisopropylcarbinyl chloride (2-chloro-2,3-dimethylbutane); N = nitrobenzene; X = *p*-xylene and D = 1,4-dioxane.

In column (14) experiments 37 and 38; [a] no rise in pressure after four hours, [b] a pressure rise of only 3 mm. was observed after seven hours.

Columns (1-4) are self-explanatory. The molarity of phenol in column (5) was obtained by using available data in the literature for the densities of the substances used in each experiment. The volume of each material was calculated (at the temperature of the experiment) and it was assumed that the solutions were perfect. This assumption probably did not introduce any appreciable error since in most cases one component comprised the majority of the solution. Once the total volume was calculated, the molarity of the phenol could be ascertained in the usual manner.

The values in column (6) represent the equilibrium pressure of hydrogen chloride that was added to the phenol before the *t*-butyl chloride was admitted to the reaction vessel. Column (7) indicates the temperatures of the experiments. The thermostat was kept at these temperatures ±0.01°. Columns (8) and (9) represent the initial and final equilibrium pressures, respectively. P_0 represents the vapor pressure of the tertiary halide plus that of phenol plus, in certain cases, the pressure of hydrogen chloride added before the start of the run, or the vapor pressure of the particular diluent employed. P_f was determined experimentally in most cases, by allowing the experiment to proceed to completion. However, it could also be calculated by extrapolation of the straight line obtained by plotting dP/dt *vs.* P to $dP/dt = 0$. When the calculated and experimental values did not agree, the experimental value was used, and it was necessary to insert the constant *b* (column (11)) into the kinetic equation. The determination and significance of the data in columns (10-14) is discussed below. The values of *a*, *b* and *C* pertain to equation (2) below, $t_{1/2}$ is the reaction half-time, and *n* is the apparent order of the reaction with respect to phenol concentration.

Vac pump. A sodium carbonate absorption tube and a Dry Ice-acetone cold trap were placed in the line before the pump. In this manner, 98.1% of the chlorine was recovered as sodium chloride in the absorption tube, and no isobutylene was obtained in the cold trap. This indicates, therefore, that the alkylation is practically quantitative and little or no dehydrohalogenation of the *t*-butyl chloride occurs.

The Henry's Law Constants for Hydrogen Chloride in Phenol.—In order to ensure that no unusual solubility behavior of hydrogen chloride in the liquid phase would influence the kinetic interpretation, the Henry's law constants for hydrogen chloride in phenol were determined at 45, 50 and 55° over a total pressure range of 200 to 900 mm. of mercury. It was found that these constants, for a given temperature, varied less than ±3%, approximately the precision of the measurements. Thus, the increase in pressure due to evolved hydrogen chloride could be employed as a reliable method of following the reaction.

Preparation of Samples.—The samples of phenol, alkyl halides and diluents were prepared in such a manner as to exclude moisture. Small amounts of moisture would lead to incorrect data because of the generation of hydrogen chloride by hydrolysis of the alkyl halides. The phenol samples were prepared in the apparatus shown in Fig. 1. Approximately 500 g. of fractionated phenol and 10 g. of aluminum triphenolate (as a drying aid) were placed in the 1-l. distilling flask (A) through the side arm (against a counter-current of dry nitrogen). The side arm was then sealed off and the phenol was frozen in (A). It was degassed by alternate freezing, evacuation and thawing. The system was then evacuated, filled with dry nitrogen and re-evacuated several times to remove oxygen. It was finally left at about 50 mm. of mercury pressure with nitrogen and heat was applied at (A). About 75 ml. of phenol was collected in the 125 ml. receiver (B), and the distillation was discontinued. The system was then filled with dry nitrogen until the pressure was 5–10 mm. below atmospheric. Vessel (B) was sealed off and discarded. The system was re-evacuated and the distillation continued. The phenol used for samples was collected in (C).

The ampoule (F), made of 15 mm. tubing, was weighed with the female half of ground joint (E). The ampoule was then attached to the system at (E), evacuated, flushed with dry nitrogen and re-evacuated and sparked. The phenol in (C) was melted with a hot-air gun and was allowed to run through 4 mm.-bore stopcock (D) into the ampoule. The phenol was frozen in the ampoule, degassed, and then sealed off in vacuum at the constriction, leaving a capillary tip for breaking with the magnetic hammer. The two halves of the ampoule were weighed, giving the weight of the sample by difference.

When a diluent was used, the ampoule was not sealed off after the phenol was added. Instead, it was filled with dry nitrogen and weighed (a stopper was used before and after to prevent oxidation and absorption of moisture). The ampoule was then connected to a small system in which the diluent had been distilled *in vacuo* and degassed according to standard vacuum techniques. The diluent was then added to the phenol, the mixture frozen and the ampoule sealed under vacuum. The weight of the diluent was then obtained from the total weight by difference.

The tertiary halide samples were prepared in a manner similar to that described in reference 3a. Standard vacuum techniques were used for distilling the halides *in vacuo* and for degassing and sealing off the samples. Care was taken to keep oxygen and traces of moisture from the samples.

Apparatus.—A schematic diagram of the rate apparatus is shown in Fig. 2. The method of following the rate of the reaction is to add a known weight of tertiary alkyl halide to a known weight of phenol in a thermostatted vessel, and to measure the increase in pressure due to the evolution of hydrogen chloride in a constant volume system. In certain experiments hydrogen chloride was added to the phenol prior to the addition of the tertiary halide, and in certain experiments the phenol contained a diluent.

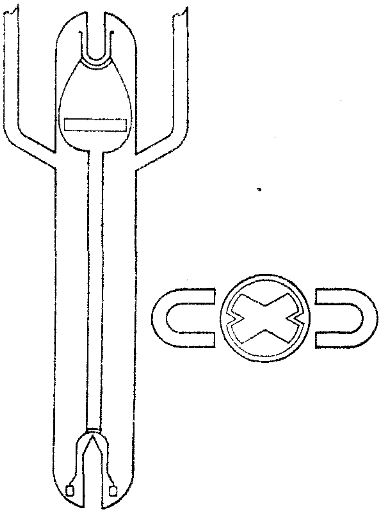
Fig. 3.—The reaction vessel.

An enlarged diagram of the reaction vessel is shown in Fig. 3. It consisted of 41 mm. tubing approximately 18 in. long, with a fulcrum extending up from the bottom and a guide tube extending down from the top. An all-glass stirrer was sealed inside the vessel. It rested on the glass fulcrum and had a tube at the top which prevented it from touching the walls of the vessel. An iron cross was sealed inside the bulb-like portion at the top of the stirrer, and the latter was operated by revolving two permanent horseshoe magnets outside the vessel, on a level with the iron cross. A bell-shaped device at the bottom of the stirrer carried four solid-glass paddles which served to stir the reaction mixture. Although there was no added lubrication, a speed of 300 r. p. m. or better was possible if the vessel was carefully constructed.

The reaction vessel contained three exit tubes immediately below the level of the bulb in the stirrer. Two of these led, through stopcocks, to the addition tubes from which the phenol and tertiary alkyl halide were added to the vessel. The third was connected to the rest of the rate apparatus. The entire reaction vessel was submerged in a thermostat.

The reagent addition tubes consisted merely of a tube which held the ampoule containing the reagent and a side-tube containing a nail sealed in glass which could break the capillary tip of the ampoule when activated with an electromagnet.

Since the reaction proceeded at a measureable rate only at elevated temperatures, it was necessary to have a condenser (G) (Fig. 2) to prevent the distillation of the reactants into the cooler parts of the system. The reaction side of the differential manometer (C) also contained a hydrogen chloride reservoir (B), lines to vacuum and dry nitrogen, and a line (H) to the hydrogen chloride generator.

The outside of the differential manometer contained an electric rest point signalling device (D) (see ref. 3a) which had both a light and a buzzer for indicating completion of the circuit. The rest of the system contained a one-liter buffer volume (E), a calibrated manometer (F) and lines leading to the vacuum and dry nitrogen sources for balancing the differential manometer. The nitrogen inlet contained a fine capillary to permit the increase in pressure on the outside of the differential manometer by very small increments.

The nitrogen source was a commercial cylinder. The nitrogen was dried over phosphorus pentoxide and the pressure was regulated by means of a mercury blowout valve set at approximately 200 mm. above atmospheric pressure. A Cenco Hy-Vac pump was the source of vacuum.

Approximately 90% of the volume of the reaction side of the system was thermostatted and the remainder of the system was at room temperature, which did not vary more than 3° during a single run.

Measurement Procedure.—When making measurements, the phenol was added to the reaction vessel, temperature and pressure equilibrium were established and hydrogen chloride was added in those cases in which its effect upon the reaction rate was being studied. Equilibrium was again established, the tertiary halide added, and time and pressure readings were made. The reaction was followed until at least 90% complete, and in many cases to essential completion.

The reagent addition tubes were sealed to the reaction vessel, the entire system evacuated, sparked, and checked for leaks. Mercury was then admitted to the differential manometer until contact was made with the upper tungsten lead. Both sides of the system were then filled with dry nitrogen and twice re-evacuated. This ensured the presence of very little oxygen in the system and therefore very little oxidation of the phenol during the course of the reaction. (When the reaction was complete, the phenol solution was only very pale yellow.)

With the system evacuated, the phenol in the ampoule was melted (if not liquid already because of diluent), the tip broken with the magnetic hammer, and the phenol was admitted to the reaction vessel. The addition tube was gently flamed and analysis showed that less than 0.1% of the phenol remained in it. The stopcock to the addition tube was then closed and the stirrer started. After thirty to sixty minutes, the halide ampoule was broken, flamed, and the halide was admitted to the reaction vessel. The stopcock was opened for about thirty seconds; the stop watch was started at the initial opening of this stopcock.

For a few minutes after addition of the tertiary halide the pressure decreased, due to solution of the halide in the phenol. Thus, readings were taken on the "break" of the contact with the mercury. When solution was complete, however, and the pressure was increasing, readings were always taken on the "make" of contact. The rate curves (Figs. 4, 5) show only the rise in pressure.

Readings were taken as frequently as possible (about one every minute) at the beginning of the reaction and less frequently as the reaction proceeded. The points obtained were very self-consistent as is indicated by the curves in Figs. 4 and 5.

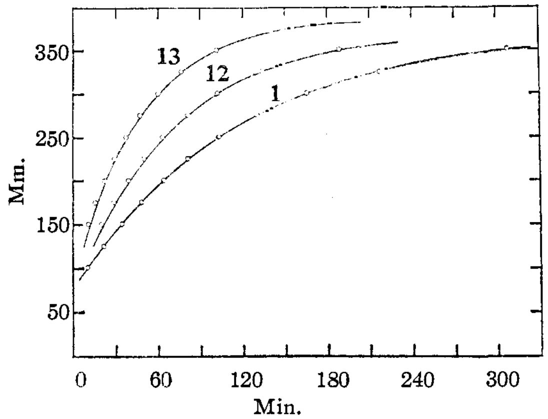

Fig. 4.—Typical rate curves for alkylation of phenol with *t*-butyl chloride at 45, 50 and 55°.

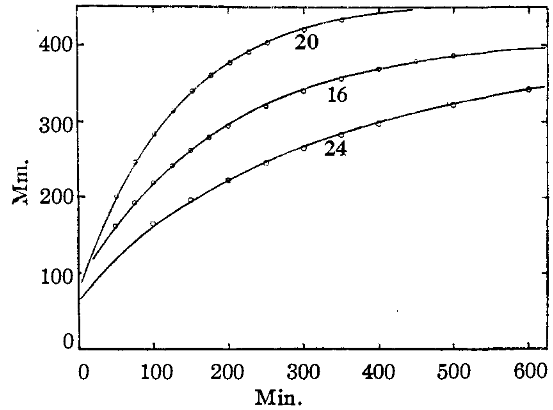

Fig. 5.—Typical rate curves for the alkylation of phenol with *t*-butyl chloride at 45° using various diluents.

When a run was completed, a break was made between stopcock (J) and condenser (G). The reaction vessel was thoroughly cleaned, dried, and re-sealed to the system for the subsequent run.

After completion of a run, the tertiary halide addition tube was removed *below* the stopcock. Ethanol was then admitted through the stopcock and the addition tube was rinsed several times with 95% ethanol. These rinsings were then analyzed for chloride by the Volhard procedure, allowing ten minutes after addition of the silver nitrate for complete reaction with the organic halide. In order to determine the weight of chloride actually used in the experiment, the weight of the alkyl halide in the ampoule was then corrected for the amount which remained behind. This correction was of the order of 1%.

Results

Numerous kinetic experiments were carried out. Space requirements prohibit a complete tabulation of the data from each experiment. A summary of the essential results obtained from thirty-eight of the experiments is given in Table I. Columns (1)–(9) have been explained in the notes to that table. Time *vs.* pressure plots were made for each run (see Figs. 4 and 5 for typical curves). These curves show the consistency of the measurements in any one experiment. Only one experimental point out of every ten is indicated on these curves, for the sake of clarity in the drawings. The solid curve is drawn using equation (2) below, and employing for each experiment shown, the corresponding constants *a*, *b* and *C* from Table I. Thus, these drawings show the closeness of fit of the calculated curve and the experimental points. In order to determine these constants a spline was used to draw a smooth curve through the experimental points, and normals to these rate curves were drawn with a plane first-surface mirror held in a small frame at right angles to the plane of the curve. The normal was drawn when the curve itself and its image appeared to give no perceptible break.[8] The slope of the rate curve at various points was then determined as the negative recip-

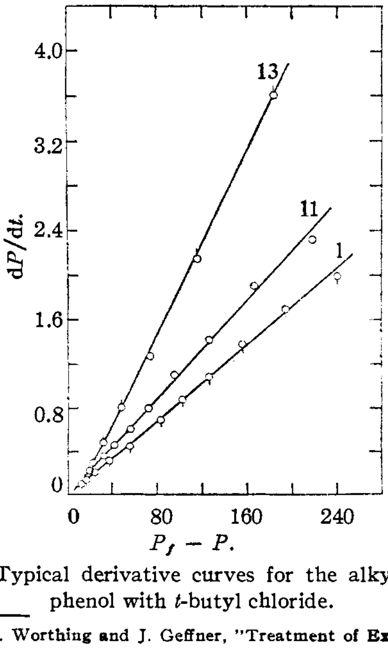

Fig. 6.—Typical derivative curves for the alkylation of phenol with *t*-butyl chloride.

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[8] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 88.

rocal of the slope of the normal. About ten slopes were measured for each curve, at regular intervals with respect to time, over the curve.

It was found that in all of the experiments, the equation

$$dP/dt = a(P_f - P) - b \qquad (1)$$

represented the data satisfactorily. In this equation P represents the instantaneous total pressure, P_f is the final equilibrium pressure, t is the time, dP/dt is the slope of the rate curve, and a and b are constants. Thus, when dP/dt was plotted against $(P_f - P)$, straight lines were obtained (see Fig. 6). The best straight line was determined by the method of least squares, and the constants a and b obtained in this manner are given in columns (10) and (11) of Table I. This equation is essentially that for a first-order reaction (when $b = 0$) in which a is a pseudo first-order rate constant. In some of the experiments, however, it was found that the straight lines did not go through the origin, and this small deviation is represented by b. This constant may arise because of the uncertainty of the zero time, and if we use half-times to compare different experiments we can do so independently of constant b.

Upon integration of (1), one obtains

$$1/a \ln [a(P_f - P) - b] + t = C \qquad (2)$$

The integration constant was determined by fitting the integrated equations to the original kinetic curves, using some experimental point near the half-time of reaction. These constants are given in column (12) of Table I. It was also possible then, after a, b and C were determined, to calculate the values of P_0 and of $t_{1/2}$ given in columns (8) and (13), respectively, of Table I.

The values of n, the apparent order of the reaction with respect to phenol, were determined only for the reaction between *t*-butyl chloride and phenol at 45°. They were obtained in the following manner. If one will plot $t_{1/2}$ *vs.* M, the molarity of phenol, using any theoretical order for the rate dependency of phenol (1st, 2nd, etc.) it is evident that in the region of $M = 9.5$ to 11.2 the curve is very nearly a straight line ($M = 11.2$ was taken as the molarity of pure phenol at 45°). The data of experiments 1, 2, 3, 4, 9 and 10 were then plotted ($t_{1/2}$ *vs.* M) and the best straight line was drawn through these points by the method of averages. This line, extrapolated to $M = 11.2$ gave a limiting theoretical value of $t_{1/2}$ (for zero *t*-butyl chloride concentration) of fifty-one and one half minutes.

It is well known[9] that

$$t \propto 1/a^{n'-1} \qquad (3)$$

where t is the time required to complete a certain fraction of a reaction, a is the initial concentration of reactants, and n' is the total order of the reaction. In two different experiments, we then have that

$$t_1/t_2 = (a_2/a_1)^{n'-1} \qquad (4)$$

In the particular case of the reaction being studied, it is known that the reaction rate is first order with respect to the tertiary halide. The half-life is therefore independent of the halide concentration. Thus, since n' in the above equation is the total order of the reaction, $n' - 1$ may be considered as the order of the reaction with respect to the phenol. Setting $n' - 1$ equal to n, the order with respect to phenol, expressing the concentrations a as molarities M, and using as our reference value the half times $t_{1/2}$, we obtain the expression

$$t_{1/2}/t^0_{1/2} = (M^0/M)^n \qquad (5)$$

where $t^0_{1/2}$ is fifty-one and one half minutes at 45°, $t_{1/2}$ is the half-time for the particular experiment (column 13 of Table I) M^0 is 11.2 at 45°, M is the molarity of the phenol for the particular experiment (column 5 of Table I). Values of n, the apparent order of the reaction with respect to phenol, could be calculated. These are the values given in column 14 of Table I.

The activation energies for the reaction of phenol with *t*-butyl chloride, *t*-amyl chloride and dimethylisopropylcarbinyl chloride were determined in the usual manner from rates at 45 and 55°. For the reaction in which nitrobenzene was used as the diluent the rate constant at 45° was corrected to the same phenol molarity as was used at 35° (see expt. 23) before calculating the Arrhenius energy of activation. The results of these calculations are given in Table II.

TABLE II

ENERGIES OF ACTIVATION FOR ALKYLATION OF PHENOL (45 to 55°)

Chloride	E, kcal./mole
t-Butyl	17.1
t-Amyl	14.8
Dimethylisopropylcarbinyl	15.9
t-Butyl[a]	13.0

[a] Using nitrobenzene as a diluent, $t = 35$ to 45°.

Discussion of Results

All of the reactions which were studied were carried out with a large (ten to twenty-fold) excess of the phenol. Thus, the rate constants a which were obtained, are pseudo first order rate constants, indicating that the reactions are all first order with respect to the tertiary alkyl halide. This is readily seen from the straight line relationship between the effective concentration of the tertiary halide $(P_f - P)$ and the over-all reaction rate dP/dt.

The determination of the order of the reaction with respect to phenol presents a more difficult problem. The amount of *t*-butyl chloride could not have been greatly increased, because too great a pressure rise for the system would have resulted. The tertiary halide could not be used in large ex-

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(9) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., 1940, pp. 1046-1047.

cess, as was the phenol, because of its low boiling point.

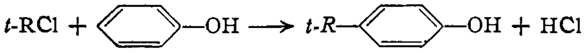
However, the order with respect to phenol was determined by using relatively small quantities of diluents of varying dielectric constants. The mathematical details of this determination were described above. The first diluent employed was *t*-butyl chloride itself, which has a dielectric constant nearly identical with that of phenol ($\epsilon_{t\text{-BuCl}} = 9.4$; $\epsilon_{C_6H_5OH} = 9.7$). Thus, in experiments 9 and 10 we see that only half of the usual quantity of phenol was employed (it still was present in tenfold excess). Although the molarity of the phenol was only slightly lowered (from about 10.6 to 9.7) it is seen from Table I that the half-time was increased from approximately eighty-five to one hundred and twenty-three minutes. These results lead to a value of approximately 6 for n.

Other diluents which also have approximately the same dielectric constants as phenol are ethylene dichloride and 1,4-dichlorobutane ($\epsilon = 8.9$). These diluents did not interfere with the reaction and led to values of about 3.7 and 4.5 for n. From experiments 15 to 19 on Table I, one may note the very large change in the reaction half-time, although the change in dielectric constant of the medium was negligible. Thus, the principal reason for the rate differences is the change in phenol concentration. Although, in the case of the 1,4-dichlorobutane diluent, the phenol concentration was only halved, the half-time ($t_{1/2}$) was increased by 1500%. Two diluents with dielectric constants lower than that of phenol, and one greater were used. *p*-Xylene ($\epsilon = 2.3$) gave a value of $n = 5.8$ and nitrobenzene ($\epsilon = 35.4$) gave $n = 2$. The dioxane ($\epsilon = 2.4$) almost completely inhibited the reaction, and an explanation for this result is discussed below.

It can be seen from experiments 5, 6, 7 and 8 that the initial hydrogen chloride pressure has little or no effect upon the reaction rate for the *t*-butyl chloride–phenol reaction. This is a significant fact when one considers that the reaction being studied is one which is typical of those catalyzed by sulfuric acid, hydrogen fluoride or aluminum chloride. Because of the fact that the kinetic activity of hydrogen chloride did not have to be considered, we can interpret the change in reaction rate with temperature as due only to the increase in available thermal energy. The values for the activation energies are indicated in Table II. The values were determined over a very small temperature range (10°) and may be in error by as much as a kilocalorie.

The relative rates of reaction for the different halides are given by *t*-butyl > *t*-amyl > > dimethylisopropylcarbinyl > > > benzyl chlorides. The half times are approximately 84, 120, 425 and 1600 minutes, respectively, at 45°. (The run with benzyl chloride (not shown in Table I) proceeded very slowly and was not carried to completion, although its $t_{1/2}$ could be estimated at 1600 min.)

The main net reaction in each case is given by



but in the case of the dimethylisopropylcarbinyl chloride, dehydrohalogenation to the olefin may have taken place to a small extent. This was indicated by the fact that when the reaction was carried out on a large scale at reflux temperature using mole for mole quantities of phenol and halide, a 42% yield of the olefin was obtained. Of course in the kinetic experiments this was diminished considerably since lower temperatures were used, and the phenol was present in a twenty-fold excess. Dehydrohalogenation to the olefin was shown to be negligible in the case of *t*-butyl chloride (see section on the Quantitative Nature of the Reaction, in the experimental part).

Only one experiment (no. 14) was carried out using *t*-butyl chloride with *p*-cresol as the phenol. The reaction proceeded far more slowly than with phenol itself, $t_{1/2}$ being 362 minutes. This means that ortho alkylation proceeded at about one-eighth of the rate of para alkylation per ortho position. Thus, if rate were the only factor, one should obtain about 20% *o*-*t*-butylphenol from the alkylation of phenol.[9a] That none of this material has been isolated indicates that if formed at all, it rearranges to the more stable para isomer. (The synthesis and reactions of ortho-*t*-butylphenol are being investigated, and some of the results have been submitted for publication.)

Experiments were performed in which anisole was used as the aromatic nucleus to be alkylated. In all of these, the starting materials were recovered unchanged, indicating that the hydrogen attached to the oxygen atom in phenol is essential to mechanism of the reaction, in the absence of any added catalysts.

Mechanism

In arriving at a mechanism for the reaction under study, the following facts must be explained: (1) first order rate dependency upon the tertiary halide, (2) a high power (approximately sixth order) rate dependency upon phenol, (3) the inhibitory power of dioxane and the effect of other diluents, (4) the low activation energy and (5) the lack of reactivity of anisole under similar conditions. There are several possible mechanisms which come to mind, one of which seems preferable to the others.

First, there is the possibility of formation of the phenyl *t*-alkyl ether as an unstable intermediate followed by the rearrangement of this ether in the presence of the generated hydrogen chloride to form the *p*-alkyl phenol.[10] In this case, the rate-

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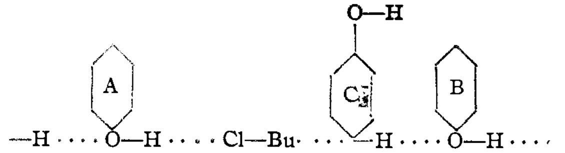
(9a) R. P. Perkins, A. J. Dietzler and V. T. Lundquist, U. S. Patent 1,972,599, claim about 1.2% *o*-*t*-butylphenol from *t*-butyl chloride and phenol using aluminum chloride as the catalyst at 50–200°.

(10) The authors are indebted to one of the referees for pointing out the work of Van Alphen (ref. 5b) on phenyl trityl and similar ethers.

determining step would have to be the formation of the ether since the reaction was not autocatalyzed by hydrogen chloride formed during the reaction, nor was it catalyzed by hydrogen chloride initially present in the phenol (see experiments 5–8, Table I). Rearrangement of the ether would have, therefore, to be intramolecular, since the involvement of five other phenol molecules in the transition state is indicated in the rate-determining (ether forming) step. If this were so, one would expect to obtain some *o-t*-butylphenol, which is not readily rearranged by concentrated hydrochloric acid,[11] and one would also expect that *p*-cresol would alkylate as readily or more so than phenol. Actually, the alkylation of *p*-cresol occurs only at one-eighth the rate of phenol, per ortho position. One might also expect the ether formation to be acid catalyzed, and it has been shown that this reaction is not catalyzed by hydrogen chloride. At any rate, one is hesitant to postulate an unstable intermediate if alternate mechanisms are more adequate.

Another possible mechanism involves the ionization of the tertiary alkyl halide to form a free or solvated carbonium ion, followed by attack of that ion upon the para position of the phenol. Since the reaction was carried out in a very large excess of phenol, it is likely that the ionization would have to be the rate-determining step. This would involve, then, the coördination of the chlorine with approximately five to six phenol molecules (either one hydroxyl of a phenol polymer or several hydroxyl groups of phenol molecules) in the ionization process. Such a mechanism could account for the observed facts, although one can show by calculations similar to those of Pearlson and Simons[3a] that the minimum energy required to form a solvated *t*-butylcarbonium ion in phenol at 45° is about 28 kcal. per mole. The experimentally determined activation energies are considerably lower than this value (14–17 kcal. per mole).

A third and preferred mechanism is here proposed, which we term the "amphoteric medium effect."[4] This mechanism involves a one-step, condensed phase reaction which makes use of the amphoteric properties of phenol. The mechanism rests on two important principles. Firstly, it is to be considered that the reaction has been studied in the liquid phase and that a large excess of phenol was present. This means that multiple collisions will be the rule, rather than the exception. The molecules are constantly in contact with and "colliding" with other molecules. The *t*-butyl chloride molecules can be considered, therefore, as essentially surrounded by phenol aggregates. Secondly, phenol is an amphoteric associated liquid which is readily capable of proton transfer in a manner analogous to that in water. The mechanism is schematically pictured below. The solid lines indicate the bonds prior to reaction, and the dotted lines indicate the shifts in the bonds when reaction occurs. The rest of the phenol molecules (3 or 4) which are involved in the transition state may be represented as coördinated linearly to the phenol molecules A and B, or may aid in the making and breaking of bonds by the polymolecular attack on the chlorine and the para hydrogen. The most important point is that bonds are being made and broken simultaneously (because of the amphoteric properties of phenol) and that at no time need there be present a high energy intermediate capable of independent existence. This mechanism is in some respects similar to the acid–base catalysis of Lowry[12] and the termolecular mechanisms proposed recently by Swain.[13] This mechanism adequately explains all of the facts which are enumerated above in the first paragraph of this section.



Summary

The reaction between tertiary alkyl chlorides and phenol was shown to be homogeneous and essentially quantitative when carried out in an excess of the phenol to form the alkyl phenol and hydrogen chloride.

The relative rates of reaction of *t*-butyl, *t*-amyl, dimethylisopropylcarbinyl and benzyl chlorides with phenol at 45° are 1:0.7:0.2:0.05. *p*-Cresol is alkylated in the ortho position at one-eighth the rate of para alkylation, per ortho position.

The rate of the reaction was first order with respect to the halide and essentially independent of the hydrogen chloride pressure. The rate was very highly dependent upon phenol concentration. The order with respect to phenol depended upon the diluent used: sixth order with *p*-xylene or *t*-butyl chloride diluent, 3.5 to 4.5 order with ethylene dichloride or 1,4-dichlorobutane, and second order with nitrobenzene as the diluent. The activation energies were experimentally determined between 45 and 55°, and were 14–17 kcal. per mole. Dioxane inhibited the reaction almost completely, and anisole would not react under conditions similar to those used with phenol in the absence of a catalyst.

The mechanism is discussed and the above facts are explained by a mechanism involving the amphoteric properties of phenol ("amphoteric medium effect").

Henry's law is obeyed within 3% by hydrogen chloride in phenol from 45 to 55° at pressures from 200 to 900 mm.

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[11] H. Hart, unpublished results.

[12] T. M. Lowry and I. J. Faulkner, *J. Chem. Soc.*, **127**, 2883 (1925).

[13] C. G. Swain, THIS JOURNAL, **70**, 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948).