The Mechanism of the Hydrogen Fluoride Catalyzed Alkylation of Toluene by t-Butyl Chloride

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The discovery by Sprauer and Simons[1] of the quantitative, homogeneous and measurable condensed phase alkylation reaction between toluene and t-butyl chloride as catalyzed by hydrogen fluoride provides a means for studying the mechanism of an alkylation reaction. Confirmation and extension of the kinetic measurements of Sprauer and Simons are, therefore, highly desirable; and herein such measurements are reported in which an entirely new apparatus was used. The question of the basicity of the promoter was raised in the previous work and we have been able to make further measurements relative to this question employing several different basic promoters. The measurements agree approximately with the kinetic equations of Sprauer and Simons, but the greater precision obtained indicates the need of an additional term.

The difficulties and hazards of attempting to postulate reaction mechanism on the basis of reaction products alone, particularly for condensed phase reactions, are well known. The complex nature of the kinetic equations for this apparently simple alkylation reaction gives emphasis to this. All such postulated mechanisms have as their foundation the assumption of one or more reaction intermediates. These intermediates always take the form of some peculiar and high energy containing molecular species, ions, or free radicals, or for variety and complexity, solvated forms of one of these. High energy containing molecular species are seldom accepted as intermediates for gas phase reactions. In the condensed phase, where intermolecular collision is continuous, the life period of the activated state would generally be conceded to be too short to permit of the species serving as an intermediate. The assumption of

ions and free radicals is, therefore, looked upon with greater favor as postulated intermediates. We have been able to calculate the rate of this reaction on the basis of either of these assumptions and show that the maximum rate so calculated is slower than the experimental rate to such an enormous extent that either of these assumptions is untenable. We have, therefore, been able to demonstrate that no mechanism can be satisfactory which postulates one or more simple or solvated intermediate molecular species in the form of activated molecules, ions, or free radicals in one or a set of stoichiometric reactions. The theory of the reaction mechanism as presented by Sprauer and Simons is confirmed within the precision and extent of the measurements.

Apparatus.—The method of quantitatively following the rate of this reaction is to add a known amount of t-butyl chloride to a mixture of toluene and basic promoter, which is under a determined pressure of hydrogen fluoride in a metallic reaction vessel in a thermostat, and to follow the pressure rise with time. The previous experiments had shown the promoting effect of water and alcohol and, therefore, the necessity of rigid drying and care in handling. Also, the possibility of promotion by metallic ions, particularly silver ions, necessitated care in the design and construction of the reaction vessel. Internally it was entirely gold plated.

A diagram of the rate measuring apparatus is shown in Fig. 1. It consists of the reaction vessel (A) held in a strap-iron frame in a thermostat. The frame was given a swirling motion by an eccentric (B) operated from above. The support and center of the motion were a ball and socket joint (C) above the center of the vessel. The reaction vessel had two diaphragm valves and a third outlet at its top. The third outlet connected through a flexible coil of $1/8$-inch copper tubing to a differential manometer, one arm (D) of which was steel tubing. On the glass side an electric rest point signalling device (E) was used. This was a simple circuit of a dry battery, 3.6 volt flashlight bulb, and tungsten contact. One of the diaphragm valves connected through a $1/8$-inch copper flexible spiral to the hydrogen fluoride reservoir (F) and through a commercial diaphragm valve to the glass manifold (G). The other valves opened to the device for introducing the reactants. The remainder of the apparatus contained a manometer (H), buffer volume (I), connection to vacuum system and nitrogen source, etc., to enable the pressure on the outside of the differential manometer to be adjusted and read.

The reaction vessel was made of a 6.5-inch length of 3-inch copper tubing closed at the ends with 0.25-inch copper plate. The ends of the tubing were machined and provided with an internal shoulder. The end plates were also machined with shoulders to match the tube but with the outside diameter 0.003 of an inch larger than the inside diameter of the tubing. The upper plate had three 0.25-inch holes drilled through it for the outlet tubes. The separate parts, including three short pieces of 0.25-inch copper tubing, were repeatedly plated with gold with intensive burnishing between platings. To assemble the chamber, the lower plate was chilled in Dry Ice–acetone while the tubing was warmed to 100°. A shrink fit joint was then made; but to ensure freedom from leaks it was silver soldered on the outside, while the inside was protected with hydrogen. Several additional platings with
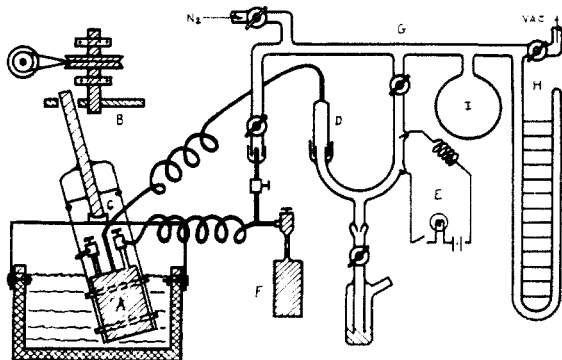

Fig. 1.—Diagram of rate measuring apparatus.

(1) J. W. Sprauer and J. H. Simons, THIS JOURNAL, **64**, 648 (1942).

gold ensured the repair of any injury to the surface that the soldering may have caused. The upper plate was fastened in the same manner and the three gold-plated outlet tubes attached with silver solder. When completed, the vessel had a capacity of 565 cc. The diaphragm valves were those used previously.[1] They were of Monel metal with copper diaphragms and a valve seat of $1/32$ of an inch diameter.

The procedure for introducing the reagents into the vessel is a critical part of the technique. The devices shown in Fig. 2 were employed. They were connected by means of S. A. E. flare fittings on copper tubing to the unencumbered diaphragm valve of the reaction vessel. The smaller diagram is for the t-butyl chloride introduction and the larger for the toluene with or without the promoter in solution. The devices consisted essentially of a brass disk connected to a copper tube, to which was fastened a glass flange (top of a round-bottom boiling flask) by means of split rings and six bolts. The gasket material was sheet Resistoflex. This substance, a polyvinyl alcohol elastomer, is quite inert toward hydrocarbon liquids and sufficiently elastic to seal the joint without undue pressure. Preliminary tests showed no visible change in texture or dimensions after six hours in refluxing toluene. Tubes sealed to the glass flanges had side arms which were provided with glass-encased iron plungers to break off the capillaries of the reagent vials. A concentric guard tube was employed in the toluene device to eliminate any tendency of the promoter to be selectively absorbed by the gasket material.

Preparation of Materials.—Hydrogen fluoride was prepared by heating potassium bifluoride purified by electrolysis.[2] It was stored in a copper container fitted with a special diaphragm valve. Since the pressure of the hydrogen fluoride was always above atmospheric pressure, any leakage would have been outward. Outgassing was, therefore, unnecessary and the possibility of atmospheric moisture entering was negligible.

The four promoters used were water, methanol, diethyl ether and hexamethylacetone. The water was redistilled in glass, methanol was distilled *in vacuo* from magnesium methylate, ether was dried over sodium and distilled *in vacuo*, and the ketone was a pure sample obtained by the kindness of Dr. F. C. Whitmore. Samples of these promoters were condensed in bulbs having capillary tips several centimeters long.

t-Butyl chloride was prepared from t-butyl alcohol and concentrated hydrochloric acid. It was dried over calcium chloride and distilled through an efficient laboratory fractionating column. A middle cut of constant index of refraction was used in the experiments. It was stored in the dark over anhydrous potassium carbonate until placed in the sample vials. The sample vials were made of 7-mm. glass tubing sealed to one-half a small ground joint and containing a capillary restriction. They were weighed and connected to a manifold by means of the other half of the ground joints. A bulb connected to this manifold contained dry potassium carbonate, and into it the freshly distilled t-butyl chloride was placed without coming in contact with moist laboratory air. Gases were removed by alternate freezing, evacuation, and thawing. The t-butyl chloride was then distilled into the vials, and they were sealed at the constriction, leaving a length of capillary for breaking in the device described above. A final weighing gave the amount of the sample. From this time on the t-butyl chloride was kept frozen in the dark in Dry Ice-acetone until use.

The toluene was repeatedly extracted with concentrated sulfuric acid until very little color developed in the acid. After washing and drying over calcium chloride, the material was distilled through an efficient fractionating column and a middle cut of constant index of refraction was used. The toluene was stored over sodium until the final drying. Sufficient toluene was prepared at the start for all of the experiments, so that variation in this substance would not have to be taken into consideration.

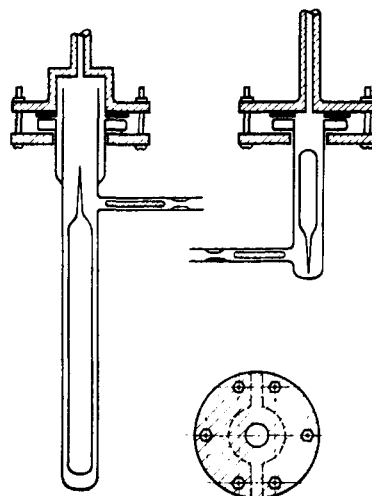(2) J. H. Simons, THIS JOURNAL, **46**, 2179 (1924).

Fig. 2.—Devices for introducing reactants.

The final drying of the toluene was accomplished with sodium triphenylmethyl. Previous experience had demonstrated that either metallic sodium or phosphorus pentoxide was an inadequate drying agent for the purpose.[3]

The toluene solution of sodium triphenylmethyl was prepared using elementary sodium. Previous workers have used a dilute sodium amalgam, and Schlenk and Marcus[4] found that p-benzhydrylphenyltriphenylmethane was formed in the presence of elementary sodium without the formation of sodium triphenylmethane. In a two-liter flask was placed one liter of purified and dried toluene and 65 g. of sodium. The mixture was heated until the sodium melted. The flask was then tightly stoppered and heated until the sodium melted. It was shaken violently until the sodium had solidified into very small particles. A mercury-sealed stirrer and reflux condenser were substituted for the stopper and a stream of carefully dried and purified nitrogen replaced the air. The nitrogen was freed of oxygen by passage through alkaline pyrogallol and dried by passage through phosphorus pentoxide. For all subsequent operations a slight positive pressure of nitrogen was maintained. A solution of 90 g. of triphenylmethyl chloride in 500 cc. of dry toluene was added. The reaction was complete within twenty-four hours at 50–60° with vigorous stirring. To prepare more of the solution, dry toluene containing the requisite amount of triphenylmethyl chloride was added to the residue and warmed with stirring until conversion was complete, as evidenced by the failure of a red color to develop on the surface of the sodium.

The preparation of a sample of rigorously dried toluene of known volume and containing a known small concentration of promoter, while avoiding the accidental admission of water such as from the atmosphere or from the water film on glass equipment, involved the employment of a special apparatus and technique. A diagram of the apparatus is shown in Fig. 3. The toluene container (1) was a liter-flask provided with a 10-mm. sidearm and connected through the tee (2) to the receiver (3). Stopcocks protected from toluene vapor by a water condenser (4) connected the flask and receiver with the vacuum and nitrogen manifolds. The receiver (3) consisted of two 200-cc. bulbs. A capillary led from their connecting tube through a stopcock (5) to the mixing chamber (6). A connection also led from the bottom of the receiver through a stopcock (9) to the sample container (10). Stopcocks (5) and (9) were in contact with liquid toluene, and the usual lubricants were unsuitable. A special glycol citrate ester

(3) J. H. Simons and E. M. Kipp, *Ind. Eng. Chem., Anal. Ed.*, **13**, 328 (1941).

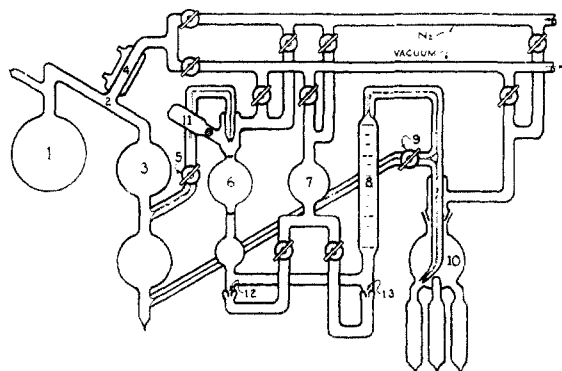(4) W. Schlenk and E. Marcus, *Ber.*, **47**, 1664 (1914).

Fig. 3.—Apparatus for sample preparation.

lubricant elsewhere described[5] was employed. The mixing chamber (6) consisted of two bulbs of 200 and 100 cc. volume connected with 10-mm. tubing. The capillary from stopcock (5) extended through a ring seal to below sidearm (11). Manifold connections were provided, and marks on the glass tubing just above and below the 200-cc. bulb established a known volume. Two connections were made at the bottom of the smaller bulb. One connected to the buret (8) and the other to the mercury reservoir (7) through a stopcock and ring-sealed orifice (12) which ensured that grease or scum on the mercury would not be carried into the toluene. The sidearm (11) served as the receiver for the promoter vial. It was provided with a right angle connection which contained a piece of iron sealed in glass for the magnetic hammer to break the tip of the promoter vial. The buret (8) was of 25-cc. capacity graduated to 0.1 cc. It was connected through scum trap (13) and a stopcock to the mercury reservoir and through a capillary to the sampling device (10). The height between the solution inlet of (8) and the top of the capillary bend above (10) was 80 cm., so that a vacuum could be maintained in (10) at the same time as an atmosphere of pressure in the mixing chamber. The sampling device (10) consisted of a one-liter bulb provided with a ground joint. To it were sealed five solution vials and a waste bulb. The upper part of the ground joint was connected to the vacuum and nitrogen manifolds. and the capillary tube entered through a ring seal and extended to a tip to divert the liquid stream into any of the vials or the waste bulb. The solution vials were calibrated so that 25 cc. of solution filled them to a mark on the neck. Their lower ends terminated in capillaries.

Preparation of Toluene Samples.—The toluene samples containing a known concentration of promoter were prepared in an all-glass apparatus, a diagram of which is shown in Fig. 3. Pure dry toluene was distilled from the solution containing sodium triphenylmethyl. A known volume of it was mixed with a weighed amount of the promoter and a measured volume of the solution added to a sample vial. The addition of pure toluene to fill the vial to a calibrated volume completed the sample. The sample vial was then sealed and removed from the apparatus.

Before use the entire apparatus shown in Fig. 3 was evacuated to less than 0.00001 mm. for several days with occasional sparking of the walls to aid in the removal of water. Dry nitrogen was then admitted. About 750 cc. of toluene containing sodium triphenylmethyl in solution was introduced into container (1). To ensure no contamination in transfer, .the introduction was made by means of a tube on the original container which entered the side tube of (1) against an opposing stream of nitrogen from the apparatus. After sealing the sidearm, the pressure in both container and receiver (3) was reduced to about 200 mm. and the receiver filled with toluene by distillation. A vial of the promoter was sealed in (11) and the mixing chamber (6) evacuated. With the lower bulb

(5) W. H. Pearlson, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 415 (1944).

of (6) filled with mercury and at a pressure of nitrogen equal to that in (3), toluene was slowly admitted to (6). The promoter was added by breaking the vial tip with the magnetic hammer. The addition of toluene was continued until the solution filled the calibrated volume of the upper bulb of (6). Mixing was accomplished by alternately raising and lowering the mercury. By means of manipulation with pressure and vacuum on the mercury in reservoir (7), the solution was introduced into buret (8). In filling the sample vials connected to (10) from the buret, a small amount of solution was first run into the waste bulb and then the desired volume placed in the vials. The solution was withdrawn from the capillary which was washed with pure toluene and the washings run into the waste bulb. The volume was then made up with pure toluene. The sample vials, when filled, were immersed in a Dry Ice–acetone bath. The pressure was reduced to remove dissolved gases and bubbles. Nitrogen up to atmospheric pressure was added to enable the necks of the vials to be thickened and drawn to heavy-walled capillaries. The pressure was again reduced and the vials disconnected by sealing the capillaries.

Measurement Procedure.—In making the measurements, the toluene sample was introduced into the reaction vessel, hydrogen fluoride admitted, and pressure and temperature equilibrium established. *t*-Butyl chloride was then added and the reaction followed with time as indicated by the increase in pressure.

With the entire system, as shown in Fig. 1, evacuated and free from leaks, the mercury was allowed to rise in the differential manometer until electrical contact was made. Despite the fact that a simple electrical circuit of a dry battery and a flashlight bulb with a mercury tungsten contact might be expected to give difficulties with fouling at the contact, under the conditions here employed in which the contact was always either *in vacuo* or dry nitrogen, no such difficulty was encountered. All measurements were subsequently made while making (not breaking) the contact. The volume of the mercury was now fixed and all valves closed. The device shown in Fig. 2 containing a vial of the toluene solution was now attached and evacuated through the sidearm to a pressure of 0.001 mm. with sparking to remove water. The sidearm was then sealed, and the vial capillary broken by the magnetic hammer. The contents of the vial were admitted to the reaction vessel by tipping it with the valve open and gently warming the assembly beyond the reaction vessel. The valve was closed, shaker started, and the sample device removed. It contained a residue of less than 0.2 cc. of toluene. The reaction vessel was opened to the manometer and the pressure read. Hydrogen fluoride was then admitted slowly with agitation until it had increased the pressure just 400 mm. The *t*-butyl chloride device containing a vial of the reagent was now attached and evacuated. The sidearm was sealed, vial capillary broken, and the device immersed in a beaker of boiling water. The valve to the reaction vessel was opened and the timer started. After forty-five seconds the valve was closed and shaking begun. The reaction was now under way.

At a convenient subsequent time the sample device was removed and quickly sealed with a brass connection. It was chilled in a Dry Ice–acetone bath, opened, and washed with alcohol. Silver nitrate and nitric acid were added, and after several days standing with occasional shaking. a chloride analysis determined the amount of the total weighed sample not transferred.

Pressure measurements were begun ninety seconds after opening the valve for the admission of *t*-butyl chloride, but pressure equilibrium was not sufficiently established for consistent readings until the elapse of three minutes. Measurement was made by increasing the pressure on the glass side of the system two to three millimeters and recording the pressure and the time at which the differential manometer reached equilibrium. The time between readings was less than a minute at the start, increasing as gas evolution slowed to a half hour or more. The reaction was followed closely for eight to ten hours, with a usual pressure rise of about 200 mm. and approximately 90%

completion. The reaction was essentially complete in less than thirty hours, at which time most experiments were terminated. In some cases observations were continued for forty-eight or seventy-two hours to evaluate accurately the total pressure rise.

Pressures on the outward side of the differential manometer were read on an absolute mercury manometer with an internal diameter of 15 mm., mounted against a mirror containing a scale, which was calibrated against a precision cathetometer. Corrected heights were used to calculate the pressure. Room temperature was maintained between 25 and 28° during an experiment to obviate errors due to temperature changes in the density of mercury. The thermostat was maintained at 25.00 ± 0.03°.

Results

The data obtained from each experiment consisted of a series of pressure measurements at determined elapsed times. These points were plotted and a smooth curve drawn through them. Normals to the primary rate curve were drawn with a plane metallic mirror held in a small frame at a right angle to the plane of the graph paper. The normal was drawn when the curve itself and its image appeared to give no perceptible break. This was checked by rotating the mirror 180° at the same point and by the appearance of the constructed normal and its image as a straight line, when the mirror was placed to form the best observable tangent to the curve. The slope of the tangent was obtained from the normal by graphically interchanging the physical lengths of the intercepts of the normal and taking the negative of the angle of a line drawn through them.

Space does not permit the reproduction of all the data, but the points for four typical experiments are shown in Figs. 4 and 5 which illustrate the consistency of the readings for any one experiment.

An analytical expression was found for the correlation of the data of any one experiment. Sprauer and Simons[1] give two equations for this purpose.

$$\frac{dP}{dt} = \frac{a (P_\infty - P)}{b - (P_\infty - P)} \qquad (1)$$

and

$$\frac{dP}{dt} = R(P_\infty - P) + S(P_\infty - P)^2 \qquad (2)$$

in which dP/dt is the tangent to the rate curve, P is the instantaneous pressure, t is the time, P_∞ is the final pressure, and a, b, R and S are constants. In (1) $(P_\infty - P)/dP/dt$ is linear with $(P_\infty - P)$ and in (2) $(dP/dt)/(P_\infty - P)$ is linear with $(P_\infty - P)$. The data of the present work fell on a straight line as well as could be expected, when plotted according to either of these equations. The constants obtained from these straight lines were used in the integrated forms of the two equations, respectively

$$\ln (P_\infty - P) - (P_\infty - P)/b + at/b = \text{constant} \quad (3)$$

and

$$\frac{1}{R} \ln \frac{P_\infty - P}{R + S(P_\infty - P)} + t = \text{constant} \qquad (4)$$

The constants of integration were determined by fitting the experimental curve at a point near the
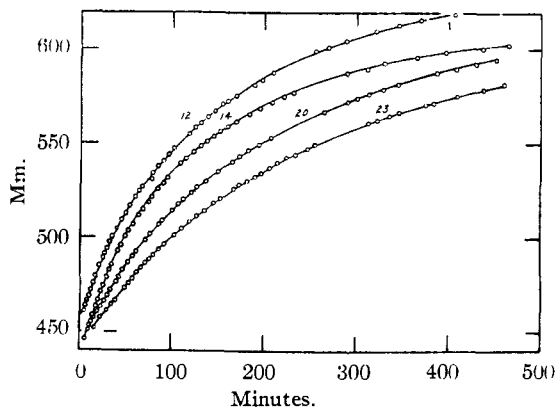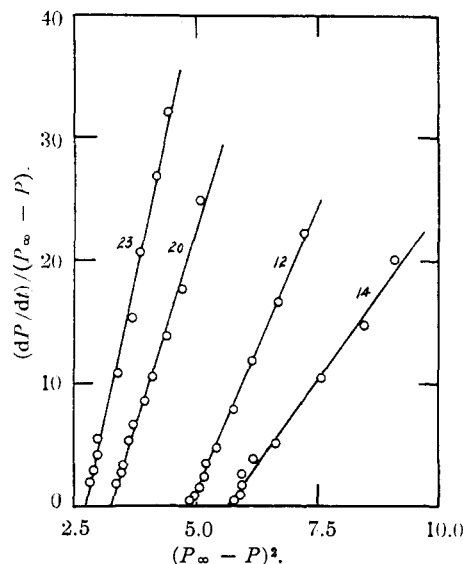

Fig. 4.—Typical rate curves.

Fig. 5.—Typical derivative curves.

center. In both cases there was a significant but small deviation of the integrated curve from the experimental points. It was higher at both ends.

TABLE I

COMPARISON OF VARIOUS RATE LAWS, EXPERIMENT 12

Pressure, mm.	Time observed, minutes elapsed	Δt[a] Eq. (6)	Δt[a] Eq. (4)	Δt[a] Eq. (8)
459	3	0	−3	− 3
469	10	+1	−2	− 2
479	18	0	−2	− 1
499	36	0	−1	+ 1
519	58	+2	0	+ 2
539	87	+2	−1	0
549	106	+1	−2	− 2
559	127	+1	−3	− 4
579	181	0	−5	−10
599	260	0	−6	−13
609	318	−1	−5	− 6
619	400	+1	−2	+43

[a] Δt is the time as calculated by the particular equation minus the experimental time at the pressure indicated.

The extent of this deviation is seen in column 4 of Table I.

To obtain a closer fit equation (2) was changed to

$$\frac{dP}{dt} = R'(P_\infty - P) + S'(P_\infty - P)^3 \quad (5)$$

$(dP/dt)/(P_\infty - P)$ plotted against $(P_\infty - P)^2$ gave straight lines as shown in Fig. 5, the points being calculated from the data and the lines obtained by the method of least squares. R' and S' are evaluated from the lines. The integrated form of the equation

$$\frac{1}{2R'} \ln \frac{(P_\infty - P)^2}{S'(P_\infty - P)^2 + R'} + t = \text{constant} \quad (6)$$

was fitted to the experimental curves at a central point to evaluate the constant of integration. The equation was found to correlate the experimental points satisfactorily, as is seen in Fig. 4 where the full line is obtained from equation (6). This is also shown in column 3 of Table I.

All experiments except 10 were correlated by this equation. For this experiment, in which the highest quantity of methyl alcohol was used, the straight line equation employed by Sprauer and Simons was used satisfactorily. It is
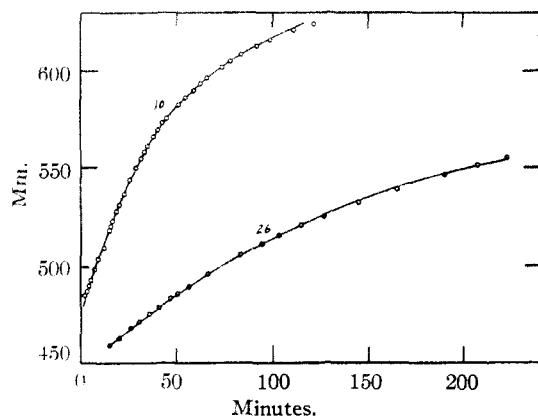
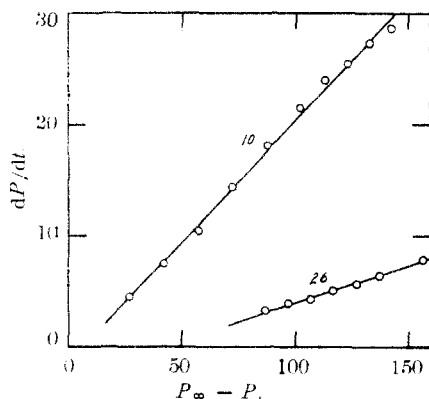$$dP/dt = b(P_\infty - P) + a \quad (7)$$

Fig. 6.—Linear rate curves.

Fig. 7.—Linear derivative curves.

or integrated

$$\frac{1}{b} \ln [a + b(P_\infty - P)] + t = \text{constant} \quad (8)$$

The smooth curve in Fig. 6 is obtained from equation (8) and Fig. 7 shows the derivative as a linear function of $(P_\infty - P)$. Experiment 26 could be correlated by either equation (5) or (8). Its correlation with equation (8) is shown in Figs. 6 and 7. Equations (7) and (8) are empirical equations found to correlate the experimental data for exceptional experiments. From their form they cannot hold to infinite time, but, over the range of the measurements, they satisfactorily correlate the data.

Table II gives a summary of the measurements. Column 1 gives the number of the experiment. Column 2 gives the concentration of the promoter. Column 3 gives the added amount of t-butyl chloride as corrected for the amount retained in the sampling device. In experiments 2, 3 and 4 the silver chloride method was not used; and in experiment 9 the precipitate was lost by accident. In these cases the initial amount of t-butyl chloride was estimated from the total rise in pressure per gram of t-butyl chloride as determined from the rest of the experiments and the observed rise in pressure in these experiments. In column 4 is recorded the initial pressure of hydrogen fluoride. Where no promoter was in the solution, this is the recorded increase in pressure on the addition of hydrogen fluoride. Where a promoter was used, a correction equal to the initial pressure of the promoter in the vessel needed to be added to the recorded increase in pressure, as the addition of the hydrogen fluoride would reduce the pressure of the promoter from the solution to a negligible amount. This was obtained by graphically obtaining the recorded pressure of the promoter-containing (HF free) solution as a function of promoter concentration, extrapolating to zero promoter concentration and subtracting the zero value from the recorded value. The thus-determined pressure without the promoter was about 33 mm. for all experiments, which is the vapor pressure of toluene plus any constant amount of nitrogen added in making up the samples. In columns 5 and 6 are found the constants of equation (5). In column 7 is the integration constant of equation (6). In column 8 is found the slope of the rate curves, dP/dt, as calculated from equation (5) for a zero time as obtained by analytical extrapolation of the curve. The actual zero time is somewhat uncertain due to the difficulty of obtaining an instantaneous addition and mixing of t-butyl chloride. This zero time slope has the advantage for use in evaluating the effects of the various promoters, in that at this time the pressure of hydrogen chloride is zero and the slope is not complicated by the apparent retarding effect of the hydrogen chloride. In column 9, K_0, the slope of the rate curve, or the rate of the reaction, is corrected to the same

TABLE II

SUMMARY OF RATE CONSTANTS IN THE REACTION OF TOLUENE AND t-BUTYL CHLORIDE AS CATALYZED BY HYDROGEN FLUORIDE AND PROMOTED BY VARIOUS BASES

W refers to water; A, methanol; E, diethyl ether; and K, hexamethylacetone.

1	2	3	4	5	6	7	8	9	10
Expt.	Promoter concn. mole/25 cc. $\times 10^4$	Initial BuCl, g.	HF pressure, mm.	R' $\times 10^3$	S' $\times 10^3$	Integration constants	$(dP/dt)_0$	K_0	K_0'
2	Dry	0.831[a]	399.1	1.469	7.345	5428	0.710	0.854	0.867
3	Dry	.869[a]	398.8	1.822	5.032	4417	.692	0.796	0.814
23	Dry	.8753	398.9	2.754	5.409	2874	.912	1.042	1.090
24	Dry	.8800	398.8	2.782	6.528	2828	.986	1.120	1.145
7	W 0.6	.9904	399.6[a]	2.313	5.473	3468	1.032	1.042	1.050
5	W 1.2	1.0181	401.5	2.442	7.393	3268	1.352	1.327	1.288
4	W 2.9	0.969[a]	400.9	2.210	5.233	3632	0.949	0.979	0.965
6	W 5.7	.9826	403.7	3.074	5.321	2581	1.108	1.128	1.055
11	A 3.7	.8917	400.9	3.072	6.969	2552	1.139	1.277	1.259
8	A 14.7	.8427	409.2	5.905	20.23	1244	2.091	2.481	2.104
12	A 14.7	.9080	412.0	4.888	10.78	1556	1.801	1.983	1.595
13	A 14.7	.9101	510.2	26.929	83.19	249	10.824	11.893	...
9	A 25.7	.914[a]	417.1	9.469	11.02	782	2.778	3.039	2.230
10	A 36.7	.8576	424.0	−163[b]	22.4[b]	59[b]	...	...	...
18	E 3.3	.9028	399.4	2.960	7.452	2651	1.175	1.302	1.321
16	E 6.6	.9410	400.3	3.226	7.060	2434	1.270	1.350	1.340
15	E 11.5	.8852	400.8	3.980	10.33	1923	1.511	1.707	1.682
14	E 23.0	.8586	402.3	5.655	18.15	1314	2.220	2.586	2.473
17	E 32.9	.9712	404.7	6.198	16.10	1211	2.845	2.929	2.679
22	K 1.3	.9180	399.3	2.761	6.825	2858	1.132	1.233	1.252
21	K 2.5	.9325	399.6	2.943	5.905	2684	1.091	1.170	1.178
20	K 5.1	.8898	400.9	3.247	7.814	2400	1.201	1.350	1.330
19	K 8.8	.8875	401.7	3.634	9.292	2127	1.397	1.574	1.531
26	W+ Ag	.9	400	−248[b]	6.49[b]	−11[b]			

[a] Estimated.   [b] Straight line law constants.

concentration of t-butyl chloride for all experiments, i. e., 1 g. per 25 cc. Assuming the rate of the reaction is proportional to the t-butyl chloride concentration, as was found by Sprauer and Simons, this is simply done by dividing column 8 by column 3. In column 10, K_0', this concentration-normalized initial rate is standardized to the same hydrogen fluoride concentration for all experiments, i. e., 400 mm. The rate of the reaction is extremely sensitive to the pressure of hydrogen fluoride. Experiments 8, 12 and 13, in which the only variation is the hydrogen fluoride pressure, show this. From these it is found that the rate is proportional to the 7.4 power of the hydrogen fluoride pressure, K_0' is then calculated from K_0 by the equation

$$\log \frac{K_0'}{K_0} = 7.4 \log \frac{400}{P_{HF}} \qquad (9)$$

It should be a function of only the promoter and its concentration.

Discussion of Results

The results obtained confirm the less precise measurements of Sprauer and Simons. The greater precision has demonstrated that their equations for the correlation of data need to be slightly modified. The effect of the promoters, while still quite significant, is much less than they found. Their reaction vessel was made of copper

joined with silver solder, whereas ours was internally entirely gold plated. In order to confirm the cause of the difference, two experiments were performed. In one copper was placed in the reaction vessel, and the reaction followed with water as the promoter. No detectable effect of the copper was found. In the other silver solder in the form of wire was added, and the same experiment repeated. The results are found in the table as experiment 26. A pronounced increase in rate was obtained. The results could be correlated by either equation (5) or (7). A reasonable explanation is that a hydrated silver ion is a strong base and an exceedingly effective promoter.

The rate of the reaction as seen in column 9 increases with the increasing concentration of the promoter. It is also to be noted that the four promoters used have approximately the same effect at the same molar concentration. These effects are shown in Fig. 8. The agreement is very satisfactory in view of the difficulty of evaluating the rate at zero time where the rate is changing rapidly.

A discrepancy was observed between experiments 2 and 3 taken at the beginning of the series and 23 and 24 taken at the end, under what were hoped to be identical conditions. This can be interpreted as a change in the reaction vessel which could have occurred abruptly or gradually

during the course of the investigation, due to either adsorption of the promoter on the walls or the gradual diffusion of silver from the silver solder through the gold plate. Since there is no evident curvature in Fig. 8, the first explanation seems more likely.
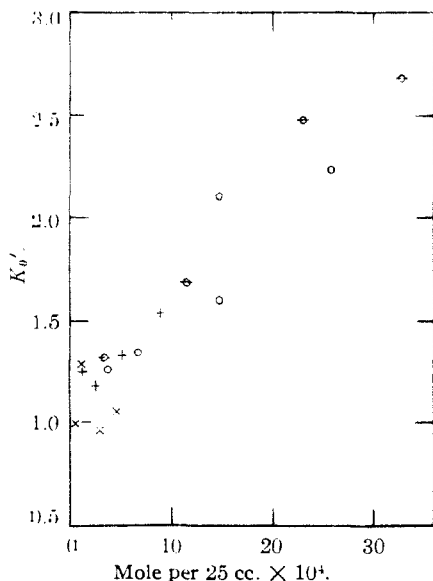

Fig. 8.—Effect of promoter on rate: water, $\times$; ether, $\ominus$: alcohol, $\bigcirc$; ketone, $+$.

Interpretation of Results

In the previous work the kinetic equations were derived on the basis of either of two mechanisms. In each of these the simultaneous action of acid and base was required in what may be called the "amphoteric medium effect." As the mechanisms required the combined actions of a number of molecules, it would be possible only for condensed phase reactions. In one of these an intermediate ionic species is formed with the evolution of hydrogen chloride by a reversible reaction as catalysed by acids and promoted by bases. This intermediate reacts in a consecutive reaction with the toluene. Equation (1) results from this mechanism. In the other the simultaneous action of the acid and base on t-butyl chloride in contact with the toluene gives rise to the organic product and hydrogen chloride. A simultaneous reversible reaction of t-butyl chloride through the action of the acid to produce hydrogen chloride accounts for the retardation phenomenon. Equation (2) results from this mechanism. Both equations (1) and (2) correlate the data equally well so on this basis no distinction can be made. There is one experimental method, however, for distinguishing between these two mechanisms. In the first mechanism, the retardation by hydrogen chloride comes from a reversal of the preliminary reaction. Hence, as the pressure of hydrogen chloride is increased, the rate at unit butyl chloride concentration decreases to zero. In the

second, the retardation results from the reversal of a side reaction, and as the pressure of hydrogen chloride is increased, the rate at unit butyl chloride concentration approaches a finite rate which is the rate of the primary reaction. Present data are insufficient to make this test, which could be accomplished by a series of experiments in which a variable initial pressure of hydrogen chloride was introduced.
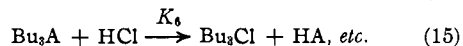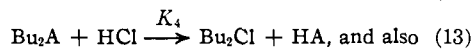
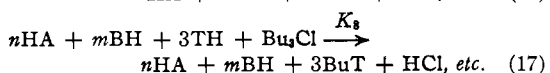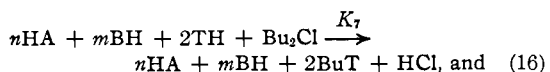Assuming a mechanism of the second type, the principal reaction is

$$n\text{HA} + m\text{BH} + \text{TH} + \text{BuCl} \xrightarrow{k_1}$$
$$n\text{HA} + m\text{BH} + \text{BuT} + \text{HCl} \quad (10)$$
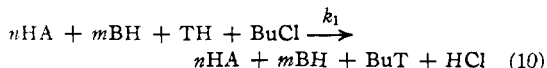
in which HA is any acidic species; BH, any basic species; TH, toluene; BuCl, t-butyl chloride; BuT, p-t-butyltoluene; n, a coefficient; and m, likewise. A significant side reaction is

$$\text{BuCl} + \text{HA} \xrightleftharpoons[K_{-2}]{K_2} \text{BuA} + \text{HCl} \quad (11)$$
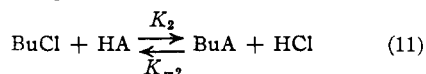
Another side reaction is experimentally known. In the previous work high molecular weight chlorides were obtained in experiments in which low concentrations of toluene were used. Similar products have been found by the action of hydrogen fluoride on tertiary chlorides.[6] Polymers have been shown to alkylate as the monomer.[7] It is not unreasonable, therefore, to postulate a second kind of side reaction of which the following are examples, where Bu $= \text{C}_4\text{H}_9$, $\text{Bu}_2 = \text{C}_8\text{H}_{17}$, $\text{Bu}_3 = \text{C}_{12}\text{H}_{2b}$:

$$\text{BuCl} + \text{BuA} \xrightarrow{K_3} \text{Bu}_2\text{A} + \text{HCl, and} \quad (12)$$

$$\text{Bu}_2\text{A} + \text{HCl} \xrightarrow{K_4} \text{Bu}_2\text{Cl} + \text{HA, and also} \quad (13)$$

$$\text{Bu}_2\text{Cl} + \text{BuA} \xrightarrow{K_5} \text{Bu}_3\text{A} + \text{HCl, and} \quad (14)$$

$$\text{Bu}_3\text{A} + \text{HCl} \xrightarrow{K_6} \text{Bu}_3\text{Cl} + \text{HA, } etc. \quad (15)$$

to form for example the di-, tri-, etc., isobutylene hydrochlorides, which it is known will alkylate to form the t-butyl containing products. The alkylation of toluene with Bu_2A, Bu_3A, etc., will have no effect on the pressure rise as hydrogen chloride is not involved. Alkylation with Bu_2Cl, Bu_3Cl, etc., will have an effect, however, in reactions similar to equation (10).

$$n\text{HA} + m\text{BH} + 2\text{TH} + \text{Bu}_2\text{Cl} \xrightarrow{K_7}$$
$$n\text{HA} + m\text{BH} + 2\text{BuT} + \text{HCl, and} \quad (16)$$

$$n\text{HA} + m\text{BH} + 3\text{TH} + \text{Bu}_3\text{Cl} \xrightarrow{K_8}$$
$$n\text{HA} + m\text{BH} + 3\text{BuT} + \text{HCl, } etc. \quad (17)$$

The total rate of the reaction becomes

$$dP/dt = K_1(\text{BuCl}) + K_2(\text{BuCl}) - K_{-2}(\text{BuA})(\text{HCl}) +$$
$$K_3(\text{BuCl})(\text{BuA}) - K_4(\text{Bu}_2\text{A})(\text{HCl}) + K_5(\text{Bu}_2\text{Cl})(\text{BuA}) -$$
$$K_6(\text{Bu}_3\text{A})(\text{HCl}) + K_7(\text{Bu}_2\text{Cl}) + K_8(\text{Bu}_3\text{Cl}), etc. \quad (18)$$

(6) J. H. Simons, G. H. Fleming, F. C. Whitmore and W. E. Bissinger, THIS JOURNAL, 60, 2267 (1938).

(7) J. H. Simons and S. Archer, ibid., 62, 451 (1940).

In this equation the contributions of the acidic and basic species and toluene have been omitted, as these can be considered constant for any one experiment. There is some contribution to the equation due to the increasing pressure of hydrogen chloride as it contributes to the acidic species. Simons and Hart[8] have shown it to be effective as an alkylating agent but only significant at higher temperatures and pressures. This effect will contribute other terms to the equation, such as $K_1'(BuCl)(HCl)$, *etc.;* but these have been neglected for the present purpose, which is only to show that the complete kinetic equation has many terms, the summation of which can be approximated within the precision of the measurements by equation (5).

Assuming, as has been previously done, that (BuA) is proportional to (BuCl) and in addition, for the same reasons, that (Bu$_2$A) and (Bu$_2$Cl) are proportional to (BuCl)^2, and also that (Bu$_3$A) and (Bu$_3$Cl) are proportional to (BuCl)^3, a rate equation can be written. (BuCl) is proportional to $(P_\infty - P)$ and (HCl) to $[(P_\infty - P_0) - (P_\infty - P)]$.

$$dP/dt = K_1(P_\infty - P) + K_2(P_\infty - P) - K_{-2}(P_\infty - P)$$
$$(P_\infty - P_0) + K_{-2}(P_\infty - P) + K_3(P_\infty - P)^2 - K_4$$
$$(P_\infty - P_0)(P_\infty - P)^2 + K_4(P_\infty - P)^3 + K_5(P_\infty - P)^3 - K_6(P_\infty - P_0)(P_\infty - P)^3 + K_6(P_\infty - P)^4 + \ldots +$$
$$K_7(P_\infty - P)^2 + K_8(P_\infty - P)^3 + \ldots etc. \quad (19)$$

$$dP/dt = [K_1 + K_2 + K_{-2} - K_{-2}(P_\infty - P_0)](P_\infty - P) +$$
$$[K_3 + K_7 - K_4(P_\infty - P_0)](P_\infty - P)^2 + [K_4 + K_5 +$$
$$K_8 - K_6(P_\infty - P_0)](P_\infty - P)^3 + K_6(P_\infty - P)^4, etc., \text{ or} \quad (20)$$

$$dP/dt = \alpha(P_\infty - P) + \beta(P_\infty - P)^2 + \gamma(P_\infty - P)^3 + \vartheta(P_\infty - P)^4, etc. \quad (21)$$

With proper adjustment of coefficients, it is seen that this equation (21) can agree with equation (5) within the precision of the measurements. All that is required is that the third power term of (5) approximate a summation of all terms of (21) over the first power term.

It should be emphasized that equation (10) represents the main reaction, and that the other effects as caused by these other known and possible reactions are of relatively small magnitude, and their contribution is required only because of the small but real apparent retardation of the hydrogen chloride. This effect becomes negligible when the main reaction is greatly accelerated, as, for example, in experiments 10 and 26 and terms in the variable of higher power than the first are unnecessary. If equation (8), which neglects powers of $(P_\infty - P)$ higher than the first, is used for a typical experiment, small deviations are found, as is seen in column 5 of Table I.

The mechanism of the reaction as postulated in equation (10) is a one-step process possible only in a condensed phase where all the various contributing molecular species are in essential contact. Such a mechanism is confirmed by the

similarity of the effects of the four promoters used. These are basic substances in the presence of hydrogen fluoride in that they have a tendency to accept a proton. They all have in common an oxygen atom, and the hydrogen bonding tendency of this oxygen atom is the basic property in the sense here used. Gordy[9] has shown this to be only slightly different for esters, aldehydes, ketones, ethers, and similar substances by means of the determination of the oxygen-deuterium frequency for deutero-methyl alcohol in various oxygen-containing organic solvents. On the basis of a mechanism which requires two or more consecutive reactions and active intermediates, it is difficult to explain the similarity of the effects of the promoters. Water, methanol, diethyl ether and hexamethylacetone are so dissimilar that any intermediates that they would form or cause would be expected to react by quite different rates.

This kinetic technique may enable measurements to be made of the relative base strength of other, and presumably weaker, bases, as, for example, organic sulfur compounds.

Experiment 10 could not be correlated on the basis of equation (10) and its rate was much higher than the concentration of alcohol would give when compared to the other alcohol-promoted experiments. An accidental inclusion of another substance may be the cause. However, as this is the highest concentration of alcohol used, it is possible that in the presence of hydrogen fluoride two liquid phases were formed. A heterogeneous catalyzed reaction on the interface of the two phases would change conditions and result in entirely different kinetic equations.

There are a number of investigations in the literature of reactions which can be readily explained on the basis of the amphoteric medium effect similar to its use in this study. The splitting of ethers by hydrogen bromide[10] is promoted by alcohol, acetic acid and water in non-polar solvents.

The reactions of tertiary halides with water and alcohols have been the subject of much controversy. Despite the numerous experiments, a definite decision between a one-step process and a mechanism involving an ionic intermediate has not been achieved. It is difficult to explain on the basis of an ionic mechanism the low energies of activation required and the retention of stereochemical configurations. On the other hand, the chemical data have been interpreted very satisfactorily. Experiments in which the simultaneous action of water and alcohol on *t*-butyl chloride to form the alcohol and ether were interpreted as the result of a one-step process.[11] While the kinetic results were successfully correlated, it was shown that the ratio of ether to alcohol was higher than the relative rate constants would pre-

(8) J. H. Simons and H. Hart, THIS JOURNAL, **66**, 1309 (1944).

(9) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

(10) F. R. Mayo, W. B. Hardy and C. G. Schultz, THIS JOURNAL, **63**, 426 (1941).

(11) A. R. Olson and R. S. Halford, *ibid.*, **59**, 2644 (1937).

dict, and an alternative ionic mechanism was put forth.[12] The hypothesis of basic promotion makes the results entirely compatible with the one-step process. If the rate of alcoholysis is increased by the presence of water to a greater extent than the hydrolysis is promoted by alcohol, the result will be a production of ether in excess of that expected from the rate constants determined in the pure solvents. In the case of benzhydryl chloride[13] this water promotion of the alcoholysis is confirmed; even in the presence of quite large amounts of water no benzhydrol was found, while the rate of formation of the ether was greatly accelerated.

Theoretical Considerations

It is well known that the assumption of ionic intermediates in non-polar media encounters difficulties from energy consideration; that is, there is not sufficient energy available to create enough ions to enable the reaction to go as rapidly as it does. Alkylation and similar condensed phase reactions proceed very rapidly at relatively low temperatures. A free radical intermediate encounters the same objections in most cases. In the mechanism (amphoteric medium effect)[5] here proposed the energy difficulties are avoided for two reasons. Due to the large number of molecules associated in the act of reaction, a large number of degrees of freedom and energy states are available for contribution to the reaction. Also, since no high energy-containing intermediate is required, the contribution of the energy of formation of the product leads to a reduction of what otherwise would be the energy of activation, as has been described in the transition state theory of reactions.[14]

Recently published data have enabled us to calculate the rates to be expected on the basis of either an ionic or free radical intermediate for this reaction and to compare them with those experimentally determined. The rates so calculated are so many fold slower than those actually observed as to leave no doubt that any mechanism for this reaction involving such intermediates is unreasonable.

The calculation of the rate of this reaction on the assumption of the t-butyl carbonium ion as the active intermediate is accomplished by calculating the energy of formation of the t-butyl and chloride ions from t-butyl chloride and from this the rate of formation of the ion intermediate. To give the maximum possible rate, it is assumed that this ion reacts instantaneously with the toluene with no energy of activation.

The energy of formation of the gaseous ions from the gas molecule is obtained from the ionization potential of the molecule and the electron affinity of the chloride ion. This energy can be

arbitrarily divided into two parts: that necessary to electrically deform the molecule into two adjacent ions, and that necessary to separate the ions against the calculable coulombic energy. If the deformation energy is independent of the medium, the energy of formation of the ions in toluene is found by adding to the deformation energy the energy of separation of the ions at the dielectric constant of toluene. This energy of formation of the ions is assumed to be the energy of activation, and the rate of the reaction calculated.

The ionization potential of the reaction

$$t\text{-BuCl(g)} \longrightarrow t\text{-Bu}^+(g) + Cl(g) + e \quad (22)$$
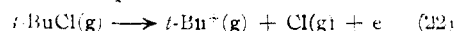
is 238 kcal. per mole.[15] The electron affinity of chlorine atoms is 93 kcal.[16] Therefore

$$t\text{-BuCl(g)} \longrightarrow t\text{-Bu}^+(g) + Cl^-(g) - 145 \text{ kcal.} \quad (23)$$
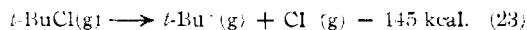
For the calculation of the energy of separation, the ion radii are necessary. That of the chloride ion can be taken as that of the ion in the crystalline alkali halides, 1.8 Å.[17] The radius of the t-butyl ion has not been experimentally determined, but it should be approximately that of the carbon–carbon bond, 1.8 Å., plus the van der Waals radius of the methyl group, 2.0 Å.,[17] or 3.8 Å. The theory of Bjerrum as developed by Fuoss and Kraus[18] is used to calculate the energy of separation in a vacuum of dielectric constant 1. It is 56 kcal. per mole. By difference from 145, this gives 89 kcal. as the deformation energy. In toluene with a dielectric constant of 2.4, a similar calculation gives 22 kcal. per mole as the energy of separation. As the effect of toluene on either the solvation of the ions or on the electrical deformation of the molecule must be small, the energy for ionization of t-butyl chloride in toluene will be the sum of 89 and 22 or about 110 kcal. per mole.

This energy can be supplied only from the thermal motion of the molecules of the solution. In order that the rate to be calculated be the fastest possible, it is assumed that every collision involving energies greater than 110 kcal. produces ions and that every t-butyl ion formed reacts instantaneously to give t-butyltoluene. The rate constant under these conditions can be calculated by the usual kinetic theory equation for a first order reaction[19]

$$K = \frac{3\pi\eta\sigma}{2m}\rho^{-E/RT} \quad (24)$$

where η, the viscosity, is 5.5×10^{-3}; σ, the diameter of the t-butyl chloride molecule, is taken as 7.6×10^{-8}; and m, the mass of the t-butyl chloride molecule, is 15×10^{-23}

$$K = 1.31 \times 10^{15} e^{-110/0.6} = 1.3 \times 10^{-67} \text{ mole per mole per second} \quad (25)$$

(12) L. C. Bateman, E. D. Hughes and C. K. Ingold, This JOURNAL, 60, 3080 (1938).

(13) N. T. Farinacci and L. P. Hammett, ibid., 59, 2542 (1937).

(14) H. Eyring, J. Chem. Phys., 3, 107 (1935).

(15) D. P. Stevenson and J. H. Hipple, This JOURNAL, 64, 2766 (1942).

(16) J. J. Mitchell and J. E. Mayer, J. Chem. Phys., 8, 282 (1940).

(17) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 350.

(18) R. M. Fuoss and C. A. Kraus, This JOURNAL, 55, 1019 (1933).

(19) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London, 1933, p. 159.

The coefficient of e, the collision factor, in the above equation is usually approximately 1×10^{13} for reactions of this type.

For comparison with the above value, the rate of the unpromoted reaction in experiments 23 and 24 is about 1×10^{-5} mole per mole per second. It is evident that a simple ionization of even so reactive a molecule as a tertiary chloride cannot be a necessary step in the mechanism of its reaction in a non-polar solvent.

The above calculation does not take into consideration the fact that substances such as hydrogen fluoride, water, alcohols and so forth, act as catalysts. It might be argued that the role of such polar molecules is to facilitate the reaction by solvating the ions, hence lowering the energy requirements to a point where a reasonable rate is possible. The experimental determination of energies of solution is extremely difficult and has been carried out in a few cases only, for inorganic salts in polar solvents. The theoretical calculation of solvation energies is as yet undeveloped. Nevertheless, it is possible to arrive at a fairly reliable estimate of the effect of solvation in a rather indirect manner.

Anhydrous formic acid is a medium of high dielectric constant, 57. In such a solvent ionic mechanisms are favored. The rate of hydrolysis of t-butyl chloride in moist formic acid has been determined to be 3.7×10^{-4} mole per mole per second.[20] By the use of radioactive chloride the rate of exchange of t-butyl chloride with chloride ions has been found to be 3×10^{-4} in anhydrous formic acid.[21] The substantial identity of these two rates for reactions rather different in appearance is most readily explained by a common rate-determining step. The ionization of t-butyl chloride, followed by very rapid combination with, in the one case, water, and in the other, chloride ions, seems a reasonable assumption.

Three factors favor ionization in a polar medium. First, solvation of the ions contributes energy toward the breaking of the bond; second, solvation increases the size of the ions; and third, the high dielectric constant decreases the coulombic forces opposing separation of the ions. Calculating the separation energy by the equations of Fuoss and Kraus for t-butyl chloride with a radius sum of 5.7×10^{-8} cm. in a medium of dielectric constant 57, it is found that at 25° the available thermal energy is more than sufficient to cause ion separation. The energy of ionization will consist, therefore, of that required to produce solvated ions from the non-polar molecule. From the observed rate in the reactions in formic acid, 10^{-4}, and the usual collision factor of 10^{13} which is but slightly affected by changes in medium and ion size, the energy of activation can be calculated from the kinetic equation (24), and it is 24 kcal. per mole.

(20) L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 1187 (1937).
(21) W. Koskoski, H. Thomas and R. D. Fowler, THIS JOURNAL, **63**, 2451 (1941).

A difference between 89 and 24 leaves 65 kcal. as the apparent solvation energy. This can be compared with the energy of hydration of lithium chloride (152 kcal.) and cesium chloride (103 kcal.).[22] Considering the increase in ionic radius from 0.6 Å. for lithium, 1.7 for cesium[23] to 3.8 for t-butyl and also the probably slightly lower solvating power of formic acid than water, the value of 65 kcal. is reasonable.

The solvation energies of small polar molecules presumably vary but slightly, as is illustrated by the similarities of the rates of ionization in anhydrous and moist formic acid. It seems, therefore, justifiable to consider the solvation of the t-butyl chloride by hydrogen fluoride in toluene solution to contribute about 65 kcal. to the solvation energy. This gives an energy to form a solvated and unseparated ion pair from the nonpolar molecule of 24 kcal. The energy of separation is reduced by the increase in size of the ions due to the layer of solvate molecules. In the metal halide salts, regardless of ion size, an increase in radius of 0.85 Å. for the cation and 0.1 Å. for the anion has been found to correlate the hydration data[24] so that an increase in radius sum from 5.7 to 6.7 Å. for the t-butyl chloride ion pair due to solvation is reasonable. Calculating the energy of the separation as before, it is found to be 17 kcal., and the total energy necessary to form the pair of ions is about 40 kcal. From equation (24) the rate is calculated to be $K = 1 \times 10^{-16}$ moles per mole per second.

Thus, even assuming a large solvation energy the maximum rate for the ionic mechanism is slower by a factor of 10^{11} than that found experimentally.

Free radicals are frequently postulated as intermediates in chemical reactions, and we can calculate the rate of this reaction assuming a free radical as the necessary intermediate. To make the rate as rapid as possible we will assume that the subsequent reaction of the free radical is instantaneous and without energy of activation.

The energy necessary to form free radicals from t-butyl chloride is approximately the energy required to break the carbon–chlorine bond. This can be estimated as follows. Electron diffraction experiments show the carbon–chlorine distance to be about the same in the tertiary chloride as in the primary chloride, about 1.8 Å.[25] The force constant from Raman spectral measurements[26] is 75% of the primary chloride. For a given bond distance it is reasonable to consider the bond strength as proportional to the force constant, that is, that the form of the force law is about the same for the two halides. Since the bond strength

(22) J. E. Mayer and L. Helmholz, *Z. Physik.*, **75**, 19 (1932).
(23) O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 220.
(24) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 109 (1939).
(25) J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **60**, 475 (1938).
(26) W. D. Harkins and R. R. Haun, *ibid.*, **54**, 3920 (1932).

in methyl chloride is 66 kcal.,[27] about 50 kcal. will be required to form the two free radicals from t-butyl chloride. There can be very little reduction of this value by effects such as solvation. Assuming as before that every sufficiently energetic collision results in the formation of a free radical (no steric factor in the kinetic equation) and that the radical so formed instantaneously reacts with toluene to form the product without energy requirements, using a collision factor of 1×10^{13}, and equation (24), the rate is calculated to be $K = 1 \times 10^{-23}$ mole per mole per second. Compared to the determined rate of 1×10^{-5} mole per mole per second, this rate is prohibitively slow.

It might be assumed that the reaction proceeds through a chain mechanism. Chain lengths in solution are usually less than 1000. One case of 50,000 is reported.[28] Assuming then even a chain length of 100,000, the rate of our reaction on a free radical mechanism is 1×10^{-18} mole per mole per second, a factor of 10^{13} slower than the experimental.

In reactions in a medium such as toluene it is generally recognized that the maximum possible concentration of a reaction intermediate, such as a carbonium ion or a simple alkyl free radical, must necessarily be very small. In many hypothetical mechanisms employing these intermediates the attempt is made to overcome this difficulty by assuming that they have only transitory existence. The above calculations show that this assumption cannot overcome the difficulty,

(27) L. Pauling. "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 49.

(28) E. A. Moelwyn-Hughes. "Kinetics of Reactions in Solution," Oxford University Press, London, 1939, p. 262.

as they give the maximum possible rate at which the intermediates can be formed and assume that this rate is the rate of the total reaction, that is, that the intermediate reacts instantaneously and completely as soon as formed to produce the final products.

Summary

A more refined apparatus has been made for and more precise measurements have been made of the reaction of t-butyl chloride and toluene as catalyzed by hydrogen fluoride.

The effect of four promoters, water, methanol, diethyl ether and hexamethylacetone, has been studied. It was found that the rate of the reaction increased with the increasing concentration of the promoter, but that all promoters gave essentially the same effect at the same molar concentration.

It was found necessary to modify the equations used by Sprauer and Simons to correlate the rate measurements in any one experiment, but their equations and theory are essentially confirmed.

The amphoteric medium effect as it contributes to the mechanism of the reaction is substantiated by these measurements and by the effects of the promoters. It is also shown to be reasonable on the basis of other investigations.

A one-step, condensed phase, catalyzed, and promoted reaction as the essential factor in the mechanism is shown to be satisfactory from kinetic considerations and reasonable from energy considerations. Mechanisms utilizing ions or free radicals as intermediates are shown to be untenable from energy considerations.

The X-Ray Investigation of Copper dl-α-Aminobutyrate

BY A. J. STOSICK

As part of the program of investigation of amino acids and proteins undertaken in these Laboratories, it has been of interest to find an improved method of determining the detailed atomic configurations of amino acids by X-rays. At the suggestion of Professor Pauling, crystalline nickel and copper salts of several of the amino acids were prepared, with the hope that the heavy metal atoms in the crystals would in most cases determine the phases of the structure factors. This would enable the investigation to reach the stage of Fourier projections more quickly than for crystals of the amino acids themselves, since the coördinates of the heavy metal atoms very likely would be determined easily. In two cases, those of copper dl-α-aminobutyrate, to be reported in this paper, and of nickel glycine dihydrate, to be

reported in a subsequent paper, these expectations were realized. The proposed method of attack however has its own inherent disadvantage. Final adjustment of parameters utilizing a comparison between calculated and estimated values for the F's is necessarily more difficult because of the preponderant contribution of the heavy atoms to the F's of all but special classes of reflections.

Since the work on copper dl-α-aminobutyrate, begun in 1939, cannot be continued at present, the results which have been obtained are presented here. The x and z parameters of all atoms have been determined, and little doubt remains as to the nature of the bonds in the molecules or the packing of the molecules in the crystal.

Crystals of copper dl-α-aminobutyrate were prepared by placing an excess of cupric oxide or