

Fig. 3.—Amperometric titration of  $\alpha$ -tocopherol in 0.1  $M$  benzoic acid–0.1  $M$  sodium benzoate–0.1  $M$  sodium chloride in 75% ethanol: I, applied potential  $-0.100$  volt; II, applied potential  $-0.075$  volt.

as the solution stood, because of spontaneous reduction of auric gold, but the decrease was no more than 2 to 3% at the end of twenty minutes and it did not appear to affect the titration. At a potential of  $-0.075$  v. the tocoquinone was not reduced, and its reduction at  $-0.1$  v. is negligibly small. Table I gives the results of several titrations.

Two straight lines were obtained, as shown in

Fig. 3. Since the tocoquinone was not reduced at a potential of  $-0.075$  v., only a few readings needed to be made before the end-point. This shortened the time of a titration considerably, and hence the titration could be carried out within thirty to thirty-five minutes. From the data in Table I it follows that  $\alpha$ -tocopherol can be determined, with an accuracy of 0.3%, in a concentration range between  $1 \times 10^{-3}$  and  $3 \times 10^{-4}$   $M$ .

A few amperometric titrations in the benzoate buffer were made with 2,5,7,8-tetramethyl-6-hydroxychroman but the results were about 2% high.

### Summary

$\alpha$ -Tocopherol, in 75% ethanol solution, can be determined rapidly, precisely, and accurately in very low concentrations, by amperometric titration. The dropping mercury electrode is used as an indicator electrode and the solution is titrated with auric chloride. The best buffer found is one which is 0.1  $M$  with respect to benzoic acid, sodium benzoate, and sodium chloride.

MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 26, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

## The Kinetics of the Hydrogen Fluoride Catalyzed Reaction between Toluene and *t*-Butyl Chloride

BY J. W. SPRAUER AND J. H. SIMONS

The recently demonstrated catalytic activity of hydrogen fluoride in promoting condensation reactions<sup>1</sup> has focused attention on the mechanism of such reactions. Kinetic studies can be most readily accomplished and interpreted provided the following conditions are met: (1) the reaction is quantitative, (2) a physical means is available for the determination of the progress of the reaction, (3) the rate is such at an easily controllable temperature that it can be readily determined, and (4) the reaction is homogeneous. The reaction between toluene and *t*-butyl chloride to form *t*-butyltoluene and hydrogen chloride when catalyzed by hydrogen fluoride was found to satisfy the above conditions.

Kinetic experiments were accomplished by varying the concentration of the reactants and the catalyst. The rate of reaction was found to be

first order with respect to *t*-butyl chloride concentration, to be retarded according to an inverse linear function of the hydrogen chloride pressure, to be catalyzed according to a high order of hydrogen fluoride pressure and to be strongly promoted by small amounts of water and methanol. These facts and other details of the kinetic results as well as the known descriptive chemistry of this reaction have been correlated on the basis of postulated mechanisms.

**Preparation of Materials.**—Hydrogen fluoride was prepared by the method described by Simons.<sup>2</sup> It was stored in a copper vessel and was withdrawn for use as the gas.

*t*-Butyl chloride was prepared from technical *t*-butanol and c. p. hydrochloric acid, dried over anhydrous sodium carbonate, and fractionated through an eight to ten plate glass-packed laboratory column. The middle sixty per cent. which had a constant boiling point and refractive index was retained,  $n_D^{20}$  1.3860 observed, 1.3868 in literature. It was stored over anhydrous sodium carbonate and carefully pipetted for use.

(1) Simons, *et al.*, THIS JOURNAL, **60**, 986, 2952, 2953, 2955, 2956 (1938); **61**, 1521, 1795, 1821 (1939); **62**, 451, 485, 1623, 1624 (1940); **63**, 608, 880, 1921 (1941).

(2) Simons, *ibid.*, **46**, 2179 (1924).

Several toluene preparations were used with no noticeable effect upon the kinetics. For some of the experiments technical toluene was repeatedly extracted with sulfuric acid and then fractionated through a twelve to fifteen plate steel-packed laboratory column with retention of the middle fifty per cent., which had about a one-half degree boiling range and  $n_D^{20}$  1.4952 observed, 1.4966 and 1.4969 in literature. For other experiments Eastman Kodak Co. sulfur-free toluene was used after fractionation and retention of the middle fifty per cent.,  $n_D^{20}$  1.4953. Eastman C. P. toluene,  $n_D^{20}$  1.4971, and a sample prepared by the hydrolysis of recrystallized toluenesulfonic acid with subsequent fractionation,  $n_D^{20}$  1.4971, were also used.

Commercial methylcyclohexane was extracted with fuming sulfuric acid and fractionated with retention of the middle seventy per cent.,  $n_D^{20}$  1.4231 observed, 1.4232 in literature.

Hydrogen chloride was prepared from c. p. sodium chloride and sulfuric acid and was dried with freshly fused calcium chloride.

The methanol used was obtained by fractionating the commercial material from sodium methylate.

**The Quantitative Nature of the Reaction.**—The reaction between 0.924 mol of *t*-butyl chloride and 1.69 mols of toluene in the presence of 26 g. of hydrogen fluoride was permitted to proceed at 0° for forty-eight hours until no more gas was evolved. 96.9% of the chlorine of the charge was accounted for as follows: 92.1% in a sodium carbonate absorption tube; 3.79% as hydrogen chloride dissolved in the product; 0.84% as *t*-butyl chloride in the cold traps following the absorption tube; 0.12% as *t*-butyl chloride in the product. A balance on the *t*-butyl group yielded 96.6% recovery as follows: as *p*-*t*-butyltoluene in the product, 95.6%; as *t*-butyl chloride in the product and cold traps, 0.96%. Toluene recovery was determined to be over 97% with lower precision since it was used in rinsing. No evidence of products other than hydrogen chloride and *p*-*t*-butyltoluene was observed.

It is concluded that the reaction proceeded practically quantitatively with formation of a single hydrocarbon product.

**Apparatus.**—A diagram of the apparatus is shown in Fig. 1. The metal system was constructed of copper with joints made with silver solder. Brass  $\frac{1}{4}$  inch S. A. E. flare fittings were used to make connections to the copper tubing. Reaction vessel (A) had a capacity of 630 cc. The valves on the reaction vessel and on the hydrogen fluoride cylinder (D) were special diaphragm valves made of monel metal with a stainless steel spindle. The diaphragm was of copper foil and the diameter of the opening of the valve seat was about  $\frac{1}{32}$  inch. These valves would hold a vacuum within the vessel for several days with less than a millimeter of mercury pressure gain. Valve (G) was a  $\frac{1}{4}$ -inch commercial brass diaphragm valve. Vessels (E) and (F) were used to introduce substances into the system. The glass manometric system was designed to measure air pressures necessary to balance a constant volume manometer (H) against the pressure in the reaction vessel. The right arm of this constant volume manometer was of  $\frac{1}{4}$ -inch nickel tubing soldered to  $\frac{1}{8}$ -inch copper tubing. The copper tubing was wound in a spiral to absorb mechanical shock during the agitation of the reac-

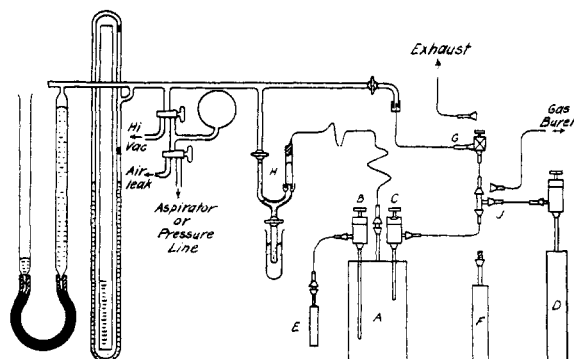


Fig. 1.—Sketch of apparatus.

tion vessel. The nickel tube was sealed with picein wax in a ring seal cup of glass. The glass system was connected through a glass-to-copper seal to the copper system at (G), so that the pressure across (H) could be equalized when necessary. (G) was usually connected to an exhaust line through suitable traps. The pressure was measured with a closed tube manometer with a bore of 10 mm. and a range from zero to two atmospheres. A gas buret with an open tube manometer connected at (J). The reaction vessel was immersed to the valves in a thermostat controlled to  $25.00 \pm 0.03^\circ$ . It was given a rotary motion by hand to effect agitation. Pressure differences were measured with an estimated precision of 0.5 mm. and corrected to mercury at 0°. The manipulation of the constant volume manometer was standardized to obtain reproducible measurements.

**Procedure.**—It was soon learned that variations of hydrogen fluoride pressure and *t*-butyl chloride concentration were not sufficient to evaluate the reaction. Water concentration had to be known and controlled, and initial hydrogen chloride pressure had an effect on the rate. In a few experiments the toluene concentration was varied by mixing it with methylcyclohexane. In two experiments oxygen was added, and in one methanol was added. The general procedure was as follows. The clean reaction vessel was filled to 50 mm. or more hydrogen chloride pressure and allowed to stand for one hour or longer, usually overnight. It was then evacuated. Air was admitted long enough to clear the constant volume manometer of mercury by gravity flow and to connect the containers (F) (40 cc.) and (E) (4 cc.) to valves (C) and (B), respectively. The vessel was evacuated through the constant volume manometer, and the containers were charged and freed of air by repeated freezing and evacuating, the toluene in vessel (F) being evacuated until after the second freezing the system developed less than 0.5 mm. pressure when isolated from the pump. With the system evacuated mercury was admitted to the constant volume manometer.

Toluene was admitted to the reaction vessel by elevating and heating its containing vessel. Valve (C) was then connected to the hydrogen fluoride cylinder (D); and the connections were evacuated, filled from the cylinder, and reëvacuated. The hydrogen fluoride cylinder was occasionally cooled to freeze its contents and evacuated to keep it free from air. It was held at a temperature at which the vapor pressure of hydrogen fluoride was about 100 mm. above the desired pressure in the reaction vessel. The

gas was then admitted in small increments with intermittent agitation. When the pressure had become constant, the *t*-butyl chloride was introduced by elevating its container above the reaction vessel and warming it. The valve (B) was then opened and the timing clock started, the container system and valve heated, the valve closed, and the vessel agitated. The valve was usually open about thirty seconds, and the vessel first agitated within one minute. The *t*-butyl chloride container was then cooled in liquid air, warmed to room temperature, and weighed to determine the net amount introduced.

The loss of hydrogen fluoride pressure to the *t*-butyl chloride container was shown to be negligible by rinsing the container with water and titrating with sodium hydroxide solution.

In most of the experiments 25 cc. of toluene and 1 g. of *t*-butyl chloride were used. Under these conditions the reaction produced a 200-mm. pressure change, one-third of the hydrogen chloride was dissolved in the liquid phase, and the toluene concentration changed from 96 to 98 mole %.

The pressure-time observations were taken by setting the pressure in the glass system above that in the reaction

vessel and observing the time at which the constant volume manometer came to the mark. An attempt was made to have agitated vigorously for at least one-half minute before the pressures became equal. With an experiment of moderate rate agitation was continuous except for the time necessary to make adjustments. In fast runs the agitation was completely continuous. Observations were usually made to 90% completion. In some of the very slow experiments a connection was made from the valve (B) to the tee (J) and the pressure adjusted through valve (G) to the pressure within the vessel in order to minimize leaks past the valve seats.

After the catalytic role of water was recognized, the reasonably dry toluene was further dried by pumping into a liquid air trap about 5% of the toluene that had already been introduced into the reaction vessel. This procedure should have reduced the water concentration by a factor of  $10^7$ , as a differential distillation calculation shows.

Hydrogen chloride and oxygen were introduced, in the experiments in which they were used, from a gas buret after the hydrogen fluoride had been introduced.

In those experiments in which the effect of water was studied, it was introduced in a number of ways: the toluene

TABLE I  
SUMMARY OF KINETIC DATA

| Expt. | Moles of <i>t</i> -butyl chloride | Moles of toluene | Moles of methylcyclohexane (M) or weight in grams of water (W) or methanol (A) <sup>N</sup> | $P_1$ in mm., pressure of toluene and/or methylcyclohexane, water, etc. | $P_2$ in mm., pressure of toluene plus hydrogen fluoride | $P_3$ in mm., $P_2$ plus pressure of hydrogen chloride or oxygen <sup>N</sup> | $P_4$ in mm. | Pressure hydrogen fluoride, $P_{HF}$ | Initial pressure of hydrogen chloride or oxygen $P_{HCl}$ or $P_{O_2}$ | $a$ or $(c)$ | $b$ or $(d)$ | $\frac{a}{b - (P_\alpha - P_0)}$ | $\frac{a}{b + 100 - (P_\alpha - P_0)}$ | $b - (P_\alpha - P_0) - P_{HCl}$ |
|-------|-----------------------------------|------------------|---|---|--|---|--------------|--------------------------------------|--|--------------|--------------|----------------------------------|--|----------------------------------|
| 1     | 2                                 | 3                | 4   | 5   | 6  | 7   | 8            | 9                                    | 10   | 11           | 12           | 13                               | 14                                     | 15                               |
| 1     | 0.0125                            | 0.234            |   | 28.0  | 300.5  |   |              | 272                                  |  |              |              | < 0.001                          |  |                                  |
| 2     | .0126                             | .233             |   | 32.0  | 399.0  |   |              | 370                                  |  |              |              | < .005                           |  |                                  |
| 3     | .0100                             | .234             |   | 30.0  | 481.0  | 717.0(O <sub>2</sub> )  | 651 Est.     | 452                                  | 236(O <sub>2</sub> )   | 1.03         | 285          | .011                             | 0.0052                                 | 97                               |
| 4     | .0112                             | .232             |   | 31.0  | 515.0  |   | 735.5        | 486                                  |  | 2.08         | 275          | .038                             | .0135                                  | 54                               |
| 5     | .0102                             | .233             |   | 30.0  | 514.0  | 699.0(O <sub>2</sub> )  | 895 Est.     | 485                                  | 185(O <sub>2</sub> )   | 1.13         | 250          | .021                             | .0073                                  | 54                               |
| 6     | .0112                             | .234             |   | 28.0  | 512.5  |   | 732.5        | 484                                  |  | 0.985        | 285          | .015                             | .0060                                  | 65                               |
| 7     | .0112                             | .232             |   | 32.0  | 516.5  |   | 739.5        | 488                                  |  | 1.61         | 285          | .026                             | .0099                                  | 62                               |
| 8     | .0099                             | .218             |   | 27.0*   | 512.0  |   | 711.5        | 484                                  |  | 1.19         | 252          | .023                             | .0078                                  | 52                               |
| 9     | .0109                             | .232             |   | 29.0  | 576.5  |   | 797 Est.     | 549                                  |  | 2.65         | 280          | .044                             | .017                                   | 60                               |
| 10    | .0224                             | .465             |   | 32.5  | 596.0  |   | 940.0        | 576                                  |  | 4.70         | 470          | .037                             | .021                                   | 126                              |
| 11    | .0106                             | .233             |   | 29.5  | 630.5  |   | 839.0        | 603                                  |  | 5.45         | 275          | .082                             | .033                                   | 66                               |
| 12    | .0114                             | .228             |   | 27.0*   | 628.0  |   | 854.0        | 600                                  |  | 4.06         | 275          | .083                             | .027                                   | 49                               |
| 13    | .0113                             | .234             |   | 27.0*   | 714.0  |   | 934.0        | 686                                  |  | 11.2         | 290          | .16                              | .066                                   | 70                               |
| 14    | .0102                             | .230             |   | 29.5*   | 786.5  |   | 984.0        | 757                                  |  | 18.9         | 290          | .20                              | .098                                   | 92                               |
| 15    | .0104                             | .231             |   | 27.5*   | 856.0  |   | 1060 Est.    | 828                                  |  | 74.5         | 275          | 1.05                             | .44                                    | 71                               |
| 16    | .0096                             | .232             |   | 30.0  | 602.5  | 702.5   | 890.0        | 574                                  | 100  | 4.28         | 335          | 0.029                            | .017                                   | 47                               |
| 17    | .0104                             | .233             |   | 30.0  | 632.5  | 738.5   | 943.0        | 604                                  | 106  | 5.45         | 340          | .040                             | .023                                   | 29                               |
| 18    | .0118                             | .233             |   | 29.5  | 630.0  | 833.5   | 1061.5       | 601                                  | 204  | 4.17         | 390          | .024                             | .016                                   | -42                              |
| 19    | .0122                             | .233             |   | 36.5  | 637.0  | 842.0   | 1081.0       | 608                                  | 205  | (0.0523)     | (16)         |                                  |  |                                  |
| 20    | .0096                             | .231             |   | 30.0  | 629.0  | 887.5   | 1073.5       | 600                                  | 259  | 5.32         | 350          | .032                             | .020                                   | -95                              |
| 21    | .0109                             | .233             |   | 31.5  | 631.5  | 938.0   | 1152.5       | 603                                  | 307  | 6.03         | 475          | .023                             | .017                                   | -47                              |
| 22    | .0111                             | .233             |   | 30.5  | 630.5  | 1002.0  | 1216 Est.    | 602                                  | { 339}   | 9.15         | 600          | .024                             | .019                                   | 47                               |
| 23    | .0096                             | .231             | 0.011W  | 41.5  | 514.0  |   | 701.5        | 485                                  | { 33 air }   | 1.59         | 230          | .037                             | .011                                   | 42                               |
| 24    | .0109                             | .231             | .018W   | 45.5  | 514.0  |   | 732.5        | 485                                  |  | 13.0         | 285          | .19                              | .078                                   | 66                               |
| 25    | .0110                             | .233             | .050W   | 53.0  | 511.0  |   | 730.0        | 482                                  |  | 4.63         | 250          | .15                              | .035                                   | 31                               |
| 26    | .0109                             | .233             | .099W   | 52.0  | 515.5  |   | 720.0        | 487                                  |  | 4.35         | 255          | .086                             | .029                                   | 50                               |
| 27    | .0111                             | .233             | .234W   | 52.5  | 513.5  |   | 726 Est.     | 485                                  |  | (0.101)      | (0)          |                                  |  |                                  |
| 28    | .0111                             | .233             | .495W   | 52.5  | 514.0  |   | 736.0        | 485                                  |  | (.172)       | (11)         |                                  |  |                                  |
| 29    | .0111                             | .234             | .011W   | 39.0  | 633.5  |   | 853 Est.     | 605                                  |  | (.171)       | (11)         |                                  |  |                                  |
| 30    | .0107                             | .230             | .282A   | 86.0  | 514.5  |   | 731.0        | 486                                  |  | (.275)       | (15)         |                                  |  |                                  |
| 31    | .0065                             | .0066            | .194M   | 49.0  | (614.5)  | 680.5   | 796.0        | 567                                  | 66   |              |              |                                  |  |                                  |
| 32    | .0094                             | .114             | .105M   | 40.0*   | 636.5  |   | 844.5        | 597                                  |  | .56          | 250          | .013                             | .0038                                  | 42                               |
| 33    | .0101                             | .0179            | .194M   | 48.0  | 657.5  |   |              | 610                                  |  |              |              |                                  |  |                                  |
| 34    | .0108                             | .0596            | .141M   | 42.5*   | 871.0  |   | 1122 Est.    | 828                                  |  | 32           | 280          | 1.1                              | .25                                    | 30                               |
| 35    | .0078                             | .0226            | .174M   | 43.5*   | 871.0  |   | 1066.0       | 827                                  |  | (.251)       | (38)         |                                  |  |                                  |

## NOTES FOR TABLE

In the table the first four columns are self explanatory. Column 5 gives the measured pressure,  $P_1$ , of each experiment. This is an apparent vapor pressure of toluene for expts. 1 to 22. The asterisks indicate those experiments in which the toluene was dried by vacuation. The differences in these figures can be attributed to three reasons, presence of air, presence of water, or differences in the technique of admitting mercury to the constant volume manometer and bringing it to level. The last named difference had no effect on subsequent measurements of pressure differences. The vapor pressure of toluene from an extrapolation of the data given in the "International Critical Tables" is 28.5 mm. at 25°. For expts. 23 to 29,  $P_1$  represents the partial pressure of toluene plus water; for expt. 30, the partial pressure of toluene plus methanol; for expts. 31 and 33, the partial pressure of methylcyclohexane; and for expts. 32, 34, and 35, the partial pressure of methylcyclohexane plus that of toluene. Column 6 records the equilibrium pressure  $P_2$  after the addition of hydrogen fluoride; column 7, the pressure  $P_3$  after the addition of hydrogen chloride or oxygen; and column 8, the equilibrium pressure at the end of the reaction,  $P_\alpha$ . The experiments in which  $P_\alpha$  was obtained by a more or less uncertain extrapolation are indicated as being estimated, (Est.).

The partial pressure of hydrogen fluoride, column 9, is calculated as  $(P_2 - 29)$  for the experiments in which toluene was used for the liquid solvent [ $(P_2 - 28)$  when final drying was done by evacuation], or  $(P_2 - 48)$  for the experiments in which methylcyclohexane was used. The partial pressures of water or methanol are assumed negligible after the addition of the hydrogen fluoride. Column 10,  $P_3 - P_2$ , represents the partial pressure of hydrogen chloride or oxygen at the start of the experiment. The constants  $a$  and  $b$  calculated for those experiments whose derivative curves are fitted by Eq. (1) are given in columns 11 and 12 of the table. The constants  $c$  and  $d$  are tabulated in columns 11 and 12 of the table for those experiments in which Eq. (4) is followed.

Expt. 6, toluene was introduced from a closed vacuated system after repeated distillations over sodium-potassium alloy. Expt. 7, toluene was pipetted after drying by passing the vapor over phosphorus pentoxide. Expt. 12, c. p. toluene used. Expt. 14, Eastman sulfur-free toluene used. Expt. 22, air assumed in the hydrogen chloride in amount to agree with solubility deviation. Expt. 23, water vapor (18 mm.) admitted. Expt. 24, introduced 0.23 g. of water with the toluene and evacuated to below saturation. Expts. 25, 26, 27, and 28, water pipetted into toluene container. Expt. 29, toluene presaturated with water at 25°. Expt. 31, hydrogen chloride solubility measurement made on sample before introduction of hydrogen fluoride. Toluene and *t*-butyl chloride introduced together after hydrogen fluoride and methylcyclohexane. 31% of total chlorine remained in the liquid product. Expt. 32, Eastman sulfur-free toluene containing 2-3% benzene used. 1.9% of the total chlorine remained in the liquid product. Expt. 33, *t*-butyl chloride introduced after hydrogen fluoride methylcyclohexane equilibrium was attained and reaction allowed to proceed for 150 minutes. Toluene was then introduced with 2-4 mm. of air. 24% of the total chlorine remained in the liquid product. Expt. 34, c. p. toluene used; 0.8% of the total chlorine remained in the liquid product. Expt. 35, c. p. toluene used; 2.1% of the total chlorine remained in the liquid product.

was saturated with it; water vapor was added through the constant volume manometer; or it was pipetted into the toluene container. Methanol was added by dissolving it in the toluene.

The effect of decreasing the toluene concentration was observed by diluting the toluene with methylcyclohexane. In these experiments the liquid product was found to contain high-boiling chlorine compounds.

In order to ensure that no unusual solubility behavior of hydrogen chloride in the liquid phase would influence the kinetic interpretation, it was ascertained that the Henry's law constant over the extremes of concentration ranges of *t*-butyl chloride, *t*-butyltoluene, and hydrogen fluoride in toluene to be encountered in the kinetic experiments varied less than  $\pm 5\%$ , approximately the precision of measurement.

Also, measurements of the solubility of hydrogen fluoride in toluene indicate no unusual behavior with significance to the kinetic interpretations.

**Results.**—A large number of kinetic experiments were performed. Space does not permit including the detailed measurements from each experiment. In the table a summary of data from thirty-five experiments is given. In Fig. 2 data from typical experiments are plotted. This plot shows the consistency of the measurements in any one experiment. From the time-pressure

curves the slopes,  $dP/dt$ , were obtained graphically; and these were plotted against the uncompleted pressure change,  $(P_\alpha - P)$ , in which

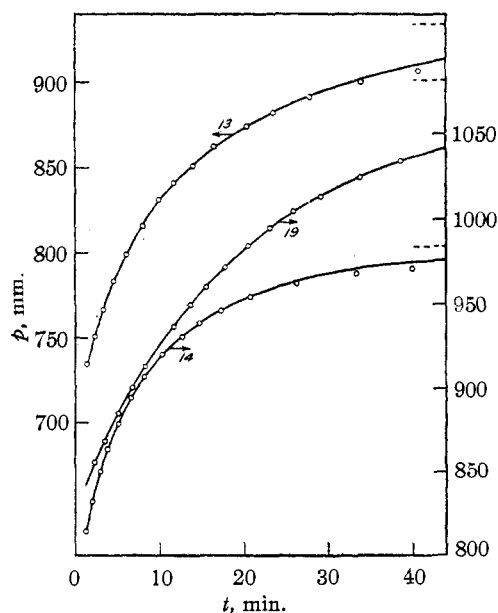


Fig. 2.—Typical kinetic data.

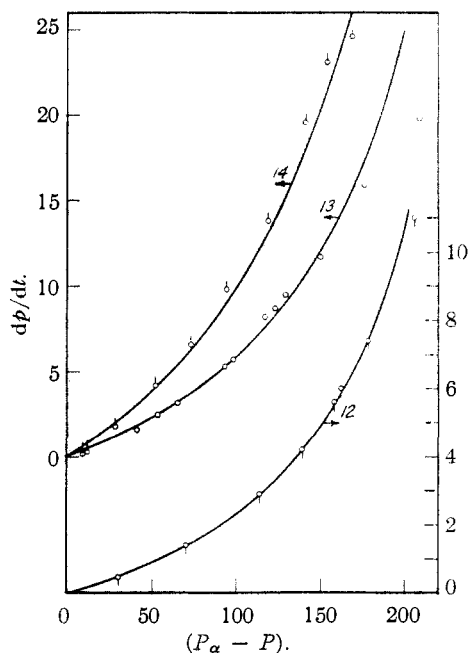


Fig. 3.—Derivative curves of the hyperbolic rate law type.

$P_\alpha$  is the final equilibrium pressure and  $P$  is the pressure at any time. Figure 3 shows the appearance of such curves as obtained from the majority of the experiments. These curves are fitted by the equation of a hyperbola of the form

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

in which  $a$  and  $b$  are constants. These constants were determined for each experiment by graphical estimation by plotting Eq. (1) as a straight line in the variables,  $(P_\alpha - P)/(dP/dt)$  and  $(P_\alpha - P)$ . The preliminary values of  $b$  thus found were then used in the integral of Eq. (1).

$$\ln(P_\alpha - P) - \frac{P_\alpha - P}{b} + \frac{a}{b}t = \text{constant} \quad (2)$$

and were adjusted to obtain a best straight line in the variables,  $\ln(P_\alpha - P) - (P_\alpha - P)/b$ , and  $t$ , after which the constant,  $a$ , was determined by the method of averages. Since the precision is less at the beginning and end of an experiment, in the evaluation of the constants, the intermediate observations were considered the more reliable. From the experiments the exact time for the start of the reaction is indeterminate. However, with  $a$  and  $b$  evaluated an effective zero time can be obtained by extrapolation according to Eq. (3). In Figs. 3 and 2 the full lines are drawn according to Eqs. (1) and (2), respectively, and the evaluated constants. The agreement with the experimental values is seen to be good.

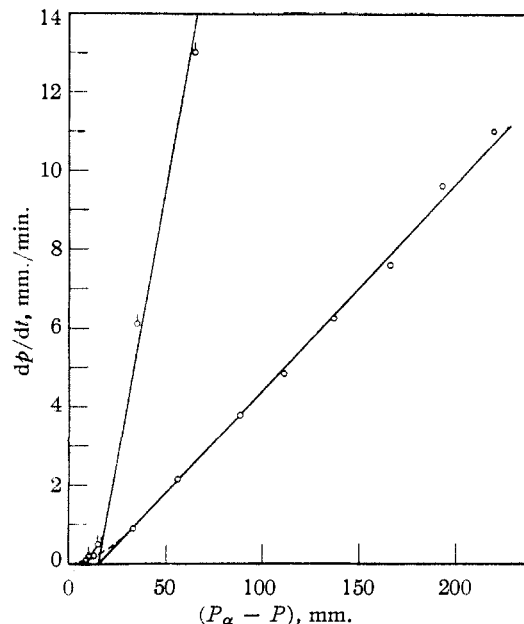


Fig. 4.—Derivative curves of the straight line rate law type, runs 19 and 30.

However, some of the experiments yield straight line derivative curves as shown in Fig. 4. These curves can be represented by the equation

$$dP/dt = c(P_\alpha - P - d) \quad (3)$$

in which  $c$  and  $d$  are constants. From the straight line graph  $d$  was determined, and  $c$  was then determined by applying the integral curve

$$\ln(P_\alpha - P - d) = -ct + \text{constant} \quad (4)$$

to the observed values. The data were extrapolated to an apparent zero time according to Eq. (4) to determine the integration constant by which the empirically fitted values were calculated. The solid lines of Fig. 4 and curve 19 of Fig. 2 are drawn according to Eqs. (3) and (4), respectively, and the determined constants.

**Assumptions and Probable Errors.**—Comparison of the total pressure increase,  $P_\alpha - P_0$ , ( $P_0$  is the initial pressure before introduction of *t*-butyl chloride, *i. e.*,  $P_2$  or  $P_3$ ) with that to be expected from the hydrogen chloride solubility measurements indicated that the tabulated amounts of *t*-butyl chloride are on the average about 5% too high, no doubt as a result of volatilization loss during handling of this material. That this discrepancy was not the result of incomplete reaction was proved repeatedly by failure to detect tertiary chlorine in the product. The chief uncertainty in comparisons of the different experiments is the uncontrollable traces of

water, since as little as 0.01 g. of water had a tremendous effect on the rate of the reaction.

The reaction was not shown to take place at any appreciable rate in the vapor phase or on the walls of the reaction vessel by preliminary experiments in which the liquid phase was not present. The small amount of scattering of the experimental points from a smooth curve, despite the fact that stirring was usually intermittent, shows also that the reaction is homogeneous. It can be shown that vapor-liquid equilibrium is established with sufficient rapidity that the results are not influenced by this process within the expected precision.

In order to interpret the data it is assumed that  $P_\alpha - P$  is linear with the fraction reacted. As the reaction proceeds the hydrogen chloride pressure increases. In addition to this there is a decrease in the pressure of *t*-butyl chloride and a probable increase in the pressure of hydrogen fluoride as a result of a decrease in the number of moles of liquid. There is also a negligible decrease in the toluene pressure and an increase in the *t*-butyltoluene pressure. When estimated for the usual conditions of the experiments, all pressure changes except the hydrogen chloride increase tend to neutralize one another within the precision of the measurements. As the solubility of hydrogen chloride in the liquid phase was shown to follow Henry's law reasonably well, the assumption is justified that  $P_\alpha - P$  is linear with the fraction reacted.

**The Effect of Hydrogen Chloride Pressure and *t*-Butyl Chloride Concentration.**—If the mechanism of the reaction corresponded to the stoichiometric equation, the rate law would be expected to follow a first order equation, since the toluene is used in large excess.  $dP/dt$  would be linear with  $P_\alpha - P$ , and this is found except for the constant  $d$  in those experiments which give straight line derivative curves. However, the hyperbolic derivative curves indicate that in these experiments the reaction is retarded by hydrogen chloride. This interpretation is tested by expts. 16, 17, 18, 20, 21, and 22 in which hydrogen chloride is present at the start of the reaction.

The pressure of hydrogen chloride at any time is given by  $P_{\text{HCl}} + (P - P_0)$  (in which  $P_{\text{HCl}}$  is the initial pressure of hydrogen chloride), so that  $b - (P_\alpha - P)$  of Eq. (1) is a linear function of the hydrogen chloride pressure. Therefore,  $b - (P_\alpha - P_0) - P_{\text{HCl}}$  should be a constant common

to all the experiments. The values of this constant are tabulated in column 15 of the table. The scattering of these data is not too surprising considering that they are fairly small differences of larger numbers, one of which, the value of  $b$ , is a constant obtained in correlating a secondary effect, the deviation from a first order rate law. In addition, the constant  $b$  is not independent of the value of the constant  $a$ , as a result of the method of their determination. To avoid this dependence, values of  $a/[b - (P_\alpha - P_0)]$ , which are recorded in column 13 of the table, may be compared. This constant may be interpreted as a rate constant for a reaction that is first order with respect to *t*-butyl chloride at zero pressure of hydrogen chloride and at a fixed pressure of hydrogen fluoride, since the constant  $a$  is obviously a function of the hydrogen fluoride pressure. The reciprocal of this constant,  $[b - (P_\alpha - P_0)]/a$ , may be expected to be linear with the initial pressure of hydrogen chloride at a fixed pressure of hydrogen fluoride. The data of interest on this point are graphically compared in Fig. 5. The equation of the solid curve of this graph is

$$\frac{a}{b - (P_\alpha - P_0)} = \frac{7.4}{P_{\text{HCl}} + 90}$$

The value of 90 is an approximate agreement with the average value of  $b - (P_\alpha - P_0)$  of expts. 3 to 15, which is 70; and 7.4 agrees roughly with 5.5 and 4.1, the values of the constant  $a$  for expts. 11 and 12 at comparable pressures of hydrogen fluoride. The constants of the dotted curve of this graph are decidedly too high.

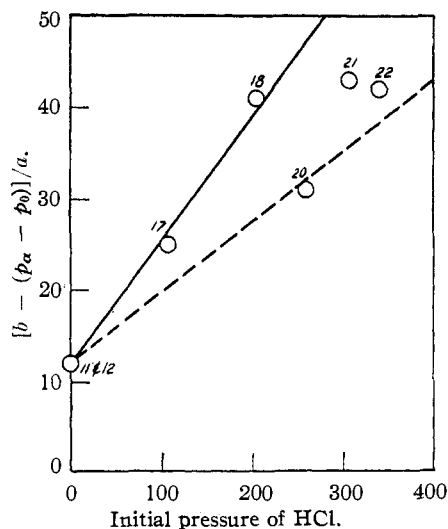


Fig. 5.—The kinetic effect of an initial pressure of hydrogen chloride.

The scattering of the points in Fig. 5 can be attributed chiefly to traces of water; and it was, in fact, in this connection that the water effect was first observed. The acceleration caused by a trace of water is so marked that it tends to mask the retardation caused by an initial pressure of hydrogen chloride. The high order of the catalytic effect of the hydrogen fluoride also increases the difficulty of obtaining a quantitative correlation of the retardation effect of hydrogen chloride. However, the close agreement of the hyperbolic rate law with the experimental data in a single experiment, in which the water concentration and the hydrogen fluoride pressure remain constant, is a good proof of the retardation effect; and the comparison of different experiments as shown in Fig. 5 supports this.

**The Effect of Hydrogen Fluoride Pressure.**—As already pointed out, comparison of the values of  $a/[b - (P_\alpha - P_0)]$  avoids the interdependence of the constants  $a$  and  $b$ . Since this constant effectively is an extrapolation to the limit of the observed data, values of  $a/[b + 100 - (P_\alpha - P_0)]$  may be more consistent and may be interpreted as an apparent first order constant at 100 mm. of hydrogen chloride pressure. Such values are recorded in column 14. These two methods of comparison show little difference in the dependence upon the pressure of hydrogen fluoride as demonstrated graphically in Fig. 6.

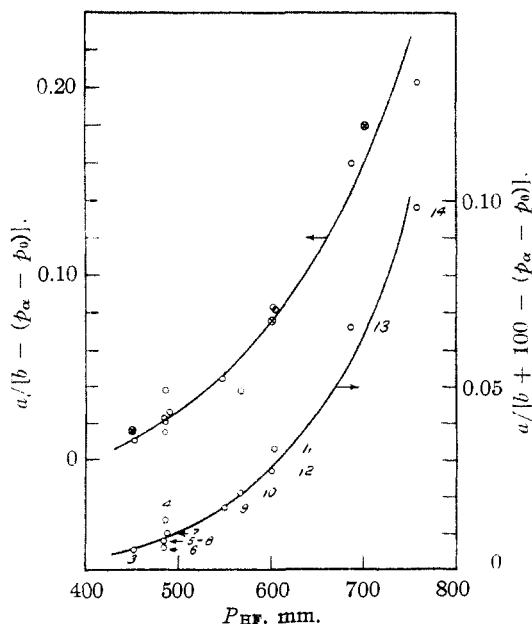


Fig. 6.—The kinetic effect of hydrogen fluoride pressure.

$$\otimes - \frac{a}{b - (p_\alpha - p_0)} = 4.10^{-17} (p - \text{HF})^{5.5}.$$

The rate of the reaction is very sensitive to the hydrogen fluoride pressure, being approximately proportional to  $P_{\text{HF}}^{5.5}$ . The group of experiments around 485 mm. of hydrogen fluoride pressure establishes the limits of reproducibility of the data. Experiment 4 is thought to be fast because of an uncontrolled trace of water.

**The Effect of Oxygen.**—Experiments 3 and 5 show that oxygen has no catalytic effect on the reaction. A very slow oxidation of the copper of the vessel took place in these experiments, but any water produced in this process had little effect on the rate, as most of the reaction was completed before sufficient water was formed. Also, the traces of water formed may be retained on the wall.

**The Effect of Water and Methanol.**—The accelerating effect of water is very marked as demonstrated by those experiments in which water was purposely added. However, as the effect is large for extremely small amounts of water, it was not possible to obtain a good quantitative correlation. Approximately 0.02 g. of water (expt. 24) can apparently increase the rate about ten-fold over the normal (expts. 5, 6, 7, and 8). It appears that a further increase in this amount of water fails to increase the rate greatly, probably as the result of the formation of a second liquid phase (aqueous phase). Experiments 23 and 29 may be the only ones with added water that are homogeneous.

In expt. 30 methanol was added in place of water. It is known<sup>3</sup> that methanol is chemically inert under these conditions. If the water effect is due to its basic character, methanol should also promote the reaction. Experiment 30 shows that it does, the effect being greater than would be caused by the same amount of water, probably because the methanol is more soluble.

The straight line rate law, according to Eq. (3), seems to apply only when water or methanol is present in quantity.

**Effect of Reduced Toluene Concentration.**—A complete investigation of the kinetic effect of toluene concentration was prevented by a complicating side reaction of *t*-butyl chloride at high toluene dilution. Methylcyclohexane, the diluent used, has been shown in this Laboratory to be unreactive under the conditions employed. In expts. 31 and 33 an examination of the reaction products after the reaction had become

(3) Simons and Passino, *THIS JOURNAL*, **62**, 1624 (1940).

very slow revealed the presence of a large portion of high-boiling, chlorine compounds. Obviously, in these cases it would be improper to force the data to a rate law and compare constants with those of the normal alkylation reaction. Similarly, comparison of the constants of expt. 35 is questionable because of the abnormally high value of the constant  $d$ , the behavior being probably related to the formation of the involatile chlorine compounds in expts. 31 and 33. Experiment 34 at 30 mole % toluene and near hydrogen fluoride saturation shows more nearly normal behavior and indicates little effect of the toluene dilution (*cf.* expt. 15). Yet expt. 32 at 50 mole % toluene indicates a considerable decrease in the rate (*cf.* expts. 11 and 12).

**The Action of Hydrogen Fluoride and Hydrogen Chloride on *t*-Butyl Chloride.**—It is known that hydrogen fluoride causes a complex reaction of *t*-amyl chloride with the liberation of hydrogen chloride.<sup>4</sup> The same is also true of *t*-butyl chloride. In the present experiments with a reduced toluene concentration such a reaction probably occurs to yield the high-boiling chlorine compounds noted in expts. 31 to 35. The kinetic behavior of this reaction was observed in expt. 33 in which the reaction was permitted to proceed for some time (150 minutes) before introduction of toluene. Figure 7 shows a comparison of these observations with those of expt. 31. Preliminary experiments in which gaseous hydrogen fluoride was added to *t*-butyl chloride show the same type of curve, and successive increases in hydrogen fluoride pressure caused successive increases in the rate of pressure change. A similar reaction, but less vigorous, was observed in experiments in which hydrogen chloride was added to *t*-butyl chloride.

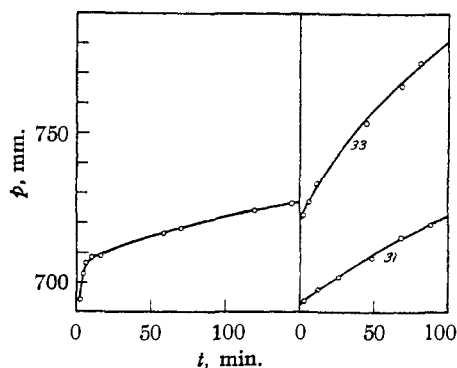


Fig. 7.—The kinetic data of runs 31 and 33.

(4) Simons, Fleming, Whitmore and Bissinger, *THIS JOURNAL*, **60**, 2267 (1938).

**The Effect of Low Hydrogen Fluoride Pressure.**—In expts. 1 and 2 at low hydrogen fluoride pressure initial kinetic effects were observed similar to the initial reaction of expt. 33 as is seen in Fig. 8. Because of these complications the data of these experiments cannot be quantitatively compared with conditions that give faster rates, but a crude estimation of an apparent first order constant has been made according to the initial rate of pressure change, recorded in column 13 of the table.

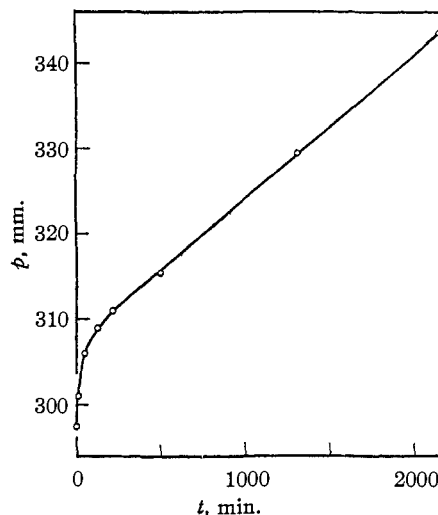
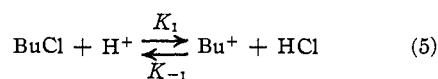


Fig. 8.—The kinetic data of run 1.

**The Mechanism.**—A set of reasonable chemical equations from which the hyperbolic rate law of Eq. (1) can be derived are



BuCl, TH, TBu, and HCl represent *t*-butyl chloride, toluene, *t*-butyltoluene, and hydrogen chloride, respectively.  $\text{H}^+$  and  $\text{H}'^+$  represent acidic species but not necessarily free protons. They are not the same substance and they may represent mixtures of acidic species.  $\text{Bu}^+$  represents an active intermediate which may be considered to be a solvated ion of the butyl group or an active intermediate, such as an ion pair, which upon reaction divides in such a manner as to transfer a butyl ion fragment, if, indeed, the two views are distinguishable.

The rate of formation of  $\text{Bu}^+$  in the above scheme is

$$d[\text{Bu}^+]/dt = K_1[\text{H}^+][\text{BuCl}] - K_{-1}[\text{Bu}^+][\text{HCl}] - K_2[\text{TH}][\text{Bu}^+] \quad (7)$$



The rate of formation of hydrogen chloride is

$$d[\text{HCl}]/dt = K_1[\text{H}^+][\text{BuCl}] - K_{-1}[\text{Bu}^+][\text{HCl}] \quad (8)$$

By eliminating  $\text{Bu}^+$  from Eqs. (7) and (8) we obtain

$$\frac{d[\text{HCl}]}{dt} = \frac{K_1[\text{H}^+][\text{BuCl}]K_2[\text{TH}] + K_{-1}[\text{HCl}](d[\text{Bu}^+]/dt)}{K_{-1}[\text{HCl}] + K_2[\text{TH}]} \quad (9)$$

The concentration of  $\text{Bu}^+$  is probably very small and  $d[\text{Bu}^+]/dt$  is also small. Then Eq. (9) becomes

$$\frac{d[\text{HCl}]}{dt} = \frac{K_1[\text{H}^+]K_2[\text{TH}][\text{BuCl}]}{K_{-1}[\text{HCl}] + K_2[\text{TH}]} \quad (10)$$

If in any one experiment  $[\text{H}^+]$  can be identified as some function of the pressure of hydrogen fluoride, it is a constant.  $[\text{TH}]$  is constant.  $[\text{HCl}] = (P_\alpha - P_0) - (P_\alpha - P)$ , and  $[\text{BuCl}] = \text{constant} (P_\alpha - P)$ . Eq. (10) then becomes

$$\frac{d[\text{HCl}]}{dt} = \frac{dP}{dt} = \frac{K_1'[\text{H}^+]K_2[\text{TH}]/K_{-1}(P_\alpha - P)}{(P_\alpha - P_0) + K_2[\text{TH}]/K_{-1} - (P_\alpha - P)} = \frac{a(P_\alpha - P)}{b - (P_\alpha - P)} \quad (11)$$

in which

$$a = \frac{K_1'[\text{H}^+]K_2[\text{TH}]}{K_{-1}} \text{ and } b = (P_\alpha - P_0) + \frac{K_2[\text{TH}]}{K_{-1}}$$

The initial rate of the reaction when the hydrogen chloride pressure is zero is  $d[\text{HCl}]/dt = K_1[\text{H}^+][\text{BuCl}]$ . This is equivalent to replacing  $P$  with  $P_0$  in Eq. (11) or

$$K'[\text{H}^+] = \frac{a}{b - (P_\alpha - P_0)} \quad (12)$$

If the reaction of Eq. (6) is rapid compared to the reverse reaction of Eq. (5) (the retardation reaction)

$$\frac{d[\text{HCl}]}{dt} = \frac{dP}{dt} = K_1[\text{H}^+][\text{BuCl}] = C[(P_\alpha - P) - d] \quad (13)$$

The constant,  $d$ , does not follow from the derivation, but is added to fit the experiments. It is a first order correction term and is necessary in order to obtain an effective *t*-butyl chloride concentration. It is probably related to the amount of *t*-butyl chloride made non-effective through side reactions.<sup>5</sup> The nature of these is indicated by the high-boiling chlorine-containing compounds found in the methylcyclohexane experiments. This shall be subsequently called polymer chloride.

The empirical Eqs. (1) and (3) which satisfactorily correlate most of the data can thus be de-

rived on the basis of a simple chemical mechanism. There are, however, several points which are not explained by this simple picture. The constant,  $d$ , is one such effect. It can be explained as the *t*-butyl chloride equivalent of the concentration of polymer chloride present. This polymer chloride may remain to the end of the reaction, it may slowly alkylate, or it may depolymerize and alkylate. Simons and Archer<sup>5</sup> have shown that a *t*-butyl polymer may alkylate as such or may produce a *t*-butyl aromatic compound. These two alkylation reactions could give rise to a slow final evolution of hydrogen chloride superimposed upon the main alkylation reaction. Obviously reduction of toluene concentration will favor such side reactions; and this effect is observed in experiments of low toluene concentration. If the alkylation and polymerization reactions have different dependence upon hydrogen fluoride pressure and particularly if the polymerization becomes relatively more important at low hydrogen fluoride pressures, then the initial kinetic effects of expts. 1 and 2 can be explained as being caused by a relatively rapid formation of polymer chloride. However, a relatively rapid reaction between *t*-butyl chloride and hydrogen fluoride to form *t*-butyl fluoride and hydrogen chloride would result in the same kinetic effect. Either of these two alternatives or a combination of them could be used to explain the initial effect in expts. 31 and 33.

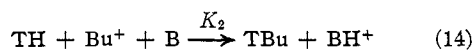
Small deviations from Eq. (1) were observed at relatively high hydrogen fluoride pressure as the reaction neared completion for experiments in which the hyperbolic rate law was otherwise followed. This is seen graphically by the deviation of the observed points from the curves of Fig. 2 and Fig. 3 as  $P_\alpha - P$  approaches zero. This effect may be the result of a small amount of a side reaction such as the ones discussed above or of the failure of the assumption of Eq. (10) toward the end of the reaction.

The high order of rate dependence upon hydrogen fluoride pressure is an interesting observation. It should be emphasized that the rate dependence to approximately  $P_{\text{HF}}^{5.5}$  should in no way be used to evaluate the complexity of the hydrogen fluoride molecule. Hydrogen fluoride undoubtedly enters into the reaction in more ways than as a source of acidity.

At least part of the accelerating effect of the

(5) SIMONS and ARCHER, THIS JOURNAL, 62, 451 (1940).

water and methanol can be correlated by including a basic catalyst in Eq. (6).



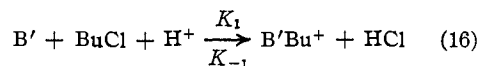
In Eq. (14), B is a basic substance and BH its conjugate acid. Eq. (10) is modified to

$$\frac{d(\text{HCl})}{dt} = \frac{K_1[\text{H}^+][K_2[\text{TH}][\text{B}][\text{BuCl}]}{K_{-1}[\text{HCl}] + K_2[\text{B}][\text{TH}]} \quad (15)$$

If B becomes large Eq. (15) reduces to Eq. (13). It must not be concluded that the reaction would not proceed in the complete absence of water or methanol, for there are present other molecular species with basic properties such as the aromatic compounds and hydrogen fluoride. In other words, the product  $K_2[\text{B}]$  of Eq. (15) may be considered to be linear combination of the products of basic catalytic constants times base concentrations for each molecular species concerned.

It is in the water promoted reactions that the straight line rate law containing the constant,  $d$ , is observed. It is, therefore, probable that the basic substances catalyze the polymerization reactions as much if not more than the alkylation reactions. The small deviations from the hyperbolic rate law were observed at somewhat lower hydrogen fluoride pressures when traces of water were present. This could be accounted for either on the basis of the polymerization reaction or by failure of the primary assumption.

If this effect were merely a hastening of Eq. (14), the observed values of the constant,  $c$ , according to Eq. (13) could not exceed the values of the constant  $a/[b - (P_a - P_0)]$  at comparable hydrogen fluoride pressure. They are in fact very much greater. As the molal solubility of water in toluene at 25° is roughly one-fortieth that of hydrogen fluoride at 600 to 700 mm. pressure, it is hard to believe that water in the toluene could increase the solubility of hydrogen fluoride enough to increase the rate as much as it does—some tenfold. It is also hard to believe that molecular complexes between water and hydrogen fluoride would be more effective acidic catalytic agents than the hydrogen fluoride alone as the complexes themselves would be the result of an acid-base reaction, *i. e.*, a partial neutralization of the hydrogen fluoride by the base, water; also the concentration of such complexes is much less than that of the hydrogen fluoride. The difficulty can be overcome by postulating a basic constituent for Eq. (5) thus—



Eq. (15) becomes

$$\frac{d(\text{HCl})}{dt} = \frac{K_1[\text{H}^+][K_2[\text{TH}][\text{B}']][\text{B}][\text{BuCl}]}{K_{-1}[\text{HCl}] + K_2[\text{B}][\text{TH}]} \quad (17)$$

B' is a base in the broad sense as it acts as an acceptor for the *t*-butyl ion. Just why these reactions require both an acid and a base may be difficult to explain.

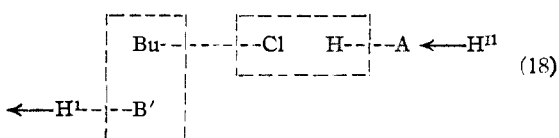
There is another and probably more serious objection to the above mechanism. This objection is common to many hypotheses of the mechanism of liquid phase reactions. We have no knowledge of the existence of the intermediate here represented as the ion  $\text{Bu}^+$ . We do not know whether or not thermal energy is sufficient to form a high enough concentration of them in this medium of low dielectric constant to account for the rate of the reaction. In general we can expect the energy of activation to be too high for this to be true. We do not dodge the issue by postulating these as free radicals, for in this case the energy situation is probably worse. Postulates of complexes with the solvent, etc., also do not completely avoid this difficulty.

In order to overcome these difficulties one of the authors (J. H. S.) wishes to suggest the following hypothesis of the mechanism of the reaction. The fundamental picture is similar to the picture sometimes used to explain the conductivity of hydrogen ions in an aqueous medium, *i. e.*, a proton is accepted by an aggregate of water molecules from a neighbor while at the same time giving a proton, but not necessarily the same one, to another neighbor. Hypotheses of a similar nature have been previously suggested for chemical reactions, for example, in studies of the mutarotation of glucose and tetramethyl-glucose.<sup>6</sup>

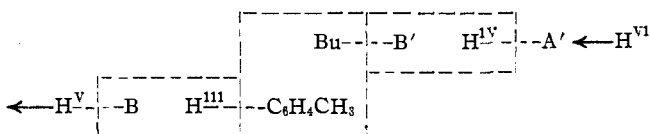
This picture can be used for each of the reactions in which both an acid and a basic constituent are required. The free existence of either an ion or a solvated ion is not necessary, for although a proton is transferred from one molecule to another, the molecule receiving it transfers another proton at the same time to some other molecule and the molecule giving it receives a different proton from a different source. The momentary formation of free ions at the chain ends gives an average concentration of them very much less than if they were the actual intermediates, and this requires a very much lower energy of

(6) Lowy, *J. Chem. Soc.*, 127, 1371 and 1385 (1925).

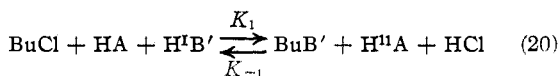
activation. The energy of activation of the transfer mechanism itself will be much lower than that which would be required for any mechanism postulating as intermediates free ions or radicals. If we assume both acid and basic factors in Eqs. 5 and 6 we could picture the processes as



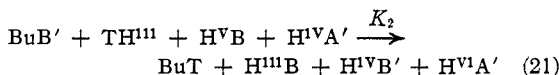
and



There is some difficulty in expressing this picture in terms of chemical equations, but an attempt to do so follows

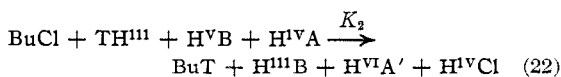


and

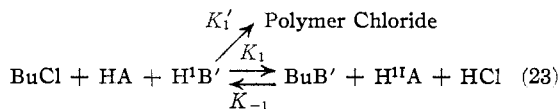


It is obvious that these chemical equations will give the same differential equations in terms of measurable quantities as derived above, Eq. 17 for example. The concentration or effectiveness of the basic constituents, Bs, and the acidic constituents, As, remains effectively constant during the reaction because equilibrium will persist between them.

In Eqs. 20 and 21 a possible reaction of the *t*-butyl chloride directly with the toluene has not been considered. In order to examine this possibility it is assumed that the alkylation reaction takes place only by this one step process and not at all by the two step process which involves a reactive intermediate as represented above. This is similar to representing BuB' in Eqs. 19 and 21 as BuCl or



A simultaneous side reaction also takes place as follows



For completeness Eq. (23) is branched to show the polymerization reaction

$$\frac{d(\text{HCl})}{dt} = K_1[\text{BuCl}][\text{AH}][\text{B}'\text{H}^{\text{I}}] + K_2[\text{BuCl}][\text{AH}^{\text{IV}}][\text{BH}^{\text{V}}][\text{TH}] - K_{-1}[\text{BuB}'][\text{HCl}][\text{AH}^{\text{III}}] \quad (24)$$

BuB' can be assumed to be proportional to the concentration of BuCl for the steady-state condition and at constant acidity, toluene concentration, base concentration, etc.; or  $[\text{BuB}'] = e[\text{BuCl}]$ . Then, as before

$$\frac{dP}{dt} = (P_\alpha - P) \left\{ (K_1[\text{AH}][\text{B}'\text{H}^{\text{I}}] + K_2[\text{AH}^{\text{IV}}][\text{BH}^{\text{V}}][\text{TH}] - K_{-1}e(P_\alpha - P_0)\text{AH}^{\text{III}}) \right\} + (P_\alpha - P)^2 K_{-1}e[\text{AH}^{\text{III}}] \quad (25)$$

For any one experiment

$$\frac{dP}{dt} = (P_\alpha - P)R + (P_\alpha' - P)^2S \quad (26)$$

where *R* and *S* are constants.

In these equations the rate of pressure increase is not restricted to the unretarded rate of the former of the two reactions, and there is no restriction imposed upon the amount of basic catalysis. Eq. (26) is equivalent to the hyperbolic law to a first approximation.

$$\frac{dP}{dT} = \frac{a(P_\alpha - P)}{b - (P_\alpha - P)} = \frac{a}{b(P_\alpha - P)} \left[ 1 + \frac{P - P}{b} + \left( \frac{P - P}{b} \right)^2 + \dots \right]$$

Calculations on the experimental data show that Eq. (26) will correlate the quantitative data of the experiments within the precision of the data. Eq. (26) also reduces to Eq. (3) when the forward reactions are rapid relative to the retardation reaction. In obtaining Eq. (26) from Eq. (25) it has been assumed that the concentration of acidic and also basic constituents remain constant during the course of an experiment. This is true in general, because equilibria between acidic and basic constituents will persist. The constant, *d*, will have the same interpretation as was previously given. The discussion of the other small end effects will not be greatly changed. Equation (23) is represented as having a basic factor. It has been noted in the results that hydrogen chloride catalyzed the decomposition of *t*-butyl

chloride. Mr. E. E. Mushlitz has confirmed this effect recently and has also shown that methanol has an accelerating effect in the presence of hydrogen chloride. As B' may be water or hydrogen fluoride, BuB' may be *t*-butyl fluoride or *t*-butyl alcohol. In either case these would subsequently react with the toluene without further effect upon the pressure.

The assumption that [BuB'] is proportional to [BuCl] is not absolutely rigorous. At the very start of the reaction [BuB'] will rise rapidly to this value. This may explain some of the initial effects in experiments such as 1, 2, 31, and 33 where the initial rate of pressure increase is high. The effect of initial pressure of hydrogen chloride from these equations will take the form  $P_{\text{HCl}} = \text{constant} - \text{constant} [a/(b - (P_\alpha - P_0))]$  whereas in the former treatment this takes the form  $P_{\text{HCl}} = \text{constant} + \text{constant} [(b - (P_\alpha - P_0))/a]$ . The data are not sufficiently accurate to distinguish between the two alternatives.

As the experimental data can be correlated by either a one-step process with a simultaneous side reaction or a two-step process with an active intermediate within the precision of the measurements, it may be considered that either one of the processes or any combination of them may occur within our present knowledge. For both processes there is postulated an acid-base or proton transfer mechanism in which both acid and basic constituents are essential. The As and the Bs may be indistinguishable in some cases, and as the catalytic activity is dependent upon functions of both acidity and basicity, it is in a sense a function of the amphoteric properties of the solution.

This proton transfer mechanism or mutual acid-base catalysis is probably effective in the polymerization of *t*-butyl chloride with hydrogen fluoride.<sup>5</sup> The products formed include *t*-butyl fluoride and a mixture of products which are chiefly tertiary chlorides. These could all be formed by this type of mechanism either as the primary product of the polymerization or as the result of the destruction of the unstable polymers upon distillation. The kinetic data for the water promoted reactions indicate that the polymerization reaction is accelerated by the presence of water. The type of process here postulated may be useful to explain the difference between hy-

drogen chloride and sulfuric or other oxygen containing acids in condensation or polymerization reactions. Hydrogen chloride has only feeble basic properties, whereas the basic properties of the oxygen-containing acids are more pronounced. The oxygen-containing acid molecule such as phosphoric acid has several hydrogen atoms available for transfer as well as several oxygen atoms upon which to receive protons. Thus, despite the higher acidity of hydrogen chloride, phosphoric acid is a more effective acid catalyst for certain reactions. There are, however, condensation reactions which are promoted by hydrogen chloride, particularly when used with solvents which have basic properties such as acetic acid or ethyl alcohol. The strong associating or polymerizing property of hydrogen fluoride coupled with its high acidity probably make it an effective proton transferring substance. Although the mechanism has been postulated for the reaction under study and that one alone, it seems reasonable to expect that a similar mechanism would hold for other hydrogen fluoride catalyzed condensations.

### Summary

The kinetic behavior of the reaction between *t*-butyl chloride and toluene when catalyzed by hydrogen fluoride has been studied by measuring the gas pressure of the evolved hydrogen chloride at constant volume.

The reaction is homogeneous and proceeds at a measurable rate at 25°. Under a wide range of conditions the reaction produces *p-t*-butyltoluene in practically quantitative amounts.

The reaction is first order with respect to *t*-butyl chloride concentration and is approximately proportional to the 5.5 power of the hydrogen fluoride pressure. The reaction is strongly promoted by water and methanol, is retarded by hydrogen chloride, and is unaffected by oxygen.

Mechanisms are proposed to correlate the kinetic data quantitatively and other known chemical facts qualitatively. An hypothetical mechanism is finally proposed which might be called a proton transfer mechanism or a mutual acid-base catalysis.

STATE COLLEGE, PENNSYLVANIA

RECEIVED SEPTEMBER 18, 1941