resulting mixture was refluxed for 15 minutes with stirring. After dilution with water, separation and drying over anhydrous magnesium sulfate, the product was distilled at 75–76° at 1 mm. (reported[19] 80.5° at 0.8 mm.) yielding 25.1 g. (72%) of colorless *p*-bromostyrene oxide, m.p. 27.1° (reported[19] 26°).

p-Bromostyrene oxide (26.9 g.) reduced with 3.0 g. (400%) of lithium borohydride, gave an 83% yield of a mixture containing 20.4 g. (91%) of a fraction distilling at 86–92° at 1 mm. [largely 1-(4-bromophenyl)-ethanol[20]] and 2.0 g. (9%) of 2-(4-bromophenyl)-ethanol, b.p. 104° at 1 mm. (reported[21] b.p. 147° at 10 mm., m.p. 36–38°).

The product of a duplicate reduction of *p*-bromostyrene oxide, obtained in 66% yield, was analyzed by infrared absorption. Comparison of the maxima at 2950, 2930, 1595, 1200, 1110, 900 and 750 waves cm.$^{-1}$ with synthetic mixtures of the two isomeric alcohols, indicated a composition of 84% of the secondary alcohol and 16% of the primary.

1-(4-Bromophenyl)-ethanol (b.p. 98–102.5° at 2 mm.) was prepared independently in 68% yield by sodium borohydride reduction of *p*-bromoacetophenone in aqueous methanol. The phenylurethan melted at 103.6–104.0° (reported[20] 103–104°). 2-(4-Bromophenyl)-ethanol (b.p. 138° at 9 mm.) was prepared in low yield by the aluminum chloride-catalyzed bromination of 2-phenylethanol. The phenylurethan melted at 127.8–129.0° (reported[21] 126°).

The phenylurethan prepared from the 1-(4-bromophenyl)-ethanol fraction of the *p*-bromostyrene oxide reduction product melted at 102.1–102.8° and did not depress the m.p. of an authentic sample of the 1-(4-bromophenyl)-ethanol phenylurethan. The urethan prepared from the isomeric fraction melted at 129.2–129.7° and did not depress the m.p. of an authentic sample of the urethan of 2-(4-bromophenyl)-ethanol.

Lithium Borohydride Reduction of *p*-Nitrostyrene Oxide.—*p*-Nitrostyrene oxide was prepared from commercial *p*-nitrophenacyl bromide by the procedure used for *p*-bromostyrene oxide. The yield of product twice recrystallized from ethanol was 55%; m.p. 84.2–85.4° (reported[26] 85–86°). A solution of 14.8 g. of *p*-nitrostyrene oxide in ether, reduced by 4.0 g. (800%) of lithium borohydride, gave upon distillation 9.4 g. (63%) of an oil, b.p. 134–142° at 2 mm., which partially solidified upon standing, and 4.3 g. (29%) of a tarry residue. The mixture was not quantitatively separable by fractional distillation. Infrared analyses of this and a duplicate product fix the composition at 62% 2-(4-nitrophenyl)-ethanol and 38% 1-(4-nitrophenyl)-ethanol, by comparison with synthetic mixtures, of the absorption at 2950, 1200, 1090, 1035, 900 and 840 waves cm.$^{-1}$.

1-(4-Nitrophenyl)-ethanol, prepared independently by the sodium borohydride reduction of *p*-nitroacetophenone,[22] boiled at 137–138° at 2 mm. (reported[23] 161–163° at 4 mm.). The phenylurethan melted at 97.3–97.6° (reported[24] 205–206°).

Anal. Calcd. for $C_{15}H_{14}O_4N_2$: C, 62.9; H, 4.9; N, 9.8. Found: C, 62.8, 62.6; H, 4.9, 5.1; N, 9.9, 10.1.

The *p*-nitrobenzoate of 1-(4-nitrophenyl)-ethanol melted at 138.0–138.4° (reported[23] 138°).

2-(4-Nitrophenyl)-ethanol, b.p. 148–149° at 2 mm. (reported[24] 189° at 16 mm.), m.p. 60.7–61.8° (reported[25] 60–61°) was prepared by the method of Ferber.[25] The phenylurethan melted at 132.6–133.0° (reported[24] 127–128°).

1-(4-Nitrophenyl)-ethyl *p*-nitrobenzoate, m.p. 137.6–138.2°, and the phenylurethan of 2-(4-nitrophenyl)-ethanol, m.p. 130.2–131.0°, prepared from impure samples of the corresponding alcohols obtained by fractional distillation of the reduction mixture from *p*-nitrostyrene oxide, showed no melting point depressions when mixed with the respective authentic samples.

A mixture containing 62% 2-(4-nitrophenyl)-ethanol and 38% 1-(4-nitrophenyl)-ethanol was treated with lithium borohydride and worked up by the technique employed on the epoxide reduction mixture. The product, once distilled, had the identical composition to the starting mixture. The yield was 61%, with a considerable amount of tarry residue remaining behind.

Lithium Borohydride Reduction of 1,2-Epoxybutane.—A solution of 14.4 g. of 1,2-epoxybutane in ether was reduced by 3.3 g. (300%) of lithium borohydride. Fractional distillation gave 8.5 g. (57%) of 2-butanol, b.p. 98°, n^{20}D 1.3957, with no trace of 1-butanol.

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(19) T. Bergkvist, *Svensk Kem. Tid.*, **59**, 205 (1947); *C. A.*, **42**, 2584 (1948).

(20) R. Quelet, *Bull. soc. chim.*, [4] **45**, 75 (1929), reported b.p. 130° at 12 mm.

(21) T. W. J. Taylor and P. M. Hobson, *J. Chem. Soc.*, 181 (1936).

(22) L. Long and H. Troutman, THIS JOURNAL, **71**, 2473 (1949).

(23) A. H. Ford-Moore and H. N. Rydon, *J. Chem. Soc.*, 679 (1946).

(24) J. v. Braun and B. Bartsch, *Ber.*, **46**, 3050 (1913).

(25) E. Ferber, *ibid.*, **62**, 183 (1929).

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Autocatalysis in Aromatic Alkylations. The Reaction of Phenols with Triphenylmethyl Chloride[1]

BY HAROLD HART AND FRANK A. CASSIS[2]

RECEIVED SEPTEMBER 23, 1953

The kinetic rate curves for the nuclear alkylation of phenol and *o*-cresol by triphenylmethyl (trityl) chloride in *o*-dichlorobenzene were S-shaped, typical of an autocatalytic reaction. When the phenol was saturated with hydrogen chloride prior to alkylation, the slow portion of the rate curves was eliminated, and the reaction followed third-order kinetics; *i.e.*, rate = k_3(phenol)(trityl chloride)(hydrogen chloride). The autocatalytic curves were fitted precisely by the expression: rate = k_2(phenol)(trityl chloride) + k_3(phenol)(trityl chloride) (hydrogen chloride). Aryl trityl ethers are rapidly cleaved by hydrogen chloride, and are probably not intermediates in the alkylation. The mechanism of the alkylation and of the catalytic function of the hydrogen chloride are discussed.

The reaction between triphenylmethyl (trityl) chloride and phenols is of interest for several reasons. In particular, it was this reaction, and analogous reactions with methanol, carried out in the presence of pyridine, which supported the postulation of termolecular mechanisms for displacement reactions in non-aqueous solvents.[3] The product of the reaction was trityl phenyl ether, and the kinetics were third order; first order in trityl halide and second order in phenol. It was of interest to investigate this same reaction in the absence of pyridine, in which case the product is exclusively the *p*-nuclearly alkylated phenol, rather than the ether.

A previous investigation[4] of the nuclear alkylation of phenol with *t*-butyl chloride showed that this reaction is polymolecular in phenol when the latter is the solvent. It was in part the purpose of

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(1) Presented at the September, 1953, Meeting of the American Chemical Society, Chicago, Ill. Taken in part from the Ph.D. thesis of Frank A. Cassis, Michigan State College, 1953.

(2) Research Corporation Fellow, 1949–1951.

(3) C. G. Swain, THIS JOURNAL, **70**, 1119 (1948).

(4) H. Hart and J. H. Simons, *ibid.*, **71**, 345 (1949).

the present work to study the reaction in dilute solution in an inert solvent, to determine more precisely the kinetic order with respect to phenol. Trityl chloride appeared to be better suited for this purpose than *t*-butyl chloride, because it permitted the use of high reaction temperatures without the danger of dehydrohalogenation or loss of reactants due to volatility. *o*-Dichlorobenzene proved to be a satisfactory inert solvent of sufficiently high boiling point and moderate polarity (dielectric constant approximately 9[5]). Furthermore, the reaction products (*p*-tritylphenol and *p*-trityl-*o*-cresol from phenol and *o*-cresol, respectively) were sufficiently soluble in this solvent to permit following the reaction to essential completion. The rates were followed by measuring the increase in pressure due to evolved hydrogen chloride in a constant volume system. In order to establish the reaction products, isolation experiments were performed on reaction mixtures from the kinetic runs. An experiment on the cleavage of trityl *o*-cresyl ether by hydrogen chloride is also pertinent to the reaction mechanism.

Experimental

Materials.—Phenol and *o*-cresol were purified as described previously.[4] The triphenylmethyl chloride was recrystallized several times from benzene–pentane solution, m.p. 110–111°, and was stored in a vacuum desiccator. The *o*-dichlorobenzene was mixed with a little benzene, then distilled in a nitrogen atmosphere, through a Vigreux column, the material boiling at 180–181° at atmospheric pressure being used as the reaction solvent.

Apparatus.—The apparatus was in principle similar to that previously described,[4] but with several modifications which permitted more precise kinetic measurements, especially at the beginning of a run. In place of the rather cumbersome stirring device, an Arthur H. Thomas magnetic stirrer was employed, the stirrer inside the reaction vessel being sealed in glass. In order that the stirring motor might be used when submerged in a constant temperature bath of hot ethylene glycol, it was fitted with a sealed copper tube to contain the lead-in wires, coated with glyptal resin, wrapped with rubber tape, and used inside a plastic container. Under these circumstances, the motor operated satisfactorily during all the kinetic runs without any bath fluid entering the motor housing. The stirrer provided very efficient mixing of the reactants, and permitted accurate pressure measurements within two minutes after adding the reagents. With the old apparatus,[4] 10 to 20 minutes was required and, as will be seen below, an important phenomenon necessitated accurate early measurements.

The apparatus was further modified in that all tubing on the reaction side of the differential manometer not immersed in the constant temperature bath was capillary tubing, thus bringing the portion of the vessel not in the bath to less than 3% of the total volume of the system. Also, instead of using a magnetic hammer to break the capillary tips on the reactant ampoules, they were broken by twisting a stopcock in which the tip was thrust. A double stopcock arrangement prevented the stopcock from sticking because of broken glass. The reaction vessel was fashioned from a 125-ml. Florence flask, and had side arms through which the reagents were added. It was attached to the rest of the system by a mercury-sealed ground glass joint. The constant temperature bath contained ethylene glycol, with temperature control to 0.01°.

Measurement Procedure.—The measurement procedure was essentially the same as that previously described,[4] with minor modifications. Both the phenol and the halide sample were made up in the solvent, *o*-dichlorobenzene. After the reaction system was thoroughly evacuated, the phenol solution was added from an evacuated ampoule and allowed to come to temperature equilibrium. Then the chloride solution was added, and pressure *vs.* time readings were made by balancing the differential manometer with nitrogen, readings always being taken on the "make" of contact with the upper tungsten lead of the manometer. The reactions were followed in most cases until 85 to 100% complete.[6] A blank experiment in which trityl chloride was heated in *o*-dichlorobenzene at 90° showed no detectable evolution of hydrogen chloride in 24 hours.

Product Isolation.—After the completion of experiment 4 (Table I) the reaction mixture was cooled and a white, crystalline solid separated, which, after recrystallization from benzene, melted at 280–281° (literature value for *p*-tritylphenol, 282°[7]). A similar procedure with the product from experiment 5 (Table I) gave a white solid which, after recrystallization from benzene, melted at 185–186° (literature value for *p*-trityl-*o*-cresol, 182–183°[8]).

Reaction of Trityl *o*-Cresyl Ether with Hydrogen Chloride.—A solution of 9.0 g. (0.0257 mole) of trityl *o*-cresyl ether[9] in 40 ml. of benzene was warmed to 60°, and dry hydrogen chloride was passed through the solution for 15 minutes. The mixture was cooled and extracted with 10% sodium hydroxide. The alkaline extracts were acidified, extracted with benzene, and dried over anhydrous sodium sulfate. An aliquot was analyzed by the method of Fritz,[10] titrating in ethylenediamine with a benzene solution of potassium methoxide, using *o*-nitroaniline as the indicator. The presence of 2.55 g. of *o*-cresol was indicated (92% of the theoretical). To prove that the phenolic material was *o*-cresol, the solvent was removed, and the residue was warmed with *p*-nitrobenzoyl chloride and pyridine for five minutes. The product, recrystallized from alcohol, melted at 94–95°, and showed no depression when mixed with an authentic sample of *o*-cresyl *p*-nitrobenzoate.

The alkali-insoluble fraction was dried over anhydrous sodium sulfate, and the solvent removed by distillation. The residue consisted primarily of triphenylmethylcarbinol, m.p. and mixed m.p. 161–162°. A total of 5.0 g. (74.8%) was recovered. There was no evidence for any unreacted trityl *o*-cresyl ether in this fraction.

Results

The data obtained from each kinetic run are a series of time *vs.* pressure readings, usually well over a hundred points per run. Some of the typical rate curves are shown in Fig. 1, where only every tenth point is plotted for the sake of clarity in the drawing. A summary of some of the pertinent kinetic runs is given in Table I, where p_0 and p_f are the initial and final pressures, respectively, and where k_2 and k_3 represent rate constants, and k is a proportionality constant, the meaning of which will be discussed below.

Experiments 1–4 represent alkylations of phenol, and experiments 5–7 represent alkylations of *o*-cresol, both with trityl chloride. Experiments 8 and 9 were check runs on the alkylation of phenol with *t*-butyl chloride at 50°, to determine whether the apparatus was functioning properly. The results are in excellent agreement with the earlier data of Hart and Simons.[4]

It will be noted from Fig. 1 that the curves for runs 4 and 5 are S-shaped, typical of an autocatalytic reaction. The same was true of all the other

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(5) C. P. Smyth, S. O. Morgan and C. Boyce, This Journal, **50**, 1536 (1928).

(6) For further details concerning the measurement procedure, and for drawings of the apparatus, see Frank A. Cassis, Ph.D. Thesis, Michigan State College, 1953.

(7) A. Baeyer and V. Villiger, *Ber.*, **35**, 3013 (1902).

(8) H. A. Iddles, K. S. French and E. F. Mellor, This Journal, **61**, 3192 (1939). For some time there was doubt as to the correct structure of this product. The reaction was thought to involve side-chain (methyl) alkylation to give 1-(2-hydroxyphenyl)-2,2,2-triphenylethane, and a variety of explanations have been offered for the unusual course of the reaction. (See, for example, J. W. Baker, "Hyperconjugation," Clarendon Press, Oxford, 1952, pp. 56–57.) The structure of the product, however, was firmly established as *p*-trityl-*o*-cresol by Iddles, *et al.*, This Journal, **62**, 71, 2757 (1940).

(9) G. S. Parsons and C. W. Porter, *ibid.*, **54**, 363 (1932).

(10) J. S. Fritz and R. T. Keen, *Anal. Chem.*, **25**, 179 (1953).

TABLE I

KINETIC STUDIES OF THE ALKYLATION OF PHENOLS WITH TRIPHENYLMETHYL CHLORIDE IN *o*-DICHLOROBENZENE AT 88.00°

P = phenol, C = *o*-cresol, B = *t*-butyl chloride

Expt.	Molarity phenol	Molarity halide	p_0 (mm.)	p_f (mm.)	k_2, (l. mole^{-1} min.$^{-1}$)	k_3k, (l.^{2} mole^{-2} min.$^{-1}$)
1	0.315 (P)	0.631	88.2	542.2	0.204	0.00174
2	.610 (P)	.629	71.5	525.5	.430	.00538
2a	.610 (P)	.629	73.8	529.0	.439	.00543
3	.9132 (P)	.6105	87.4	657.0	.786	.00815
4	1.184 (P)	.5935	126.2	670.5	1.087	.0131
5	1.184 (C)	.5921	101.5	757.5	0.333	.0103
6	1.368 (C)	.3571	162.0	435.0	.355	.0101
7[a]	1.368 (C)	.3571	279.1	553.4	...	.00978
8[b]	10.55 (P)	.01112 (B)	107.8	506.2	.0124	($t_{1/2}$ = 55.2 min.)
9[b]	10.61 (P)	.009881 (B)	104.5	499.7	.0136	($t_{1/2}$ = 53.1 min.)

[a] Hydrogen chloride added initially. [b] The temperature for these experiments was 50.00 ± 0.01°.

experiments except 7, 8 and 9. The substance most likely to be functioning as the autocatalyst was thought to be hydrogen chloride, and, in order to test this hypothesis, run 7 was made. In this experiment the conditions were identical with those in experiment 6 except that the *o*-cresol was saturated with hydrogen chloride before the run was started. It can be seen from Fig. 1 that the induction period has been eliminated from the kinetic curve, and therefore that it is indeed the hydrogen chloride which is functioning as the autocatalyst. With this information, it became possible to fit the experimental rate curves with kinetic equations.

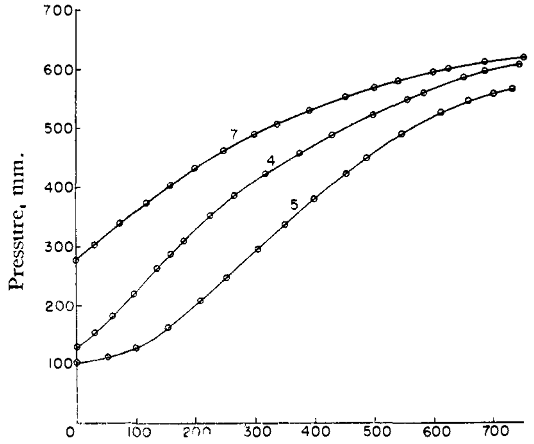

Fig. 1.—Experimental rate curves for experiments 4, 5 and 7 of Table I.

It was thought that the latter (major) portion of the rate curves might represent a reaction first order in each of the reactants, phenol (P), trityl chloride (TCl) and hydrogen chloride.

$$\text{rate} = k_3(\text{P})(\text{TCl})(\text{HCl}) \qquad (1)$$

These concentrations can be expressed in terms of measured quantities as

$$(\text{HCl}) = k(p - p_0)$$

$$(\text{TCl}) = b\left(1 - \frac{p - p_0}{p_f - p_0}\right)$$

and

$$(\text{P}) = a\left(1 - \frac{p - p_0}{p_f - p_0}\right)$$

where p represents the instantaneous pressure, p_0 the initial pressure (which consists primarily of the vapor pressure of the solvent, with small terms from the dissolved phenol and halide, and which also is a function of the volume of materials used), p_f the final equilibrium pressure, a and b the initial concentrations of the phenol and halide, respectively, and k is a Henry's law constant for the solubility of hydrogen chloride in the reaction medium. Substituting in equation 1 and rearranging terms we get

$$\frac{\mathrm{d}p}{(p_f - p)^2(p - p_0)} = \frac{k_3kab}{(p_f - p_0)^2}\,\mathrm{d}t \qquad (2)$$

which can be integrated to

$$\left[\frac{1}{p_f - p} + \frac{1}{p_f - p_0}\ln\frac{p - p_0}{p_f - p}\right] = \frac{k_3kab}{(p_f - p_0)}\,t + C(p_f - p_0) \qquad (3)$$

which is in the form of a straight line. A plot of the function Y, which is the left side of equation 3, against t was linear for the latter part of each autocatalytic run.

A second-order rate expression

$$\text{rate} = k_2(\text{P})(\text{TCl})$$

was found to fit the first portion of the autocatalyzed runs. Substituting and rearranging as above, we get

$$\frac{\mathrm{d}p}{(p_f - p)^2} = \frac{k_2ab}{(p_f - p_0)^2}\,\mathrm{d}t$$

which integrates to

$$\frac{1}{p_f - p} = \frac{k_2ab}{(p_f - p_0)^2}\,t + C$$

When $t = 0$, $p = p_0$ and the integration constant C becomes $1/p_f - p_0$. We then get

$$\frac{1}{p_f - p} = \frac{k_2ab}{(p_f - p_0)^2}\,t + \frac{1}{p_f - p_0} \qquad (4)$$

and a plot of $1/(p_f - p)$ *vs.* t should be linear. This was found to be the case for the early part of each autocatalyzed experiment.

From these results it appeared that the autocatalyzed runs should fit the expression

$$\text{rate} = k_2(\text{P})(\text{TCl}) + k_3(\text{P})(\text{TCl})(\text{HCl}) \qquad (5)$$

When substitutions in equation 5 were made, as done previously, and the resulting expression integrated, the equation obtained was too complex for a simple evaluation of the rate constants. We therefore worked with the differential equation which, after rearrangement of terms, gives

$$\frac{\mathrm{d}p/\mathrm{d}t}{(p_t - p)^2} = \frac{k_2ab}{(p_t - p_0)^2} + \frac{k_3kab}{(p_t - p_0)^2}(p - p_0) \quad (6)$$

Thus, a plot of $\mathrm{d}p/\mathrm{d}t/(p_t - p)^2$ *vs.* $(p - p_0)$ should be linear throughout the entire kinetic experiment, and should permit the evaluation of k_3k from the slope and k_2 from the intercept. In order to test equation 6 it was necessary to determine $\mathrm{d}p/\mathrm{d}t$, and this was done in a manner similar to that described in a previous paper.[4,11] Such plots were then made, and found to give excellent straight lines. A typical example is shown in Fig. 2 for the data from experiment 5. The best straight line was determined in each case by the method of least squares, and the constants obtained in this way for runs 1–6 are given in the last two columns of Table I.

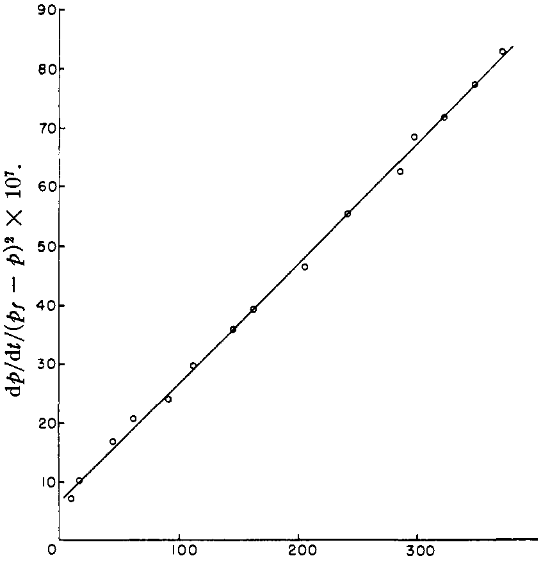

Fig. 2.—Data for experiment 5 plotted according to equation 6.

The accuracy of rate constants determined this way is illustrated in Fig. 3, which shows a calculated rate curve for experiment 5, using the experimental points chosen at random, and it is seen that an excellent fit is obtained for the entire reaction. Furthermore, experiments 2 and 2a are duplicate experiments, and it is seen that the rate constants evaluated by the procedure just outlined agree within 2–3%.

The treatment of experiment 7, in which the slow portion of the alkylation was eliminated by prior saturation with hydrogen chloride, was somewhat different. This run followed third-order kinetics (equation 1), but the concentration term for hydrogen chloride now involves $(p - p_0{}^1)$ rather than $p - p_0$, where $p_0{}^1$ represents the initial pressure in experiment 6. Since experiment 6 was identical with 7, except for the added hydrogen chloride, the term $p - p_0{}^1$ represents the sum of the hydrogen chloride originally added $(p_0 - p_0{}^1)$ and that which is formed during the alkylation $(p - p_0)$. A linear plot was obtained when $\mathrm{d}p/\mathrm{d}t/(p_t - p)^2$ was plotted against $(p - p_0{}^1)$ for experiment 7, and the value for k_3k in Table I was calculated from the slope of this line, $k_3kab/(p_t - p_0)^2$.

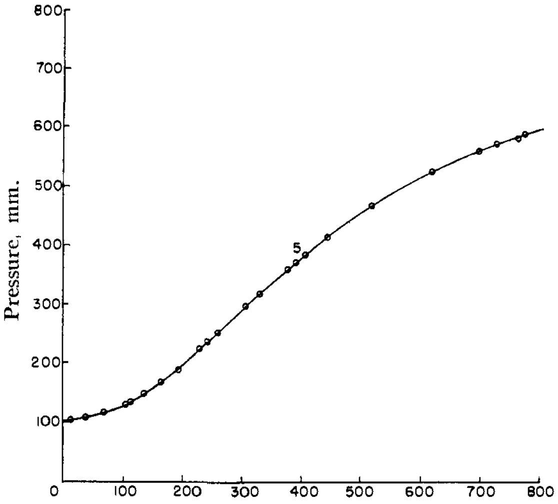

Fig. 3.—Calculated rate curve for experiment 5, with several experimental points.

The rate constants k_2 and k_3k fit the data for any individual kinetic run extremely well, as shown by the precise fit of the calculated curve with the experimental points for the entirety of a run (Fig. 3). Furthermore, these constants are reproducible as shown by duplicate runs 2 and 2a, and by the k_3k values for runs 6 and 7. From the present data, it is not possible to separate k_3 from k, but the numerical value of their product has the dimensions of a third order rate constant expressed as l.^{2} mole^{-2} min.$^{-1}$. Increasing values of k_3k obtained as the concentration of phenol was increased (experiments 1–4) may be due in part to an increase in k (solubility of hydrogen chloride in the reaction medium should increase with increasing phenol concentration). Since k_2 increases simultaneously, however, we believe that the major cause of the increase in rate constants is an increase in the ionizing power of the solvent. The initial phenol concentrations (0.3 to 1.2 *M*) were rather large from the kinetic viewpoint, and changes in them probably affected the polarity of the medium. Despite the variation of rate constants with initial phenol concentrations, however, all of the runs followed the same rate law (equation 5).

A comparison of the k_3k values for experiments 6 and 7 is of interest. They agree within 3%, demonstrating that in experiment 7 (cresol initially saturated with hydrogen chloride) one is essentially meas-

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(11) Brief mention of the method of evaluating the other terms in equation 6 will be made here. The initial molarities of phenol and halide (a and b) were calculated from measured densities of phenol and halide solutions in *o*-dichlorobenzene, and the assumption of no volume change on mixing. The initial pressure p_0 was determined by extrapolation of the experimental rate curve to zero time, a very good extrapolation since the curves were very flat near $t = 0$. The final pressure p_f was determined experimentally in all but the very slow phenol runs (for example, experiment 1). In these runs, it was found that the data near the end of the reaction gave a linear plot of $\mathrm{d}p/\mathrm{d}t$ *vs.* p, which on extrapolation to $\mathrm{d}p/\mathrm{d}t = 0$ gave p_f. Checks of this procedure against experimental values in faster runs showed agreement better than 1%.

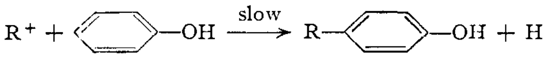
uring the rate constant for the catalyzed portion of experiment 6.

Discussion

Autocatalysis by Hydrogen Chloride.—Alkylation of the aromatic nucleus by an alkyl halide, olefin or other source of alkyl group normally requires an acidic catalyst, either of the electron-deficient ($AlCl_3$, BF_3, etc.) or proton-donating (H_2SO_4, HF, etc.) type. It is not unreasonable, then, that the seemingly uncatalyzed alkylation of phenols by reactive halides should be autocatalyzed by the hydrogen chloride formed during the reaction.[12] The elimination of the induction period when the phenol was saturated with hydrogen chloride prior to alkylation, and the close fit (Fig. 3) of the experimental data by equation 5 clearly demonstrate autocatalysis by hydrogen chloride. This fact went undetected in previous work[4] primarily because of poor stirring which prevented precise rate measurements at the beginning of a kinetic run. Autocatalysis became apparent, however, when dilute solutions of reactants were used and when the apparatus was improved to permit accurate rate measurements at the start of a run.

Mechanism.—The most probable mechanism for nuclear alkylation consistent with all the facts is given in equations 7 and 8.

$$RCl \overset{\text{fast}}{\rightleftarrows} R^+ + Cl^- \qquad (7)$$



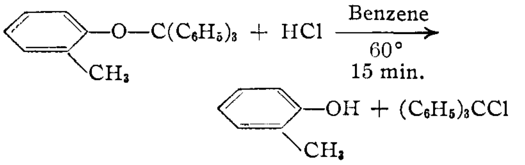
(8)

The first step is a rapid and reversible ionization of the tertiary halide to form a carbonium ion, the process being favored by an ionizing solvent (such as phenol), or by other groups which can stabilize the ions. The second step is a rate-determining attack by the carbonium ion on the aromatic nucleus, and will be favored by ring-activating substituents such as hydroxyl. Equations 7 and 8 could be combined in a concerted process, but when R is triphenylmethyl, the ionization mechanism would appear preferable. Anisole is not readily alkylated without a catalyst presumably because it does not aid in ionizing the alkyl halide, although the methoxyl group is apparently equally as ring-activating as the hydroxyl group.[13]

Hydrogen chloride acts as a catalyst for the reaction, probably by facilitating ionization of the alkyl halide, as shown in equation 9. Its role is similar to that of other acidic alkylation catalysts,[14] and the catalysis is in some ways analogous to the hydrogen chloride-catalyzed isomerization of camphene hydrochloride to isobornyl chloride.[15] The precise nature of the product of equation 9 (that is, the extent to which it is ionic) cannot be ascertained from kinetic data alone. A study of the ionization of trityl halides in an inert solvent, in the presence of hydrogen chloride would help us to establish this point, and is planned. Equation 9 coupled with 8 will satisfy the observed third order kinetics. Alternative explanations of hydrogen chloride catalysis are possible, but we favor the one presented here.

$$(C_6H_5)_3C\text{—}Cl + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (C_6H_5)_3C^+\ Cl^{\ominus}\ldots H\text{—}Cl \qquad (9)$$

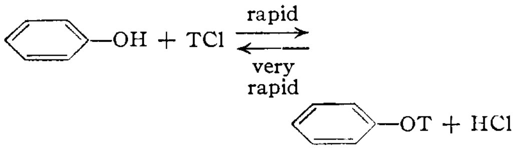
The Ether as a Possible Intermediate.—Because alkyl aryl ethers such as phenyl trityl ether, give the corresponding *p*-alkylated phenol when treated with hydrogen chloride, and because anisole is not readily alkylated without a catalyst, whereas phenol is, the ethers have often been cited as intermediates in the uncatalyzed alkylation of phenols.[16] That this is probably not the case is shown here. When *o*-cresyl trityl ether was treated, in benzene solution, with hydrogen chloride the first reaction which occurred was a rapid cleavage to *o*-cresol and trityl chloride.



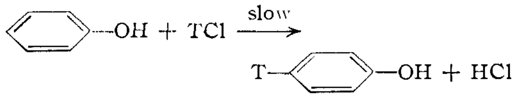
(10)

Van Alphen had performed this reaction without a solvent at 180° for one hour. Under such circumstances the product was the alkylated phenol, but clearly this product arose from rapid cleavage followed (under van Alphen's conditions) by nuclear alkylation. Under the milder conditions which we employed, chosen purposely because the alkylation proceeds only very slowly under these circumstances, the cleavage was still a very rapid reaction.[17] Since the reaction of the ether with hydrogen chloride causes cleavage to the original reactants, it would seem unlikely then that the ether should be an intermediate in the nuclear alkylation.

At this point, we would like to offer an explanation of why O-alkylation occurs in the presence of pyridine,[3] whereas in its absence C-alkylation results. This can be expressed in terms of two competing reactions



(11)



(12)

where T is the triphenylmethyl group. T^+ reacts more rapidly at the oxygen of phenol than at a ring position, but the reaction at the oxygen (to form ether) is reversible, whereas the nuclear alkylation is not. Pyridine prevents the reversal of 11. A rough comparison of Swain's data[3] for 11 in the for-

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[12] Hydrogen chloride is, in fact, a catalyst for the alkylation of aromatic hydrocarbons at high temperatures and pressures (see J. H. Simons and H. Hart, This Journal, **66**, 1309 (1944)).

[13] R. H. Rosenwald, *ibid.*, **74**, 4602 (1952).

[14] H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

[15] P. D. Bartlett and I. Pockel, This Journal, **60**, 1585 (1938). This reaction is also catalyzed by phenols (P. D. Bartlett and J. D. Gill, Jr., *ibid.*, **63**, 1273 (1941)) demonstrating that reactions such as 7 are facilitated by phenols.

[16] See, for example, J. van Alphen, *Rec. trav. chim.*, **46**, 287 (1927), who claimed that hydrogen chloride brought about a "rearrangement" of the ether to the alkylated phenol.

[17] A paper on the stereochemistry and kinetics of these ether cleavages is forthcoming (with H. S. Eleuterio and R. Elia).

ward direction indicates that the reaction is considerably more rapid than the rates we observed for 12.

Acknowledgment.—We express our appreciation to the Research Corporation for financial aid during most of the time this work was in progress.

EAST LANSING, MICHIGAN

[CONTRIBUTION OF THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

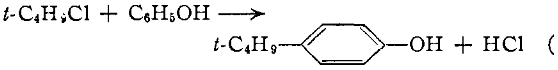
Inhibition of Phenol Alkylations by Ethers. Kinetic Evidence for Phenol–Ether Complexes

BY HAROLD HART, FRANK A. CASSIS AND JOHN J. BORDEAUX

RECEIVED OCTOBER 10, 1953

The nuclear alkylation of phenol by *t*-butyl chloride is inhibited by dioxane, the decrease in reaction rate being proportional to the concentration of dioxane. The inhibition can be quantitatively accommodated by assuming that a hydrogen-bonded complex of 2:1 phenol:dioxane is formed, and that phenol so bound cannot participate in the alkylation reaction. The same explanation fits the data for tetrahydropyran if a 1:1 complex is assumed. The availability of the phenolic hydroxyl, presumably for solvating the halogen of the alkyl halide, thus appears significant in the alkylation reaction.

It has been observed[1] that the nuclear alkylation of phenol by *t*-butyl chloride (equation 1) is prevented when the phenol contains about 21 mole per cent. of dioxane. An equivalent amount of *p*-xylene, which has about the same dielectric constant as dioxane, causes only the decrease in rate expected from dilution of the reactants. It was the purpose of the present work to examine this inhibition in more detail. Accordingly, the rate of the alkylation reaction was determined with several different concentrations of dioxane, and of tetrahydropyran in the reaction mixture.



$t\text{-}C_4H_9Cl + C_6H_5OH \longrightarrow t\text{-}C_4H_9\text{-}C_6H_4\text{-}OH + HCl$ (1)

Experimental

Materials.—Phenol and *t*-butyl chloride were purified as described previously.[1] Dioxane was purified according to the procedure of Fieser.[2] Tetrahydropyran was prepared by the catalytic hydrogenation of du Pont dihydropyran over Raney nickel at low pressure.

Apparatus.—The apparatus and rate measurement procedure already have been described.[1,3]

Results

The reaction was followed, as in earlier work, by the rate of evolution of hydrogen chloride with time, a series of time *vs.* pressure readings being obtained. Since phenol was used in excess in all of these experiments, and since the number of moles of hydrogen chloride generated was small compared with the total moles of phenol,[3] the reaction followed pseudo-first-order kinetics

$$\text{rate} = k(t\text{-butyl chloride})$$

Plots of log ($p_f - p$) (which is equivalent to the concentration of unreacted halide) against t yielded straight lines,[4] from the slopes of which k was calculated. Some of these plots are shown in Fig. 1. A summary of the data for pertinent experiments is given in Table I.

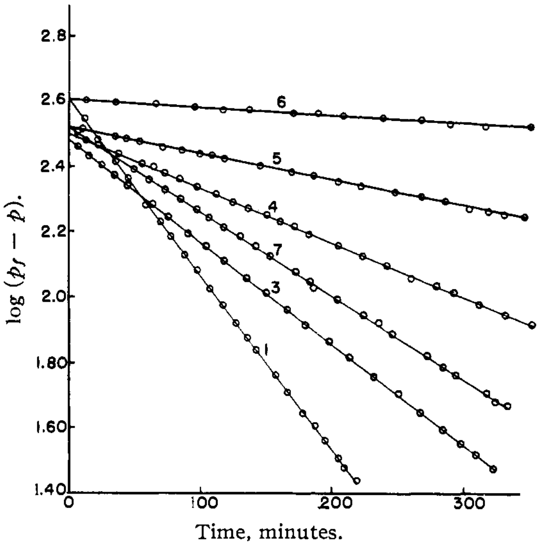


Fig. 1.—Adherence of observed data to first-order rate law.

The first two experiments were performed to furnish standard conditions for the reaction without any diluent added. The results agree closely with those previously obtained.[1] Experiments 3–7 show the effect of increasing amounts of dioxane. At a mole percentage (dioxane in phenol–dioxane mixture) of only 14%, the apparent rate constant is reduced to about 3% of the value without added dioxane, clearly showing the marked inhibition by dioxane. Experiments 7–9 show that tetrahydropyran also exhibits this effect, although to a lesser extent, a similar concentration (14 mole per cent.) causing a decrease to 13% of the value without added tetrahydropyran. For comparison, one run (no. 10) was made with *p*-xylene. The effect is even less, the rate constant only being reduced to 36% of the value for an undiluted run. These effects are discussed in more detail below.

Discussion

It is clear from the data that ethers are more effective at decreasing the alkylation rate than is *p*-xylene. We assume, therefore, that the role of *p*-xylene is principally one of a diluent, and that the observed decrease in reaction rate is due to a decrease in the concentration of reactants (particularly the phenol). It was shown previously[1] that

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(1) H. Hart and J. H. Simons, THIS JOURNAL, **71**, 345 (1949).

(2) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc, New York, N. Y., 1941, p. 368.

(3) H. Hart and F. A. Cassis, THIS JOURNAL, **76**, 1634 (1954).

(4) The symbols have the same meaning as in previous papers (ref. 1 and 3).