THE EFFECT OF HALOGEN ATOMS ON THE S_N1 REACTIVITY OF OTHER HALOGEN ATOMS ATTACHED TO THE SAME CARBON ATOM

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THE EFFECT OF HALOGEN ATOMS ON THE S_N1 REACTIVITY OF OTHER HALOGEN ATOMS ATTACHED TO THE SAME CARBON ATOM

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CHAPTER I

INTRODUCTION

Olivier and Weber[1] found the rate of hydrolysis of alpha-chloro-substituted toluenes, in 50% aqueous acetone, to follow the order,

$$C_6H_5CCl_3 > C_6H_5CHCl_2 > C_6H_5CH_2Cl,$$

and found the rate of hydrolysis of $C_6H_5CCl_3$ and $C_6H_5CHCl_2$ to be independent of the concentration of the hydroxide ion present.

For this reason, it has been stated[2] that the hydrolysis proceeds by the carbonium ion mechanism, and that the alpha-halogen atoms stabilize the carbonium ions by resonance, thus increasing their rate of reactivity.

In order to determine if alpha-bromination and alpha-fluorination have the same effect as alpha-chlorination, and to compare the relative magnitude of the effects due to chlorine, bromine, and

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[1] S. C. J. Olivier and A. P. Weber, Rec. trav. chim., 53, 869 (1934).

[2] E. D. Hughes, Trans. Faraday Soc., 37, 603 (1941).

fluorine, it was decided to determine the rates of hydrolysis, in 50% aqueous acetone, of all the alpha-chloro, alpha-bromo, and alpha-chloro-bromo derivatives of toluene, as well as one fluorine derivative, benzodifluorochloride.

CHAPTER II

THEORETICAL DISCUSSION

According to the theory developed by Ingold and Hughes,[1] substitution reactions may be divided into nucleophilic substitution (S_N) reactions and electrophilic substitution (S_E) reactions. Either type reaction may be subdivided into monomolecular (S_N1 or S_E1) or bimolecular (S_N2 or S_E2) reactions. In the case of the nucleophilic substitution reaction, the following examples are illustrative:

$$(S_N1) \qquad RX \xrightarrow{slow} R^+ + X^-$$

$$R^+ + Y \xrightarrow{fast} RY$$

$$(S_N2) \qquad RX + Y \longrightarrow RY + X$$

The chief characteristic of the S_N1 reaction is considered to be the formation of a carbonium ion. Since the reaction of a carbonium ion, such as $C_6H_5CHCl^+$, would be immeasurably fast, it is the formation of this ion that would be the rate-controlling step. Thus, those factors that would influence the formation of the carbonium ion would influence the S_N1 reactivity.

Olivier and Weber[2] found the rate of hydrolysis of $C_6H_5CH_2Cl$,

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[1] A. Edward Remick, Electronic Interpretations of Organic Chemistry (New York: John Wiley & Sons, Inc., 1949), p. 73.

[2] Olivier and Weber, loc. cit.

in aqueous KOH solution, to increase with an increase of concentration of hydroxide ion, while the rate of hydrolysis of $C_6H_5CHCl_2$ and of $C_6H_5CCl_3$, in aqueous KOH solution, was independent of the concentration of hydroxide ion present.

Hughes[3] cites this evidence as proof that in the case of the latter two compounds, the hydrolysis proceeds by the carbonium ion, or S_N1, mechanism. By the line of reasoning outlined in the next few paragraphs, it would seem that an S_N1 mechanism is indeed indicated in the case of the alpha-halo-substituted toluenes, although by no means is actual proof established.

In the hydrolysis of an alkyl halide, in a pure water solvent, the substituting group comes from a source of sufficient quantity that its concentration may be considered to be constant. Thus the reaction will be first order, whether the mechanism is S_N1 or S_N2. If, upon increasing the concentration of the hydroxide ion, the rate of reaction increases, it is safe to consider the mechanism, of that part of the reaction that depends on the hydroxide ion concentration, as being S_N2. On the other hand, if an increase in the concentration of hydroxide ion has no effect on the rate of hydrolysis, it may be considered that (1) the added hydroxide ion is not as strong a nucleophilic agent as is the pure solvent, water, or (2) the mechanism is not S_N2.

Since the hydroxide ion is a stronger base than is water, it would be expected to be a more nucleophilic agent than is water. Also, with most S_N2 reactions, such as the hydrolysis of n-butyl chloride,

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[3] Hughes, loc. cit.

increased hydroxide ion concentration causes an increase in S_N2 reactivity. For these reasons, it seems likely that if an increased concentration of hydroxide ion does not increase the rate of hydrolysis, the mechanism is not S_N2.

This line of reasoning is supported by the work of Petrenko-Kritchenko and Opotsky,[4] who show that methyl halides, which are known to react by an S_N2 mechanism, are more reactive than methylene halides. This indicates that alpha-halogenation decreases the S_N2 reactivity of the methyl halides. With the benzyl halides, alpha-halogenation increases the reactivity. Since this does not follow the order of S_N2 reactions, benzyl halides probably hydrolyze by an S_N1 mechanism.

Due to the lack of more concrete evidence, it will be assumed, for the purpose of this paper, that the hydrolysis of alpha-halo-substituted toluenes, in 50% aqueous acetone, proceeds by an S_N1 mechanism.

Olivier and Weber[5] also found the rate of hydrolysis of the alpha-chloro toluenes, in 50% aqueous acetone, to follow the order,

$$C_6H_5CCl_3 > C_6H_5CHCl_2 > C_6H_5CH_2Cl.$$

Hughes[6] cites this evidence as proof that the alpha-halogen atoms stabilize carbonium ion formation by resonance,

$$C_6H_5\overset{H}{\underset{\oplus}{C}}\text{-}\overline{Cl}| \longleftrightarrow C_6H_5\overset{H}{C}=\overline{Cl}|_{\oplus}.$$

It might then be expected that the tetra-halo derivatives of

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[4] P. Petrenko-Kritchenko and V. Opotsky, Ber., 59B, 2137 (1926).

[5] Olivier and Weber, loc. cit.

[6] Hughes, loc. cit.

methane, with the opportunity of resonance stabilization by three remaining halogen atoms, would hydrolyze by an S_N1 mechanism. The actual unreactivity of these tetra-halo derivatives is explained by Hückel[7] as being due partly to the increased carbon-halogen bond strength, and partly to the shielding effect of the negatively charged halogen atoms.

Another factor that should greatly influence the carbonium ion formation, and thus the S_N1 reactivity, is the inductive effect of the alpha-halogen atoms. The electronegative halogens, as compared to carbon, should make the central carbon atom more positive, thus decreasing the tendency for carbonium ion formation. This tendency should be more apparent with increasing alpha-halogenation, and would oppose the effect of resonance stabilization of the carbonium ion.

The only other apparent factor which might influence the carbonium ion formation is the possibility of "B" strain,[8] caused by the steric effect of the large halogen atoms. This effect, by promoting a less strained carbonium ion, would increase the S_N1 reactivity. However, although this factor cannot be entirely disregarded, an examination of models, based on atomic measurements, shows this effect to be improbable.

For the purpose of this investigation, it will be necessary to make two more assumptions. First, we will assume that the replacement

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[7] W. Hückel, Ann., 540, 274 (1939).

[8] H. C. Brown and R. S. Fletcher, J. Am. Chem. Soc., 71, 1845 (1949).

of the first halogen atom is the rate-controlling step. In agreement with this assumption, it is known that benzoyl chloride, a possible intermediate in the hydrolysis of $C_6H_5CCl_3$, hydrolyzes at a rate too fast to be measured under the conditions used in this investigation. It seems likely that a compound containing a halogen atom and a hydroxyl group, on the same carbon atom, would decompose at a rate too rapid to be measured, since no such compound has been reported to be isolated. This makes it even more likely that the replacement of the first halogen atom is the rate-controlling step. Secondly, we will assume that in the case of a compound containing both bromine and chlorine, the bromine will be replaced initially, rather than the chlorine. This second assumption is in accord with the fact that in nucleophilic substitution reactions, bromides have invariably been found to be much more reactive than the corresponding chlorides. However, it must be realized that this relation between the reactivities of bromides and chlorides will not necessarily be true for a compound containing both bromine and chlorine, since the environment of the bromine in $C_6H_5CHClBr$ is not the same as the environment of the chlorine in the same compound.

In the case of the single fluorine compound, it will be assumed that the chlorine atom is replaced initially.

In view of the considerations discussed above, it would be difficult to accurately predict the effect of halogen atoms on the S_N1 reactivity of other halogen atoms attached to the same carbon atom. However, some conclusions can be drawn.

The data reported for the hydrolysis of the chlorine series,

$C_6H_5CH_2Cl$, $C_6H_5CHCl_2$, $C_6H_5CCl_3$, shows that the effect of a chlorine atom on the S_N1 reactivity of another chlorine atom attached to the same carbon atom, as opposed to the effect of a hydrogen atom on the S_N1 reactivity of a chlorine atom attached to the same carbon atom, is to increase the S_N1 reactivity. This increased S_N1 reactivity indicates that resonance stabilization of the carbonium ion has a greater effect on S_N1 reactivity than does the inductive effect of the chlorine atoms of the carbonium ion.

Since we have assumed that the rate-controlling step in the hydrolysis of halides is the replacement of the first halogen atom, and that in the case of chloro-bromides this first halogen atom would be bromine, hydrolysis would give an identical environment for all of the alpha-chloro-bromo-substituted derivatives of toluene. Thus, the only change in reactivity would be due to the nature of the carbonium ion formed. A comparison of the rates of hydrolysis of the series $C_6H_5CBr_3$, $C_6H_5CClBr_2$, $C_6H_5CCl_2Br$, should give the information desired. In the case of fluorine, the only possible comparison would be between the benzodifluorochloride, and benzotrichloride.

Due to the fact that fluorine is in an earlier period of the periodic table than is chlorine, fluorine should have a greater tendency for double bond formation than chlorine. For the same reason, chlorine should have a greater tendency for double bond formation than bromine. Since the hydrolysis of the chlorine series has indicated that resonance stabilization of the carbonium ion by double bond formation is predominate over the opposing inductive effect of the alpha-chloro atoms, it would be expected that the results of the hydrolysis of the various

alpha-halo derivatives of toluene would show, as regards the effect of halogen atoms on the S_N1 reactivity of other halogen atoms attached to the same carbon atom, the following order,

$$\text{Fluorine} > \text{Chlorine} > \text{Bromine}.$$

CHAPTER III

EXPERIMENTAL

A. PREPARATION OF MATERIALS

It was found necessary to synthesize the majority of the alpha-halo toluenes used in this work. The preparation and purification of these compounds, as well as the purification of the available compounds, is given in the following section.

Benzyl chloride. Benzyl chloride (Eastman Kodak Company, White Label) was fractionated once, at atmospheric pressure, using a Todd Scientific Company Precise Fractionation Assembly, of 40 theoretical plates. The 36 inch column, with an inside diameter of 12 mm., was packed with glass helices, and equipped with an upper and a lower variable heating element. From the still-head extended an all-glass take-off device, equipped with a stop-cock, by means of which the reflux ratio could be adjusted.

The main fraction distilled at 178-179°C (745 mm.), as compared to 179.35°C (760 mm.), reported by Timmermans.[1]

Benzal chloride. Benzal chloride (Eastman Kodak Company, White Label) was fractionated three times, at atmospheric pressure, using the Todd still (page 10).

The main fraction distilled at 206-207°C (740 mm.), as

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[1] J. Timmermans, Chem. Centr., 618 I (1914).

compared to 205.2°C (760 mm.), reported by Timmermans.[2]

Benzotrichloride. Benzotrichloride (Eastman Kodak Company, White Label) was fractionated twice, under reduced pressure, using the Todd still (page 10).

The main fraction distilled at 85-86°C (8 mm.), as compared to 105°C (25 mm.), reported by Timmermans.[3]

Benzyl bromide. 918 grams (9.96 moles) of toluene (Eastman Kodak Company, Practical Grade) was heated to reflux in a 3-liter, round-bottomed, 3-necked flask, equipped with a reflux condenser and a dropping funnel. All glassware was Pyrex, with ground-glass, standard-taper joints. 1120 grams (7 moles) of bromine was placed in the dropping funnel, and added to the refluxing toluene during a period of 2.5 hours. The bromine was added at such a rate that at no time was there a large amount of unreacted bromine present in the reaction flask. A 300-watt, unfrosted, tungsten bulb, equipped with an asbestos reflector, was placed very close to the reaction flask. To the top of the condenser was attached a calcium chloride drying-tube, from which ran a rubber tube to a glass funnel inverted over a beaker of water, for the purpose of absorbing the hydrogen bromide evolved during the reaction. The heating element consisted of a Glas-col mantle, controlled by a variable transformer.

Upon completion of the reaction, the reflux condenser was

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[2] Loc. cit.

[3] Loc. cit.

replaced by a simple fractionation column, and the mixture fractionated under a slight vacuum. This slight vacuum was maintained by extending a rubber tube from one neck of the reaction flask to a water aspirator. A suitable safety trap was placed between the flask and the aspirator. In the other neck of the flask was placed a cork, through which a long piece of glass tubing extended well into the liquid in the flask. By this means, a constant pressure was maintained slightly below atmospheric pressure. A few pellets of sodium hydroxide were added to the mixture, to absorb any free hydrogen bromide.

450 ml. of material distilled over during the first 2 hours, at a temperature of 90-110°C (the majority distilled at 108°C). The temperature then rose rapidly to 190°C, but began to drop when put on total reflux. About 150 ml. of material was taken as fore-run, as the temperature fell slowly but steadily. As it was evident that this falling temperature, at total reflux, was caused by decomposition, it was decided to take the main fraction rather rapidly. Accordingly, 690 grams of distillate was collected at a temperature of 195-197°C, at a rate of 3 drops per second, during a period of 2.5 hours.

This main fraction (b.p. 195-197°C) was fractionated at a pressure of 9 mm., using a 36 inch, vacuum-jacketed column, with an inside diameter of 12 mm. The column was packed with glass helices and wrapped with glass wool, but not equipped with a heating element. The column was provided with a device by means of which the reflux ratio could be adjusted.

10 ml. of a fore-run at 73-76°C was discarded, and the main

fraction distilled at 76°C (9 mm.), as compared to 198-199°C (760 mm.), reported by Kekulé.[4]

Using an Abbé Refractometer, the index of refraction was obtained, n_D^{22} = 1.5749, as compared to n_D^{22} = 1.5742, reported by Baker and Nathan.[5]

Benzal bromide. The residue from the simple distillation, under slight vacuum, of benzyl bromide (page 12) was subjected to fractional distillation under reduced pressure, using the apparatus described on page 12.

A middle fraction of 110-115°C (8 mm.) was refractionated, using the same apparatus.

The main fraction distilled at 108-109°C (6 mm.), as compared to 156°C (23 mm.), reported by Curtius and Quedenfeldt,[6] and the conflicting temperature, 105-107°C at 12-15 mm., reported by Vorländer.[7]

The melting point was 0-1°C.

Using an Abbé Refractometer, the index of refraction was obtained, n_D^{22} = 1.6106, as compared to n_D^{22} = 1.541, reported by Curtius and Quedenfeldt.[8]

Using a Pyrex specific gravity bottle, equipped with a ther-

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[4] F. A. Kekulé, Ann., 137, 190 (1866).

[5] J. W. Baker and W. S. Nathan, J. Chem. Soc., 519 (1935).

[6] T. Curtius and E. Quedenfeldt, J. prakt. Chem., (2) 58, 389 (1898).

[7] D. Vorländer, Ann., 341, 22 (1905).

[8] Curtius and Quedenfeldt, loc. cit.

mometer, and with a capacity of 9.86 ml., the density was obtained, $d^{28} = 1.8365$, as compared to $d^{15} = 1.51$, reported by Curtius and Quedenfeldt.[9]

From a comparison of the above physical constants, as well as other reported properties, it is apparent that Curtius and Quedenfeldt had not obtained the correct compound. Vorländer's work supports this conclusion.

Benzotribromide. Benzyl bromide was photobrominated in the apparatus described on page 11.

565 grams (3.3 moles) of benzyl bromide (page 11) was heated to 120°C. By means of the dropping funnel, 1015 grams (6.35 moles) of bromine was added to the benzyl bromide over a period of 45 minutes. During the reaction, some bromine was carried off with the hydrogen bromide. At the end of three more hours, the reaction was apparently complete, and the heating was discontinued.

Simple distillation of the clear, reddish reaction mixture was attempted. The mixture began to boil at 130-160°C, but so much decomposition occurred, the operation was discontinued. Some reddish liquid, as well as colorless, had distilled over, and a large amount of crystals had collected in the still-head and condenser.

Some of the crystals from the still-head were recrystallized from hexane, and found to melt at 195-198°C. A solution of these crystals in acetone gave a precipitate almost immediately with

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[9] Loc. cit.

alcoholic silver nitrate, but did not react with sodium iodide in acetone even after standing for 5 minutes at room temperature. The crystals were insoluble in water and in dilute alkali, slightly soluble in hexane and in acetone, and soluble in chloroform. The crystals did not decolorize bromine in chloroform.

The reaction mixture was filtered, and distilled in the apparatus described on page 12.

Distillation commenced at 77°C, but the temperature rose very rapidly. At a temperature of 87 ± 2°C (2 mm.), 100 ml. of distillate was collected and discarded. The temperature then rose to 123°C, at the same pressure. 20 grams of this distillate was discarded as fore-run, and the next 120 grams collected as the main fraction. During this collection, the temperature and pressure both varied somewhat, but it was judged that the average would be 123°C (4.5 mm.), as compared to 130-140°C (2 mm.), reported by Heble, Nadkarni, and Wheeler.[10]

The last portion of this fraction solidified in the condenser, and had to be melted with steam. During the entire distillation, bromine was constantly evolved, giving the distillate a reddish color. The entire distillate solidified at room temperature.

The flask of distillate was placed in an evacuated desiccator for three hours, but bromine fumes were still being given off. The distillate was then dissolved in 50 ml. of hexane, and boiled. This

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[10] L. S. Heble, D. R. Nadkarni, and T. S. Wheeler, J. Chem. Soc., 1322 (1938).

caused the reddish solution to change to a light yellow color. On standing in a refrigerator for several days, large white crystals were precipitated. These crystals were decanted from the mother liquor, washed with hexane, and filtered under a rubber dam. They were then placed in an evacuated desiccator. After drying, they gave a melting point of 56-57°C, as compared to 60°C, reported by Heble, Nadkarni, and Wheeler.[11]

A weighed sample was placed in a flask, hydrolyzed, and the equivalent weight, as an acid obtained:

82.21 Calculated
81.55 Found

Benzal chlorobromide. Benzyl chloride was photobrominated in the apparatus described on page 11.

1000 grams (7.9 moles) of benzyl chloride (page 10) was heated to reflux. 800 grams (5 moles) of bromine was placed in the dropping funnel, and added to the reaction flask during a period of 1 hour.

The reflux condenser was then replaced by a Claisen still-head and condenser, and the reaction mixture distilled at atmospheric pressure. Distillation commenced at 175°C, but the temperature rose rapidly to 177°C. This portion was discarded as fore-run. 250 ml. of distillate was collected at 177-183°C, and was discarded as unreacted benzyl chloride. The temperature then began to drop, and the distillation was discontinued.

The residue was subjected to vacuum distillation in the Todd

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[11] Loc. cit.

still (page 10). A middle fraction was taken at 93-94°C (7 mm.), as compared to 92-95°C (2-3 mm.), reported by Heble, Nadkarni, and Wheeler.[12]

To a weighed sample of the benzal chlorobromide was added standard silver nitrate solution. The excess silver was titrated with standard potassium thiocyanate solution, and the value for side-chain halogen obtained:

56.14 Calculated
55.66 Found

The following physical properties were obtained:

Melting point = -11 to -8°C
Density, d_4^{25} = 1.5478
I.R., n^{25} = 1.5808

Benzochlorodibromide. Benzal chloride was photobrominated in the apparatus described on page 11.

127 grams (0.79 moles) of benzal chloride (page 10) was heated to a temperature of 140°C, and stirred. 127 grams (0.79 moles) of bromine was placed in the dropping funnel, and added to the reaction flask during a period of 3 hours. The resultant mixture was distilled from a Claisen flask at about 15 mm. pressure, then subjected to vacuum distillation in the Todd still (page 10).

About 50 ml., of several fractions between 82°C (6 mm.) and 110°C (4.5 mm.), was discarded as fore-run. 10 ml. of a main fraction

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[12] Loc. cit.

was taken at 110-111°C (4.5 mm.), as compared to 98-103°C (1 mm.), reported by Heble, Nadkarni, and Wheeler.[13]

The value for side-chain halogen (page 17) was obtained:

71.10 Calculated
71.01 Found

The following physical properties were obtained:

Melting Point = 27-30°C

Density, d_4^{32} = 1.9017

I.R., n^{32} = 1.6089

Benzodichlorobromide. 266 grams (1.4 moles) of benzotrichloride (page 11), 490 grams (4.8 moles) of dry sodium bromide (J. T. Baker Company, U. S. P.), and 20 grams (0.0056 moles of mercuric bromide (J. T. Baker Company, C.P.) were placed in a 100 ml., 3-necked, standard-taper flask, equipped with a stopper, reflux condenser, and a mercury sealed stirrer. The oil bath, in which the flask was placed, was heated to a temperature of 150°C, and the contents of the flask stirred.

At the end of 5 minutes, the colorless solution had turned to a yellow-brown color, which slowly turned to a dark reddish-brown color. At the end of 140 minutes, the reaction seemed complete, so the heating and stirring was discontinued. The mixture was decanted through a sintered suction funnel, and the residue washed with an amount of carbon tetrachloride twice the volume of the original filtrate.

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[13] Loc. cit.

The carbon tetrachloride solution was distilled at atmospheric pressure. The first fraction consisted of carbon tetrachloride, bromine, and 15 ml. of liquid that was discarded as fore-run. The next 70 ml. was taken as the main fraction. A residue of approximately 70 ml. was discarded.

The main fraction from the simple distillation was subjected to vacuum distillation in the Todd still (page 10). The first 21 ml. distilled at 78-84.7°C (5 mm.), and was discarded as fore-run. The next 22 ml. distilled at 84.5-85°C (5 mm.). This fraction gave a density value corresponding to that of benzotrichloride, and was discarded. The main fraction distilled at 98°C (4.2 mm.), as compared to 88-94°C (1 mm.), reported by Heble, Nadkarni, and Wheeler.[14]

The value for the equivalent weight, as an acid (page 16), was obtained:

60.00 Calculated
60.87 Found

The following physical properties were obtained:

Melting Point = 4-7°C

Density, d_4^{28} = 1.6379

I.R., n^{28} = 1.5846

Benzodifluorochloride. A sample of benzodifluorochloride was obtained through the courtesy of The Hooker Electrochemical Company. The sample was not repurified.

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[14] Loc. cit.

The index of refraction was obtained, $n^{24.7} = 1.4622$. Also, the density was obtained, $d^{26.2} = 1.2437$, as compared to $d^{13} = 1.25445$, reported by Swarts.[15]

[15]Swarts, Fred., Chem. Centr., 26 II (1898).

B. PROCEDURE

Approximately 0.01 moles of the halide, weighed to the nearest 0.0001 gram on a Fisher Company Analytical Balance, was placed in a 100 ml. Pyrex volumetric flask, and diluted to the calibrated mark with redistilled acetone.

25 ml. of distilled water and 20 ml. of redistilled acetone were placed in each of several 100 ml. Pyrex volumetric flasks. The flasks were placed in a water bath and allowed to come to thermal equilibrium (approximately 45 minutes). The water bath was a Sargent Constant Temperature Water Bath, Model S-84805, equipped with a combination stirrer and heating element. The heating element was controlled by a mercury thermostat, with an accuracy of $\pm 0.02^{\circ}$.

By means of a calibrated Pyrex pipette, 5 ml. of the halide-acetone stock solution was placed in each of the thermally equilibrated water-acetone flasks, and the contents well shaken while still in the bath. The beginning of the reaction was taken as the time when the pipette, delivering the halide-acetone solution to the reaction flask, was half-emptied. The clamp holding the flask in the water bath had been loosened, so that the flask could be shaken immediately upon completion of the addition of the halide-acetone solution to the reaction flask.

At predetermined intervals, the reaction flasks were removed from the water bath and plunged immediately, with vigorous swirling, into a dry ice-acetone bath. This brought the contents of the flask to $-5^{\circ}C$ in 25 seconds. The end of the reaction was taken as that time

when the reaction flask entered the dry ice-acetone bath.

Two drops of phenolphthalein indicator solution was then added, and the contents of the flask titrated with standard NaOH solution (approximately 0.05 N). During the titration, the contents of the flask were shaken vigorously, and the addition of the standard NaOH solution so timed that the end-point was reached as the last frozen crystals of the solution had melted. As an aid to rapid titration, the approximate amount of standard NaOH solution needed had been previously calculated.

A blank was determined for each halide-acetone stock solution prepared. This was accomplished by freezing the contents of one of the water-acetone reaction flasks, adding 5 ml. of the halide-acetone stock solution, with 2 drops of phenolphthalein indicator solution, and titrating with the standard NaOH solution.

In the case of the slowly hydrolyzing halides, such as benzyl chloride and benzyl bromide, the cooling of the solution before titration was omitted.

C. CALCULATION OF RATE CONSTANTS

The rate constants were calculated by means of a modification of the first order rate equation,[16]

$$k = \frac{2.303}{t} \log \frac{ml_\infty}{ml_\infty - ml_t},$$

where t is the reaction time in minutes, ml_t is the ml. of base required to neutralize the acid formed in time t, and ml_∞ is the ml. of base required to neutralize the total amount of acid formed in the reaction.

The value for ml_∞ may be obtained by calculating the ml. of base required to neutralize the theoretical amount of acid formed in the hydrolysis reaction. It was this method that was used in calculating the rate constants presented in this paper.

An alternative method for obtaining the value of ml_∞ is to titrate the contents of one of the reaction flasks, when the reaction is at least 99.99% completed. It was this method that was used in calculating the rate constants presented in the original publication of this work.[17]

The value of the appropiate blank was, of course, subtracted from each titration value.

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[16] Farrington Daniels, Outlines of Physical Chemistry, (New York: John Wiley & Sons, Inc., 1948), p. 345.

[17] Jack Hine and Donald E. Lee, J. Am. Chem. Soc., 73, 22 (1951).

CHAPTER IV

DISCUSSION OF RESULTS

A. EXPERIMENTAL RESULTS

The following section consists of a series of tables in which are listed the results of the hydrolyses of the alpha-halogenated toluenes.

In each table, the fundamental data are given before the tabulation of experimental results.

The fundamental data are followed by a summary, in tabulated form, of the results of the hydrolysis reaction concerned. This summary consists of a solution number, the length of time of reaction, the net amount of standard base required for neutralization of the acid formed during the reaction, the per cent completion of the reaction, and the rate constant as calculated on page 23. In some of the tables are listed the observed infinity points, obtained from the neutralization values at 99.99 per cent completion of the reaction.

Following this tabulation is found the average value of the rate constant, which, however, is given only in the cases where results were consistent.

For the calculations of the average rate constants, only those constants were used that fell within the limits of 10 to 85 per cent completion. Also, the constants that deviated by more than six times

the average deviation were omitted from the average. All omitted constants are indicated in the tables.

Since a few of the tables show a variance from normal procedure, the following explanations are given:

Table I, $C_6H_5CH_2Cl$ at 30°C. Before the first point could be taken, the temperature rose in the water bath. Therefore, one of the solutions was titrated at 4993.5 minutes, and the obtained value used as a blank for solutions 1, 2, 3, and 4.

After taking the above points, the power supply failed for several hours, thus necessitating the preparation of new solutions for 5, 6, and 7.

Table V, $C_6H_5CHCl_2$ at 30°C. In spite of attempts to purify the $C_6H_5CHCl_2$ by three fractional distillations, the initial rate of hydrolysis showed that a highly reactive substance, probably C_6H_5COCl, was still present. Accordingly, the first 5 per cent of the reaction was disregarded, and a point at 101 minutes was taken as the starting point of the reaction.

Table VI, $C_6H_5CHCl_2$ at 45°C. The same condition was found to be present as with $C_6H_5CHCl_2$ at 30°C. Due to the increased temperature, a point at 25 minutes was found to be sufficient for the starting point of the reaction.

Tables VIII and IX, $C_6H_5CCl_3$ at 30°C. The results shown by these tables made it necessary to purify the $C_6H_5CCl_3$. The correct constants, after redistillation of the compound, are in Table X.

Table XVI, $C_6H_5CHBr_2$ at 45°C. It was necessary to prepare more stock solution for solutions 5 and 6.

Table XXXII, $C_6H_5CF_2Cl$ at 45°C. Due to lack of time, it was impossible to obtain sufficient points for an adequate range of reaction time.

Table XXXIII, $C_6H_5CF_2Cl$ at 60°C. After the first three points were taken, the temperature of the water bath rose, making it necessary to prepare new solutions for the remaining points.

TABLE I

HYDROLYSIS OF $C_6H_5CH_2Cl$ at 30°C

For points 1, 2, 3, and 4. 5 ml. of an acetone solution of $C_6H_5CH_2Cl$ (1.2610 gm. per 100 ml.) was used, giving an original concentration of 0.09968 M.

A point at 4993.5 minutes (1.47 ml. 0.0441 N NaOH) was taken as the starting point, giving a calculated infinity point = 10.01 ml. 0.0441 N NaOH.

For points 5, 6, and 7. 5 ml. of an acetone solution of $C_6H_5CH_2Cl$ (1.2724 gm. per 100 ml.) was used, giving an original concentration of 0.1006 M.

Calculated infinity point = 11.40 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	4235	0.88	8.8	0.2174*
2	10031	2.01	20.1	0.2235
3	10587	2.08	20.8	0.2201
4	10591	2.07	20.7	0.2188
5	15765	3.47	30.4	0.2303
6	26021	5.08	44.6	0.2267
7	37009	6.39	56.1	0.2222

*Omitted from average.

Average $k = 0.2236 \pm 0.0033 \times 10^{-4}$ min.$^{-1}$

TABLE II

HYDROLYSIS OF $C_6H_5CH_2Cl$ at 45°C

5 ml. of an acetone solution of $C_6H_5CH_2Cl$ (1.2724 gm. per 100 ml.) was used, giving an original concentration of 0.1005 M.

Calculated infinity point = 11.40 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	890	1.17	10.3	1.217
2	2495	2.84	24.9	1.148
3	4280	4.44	39.0	1.153
4	7460	6.56	57.5	1.149
5	11350	8.48	74.4	1.200

Average $k = 1.174 \pm 0.028 \times 10^{-4}$ min.$^{-1}$

TABLE III

HYDROLYSIS OF $C_6H_5CHCl_2$ at 30°C

5 ml. of an actone solution of $C_6H_5CHCl_2$ (1.6502 gm. per 100 ml.) was used, giving an original concentration of 0.1025 M.

Calculated infinity point = 20.41 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$	Observed infinity
1	15	0.20	1.0	6.571	19.37
2	31	0.55	2.7	8.811	19.68
3	1355	6.88	33.7	3.035	20.47
4	2853	10.96	53.7	2.699	20.81
5	5826	16.98	83.2	3.062	21.61

Not used in summary

TABLE IV

HYDROLYSIS OF $C_6H_5CHCl_2$ at 30°C

5 ml. of an acetone solution of $C_6H_5CHCl_2$ (1.5208 gm. per 100 ml.) was used, giving an original concentration of 0.09447 M.

Calculated infinity point = 18.81 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4	Observed infinity
1	76	0.66	3.5	4.706	
2	1015	4.24	22.5	2.290	19.14
3	4154	11.87	63.1	2.401	19.16
4	7089	15.35	81.6	2.389	
5	7091	15.38	81.8	2.400	
6					19.09

Not used in summary

TABLE V

HYDROLYSIS OF $C_6H_5CHCl_2$ at 30°C

5 ml. of an acetone solution of $C_6H_5CHCl_2$ (1.5630 gm. per 100 ml.) was used, giving an original concentration of 0.09707 M.

A point at 101 minutes (1.00 ml. 0.0502 N NaOH) was taken as the starting point, giving a calculated infinity point = 18.34 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4
1	49	0.17	1.0	1.908*
2	214	0.82	4.5	2.138*
3	680	2.62	14.3	2.268
4	1063	3.85	21.0	2.217
5	3182	9.22	50.3	2.196
6	4142	11.12	60.6	2.251
7	5308	13.44	73.3	2.487*

*Omitted from average.

Average k = 2.233 ± 0.027 x 10^{-4} $min.^{-1}$

TABLE VI

HYDROLYSIS OF $C_6H_5CHCl_2$ at 45°C

5 ml. of an acetone solution of $C_6H_5CHCl_2$ (1.6370 gm. per 100 ml.) was used, giving an original concentration of 0.1017 M.

A point at 25 minutes (1.22 ml. 0.0502 N NaOH) was taken as the starting point, giving a calculated infinity point = 19.03 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$
1	77	1.91	10.0	13.74
2	125	2.99	15.7	13.68
3	245	5.35	28.1	13.50
4	373	7.71	40.5	13.93
5	485	9.48	49.8	14.22
6	542	9.91	52.1	13.57
7	635	11.10	58.3	13.79
8	767	12.25	64.4	13.46
9	822	14.60	76.7	17.74*

*Omitted from average.

Average $k = 13.74 \pm 0.18 \times 10^{-4}$ min.$^{-1}$

TABLE VII

HYDROLYSIS OF $C_6H_5CCl_3$ at 20°C

5 ml. of an acetone solution of $C_6H_5CCl_3$ (0.9744 gm. per 100 ml.) was used, giving an original concentration of 0.04985 M.

Calculated infinity point = 19.86 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4	Observed infinity
1	46	3.00	15.1	35.62	20.22
2	90.25	5.42	27.3	35.32	20.35
3	160	8.52	42.9	35.03	20.21
4	244	11.62	58.5	36.07	20.31
5	390	15.09	76.0	36.58	20.41

Average k = 35.72 ± 0.48 x 10^{-4} min.$^{-1}$

TABLE VIII

HYDROLYSIS OF $C_6H_5CCl_3$ at 30°C

5 ml. of an acetone solution of $C_6H_5CCl_3$ (1.9506 gm. per 100 ml.) was used, giving an original concentration of 0.09979 M.

Calculated infinity point = 45.25 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	5	2.62	5.8	119.4*
2	14	7.27	16.1	125.1*
3	21	9.85	21.8	116.9
4	35	15.47	34.2	119.6
5	60	22.67	50.1	115.9
6	100	30.97	68.5	115.4

*Omitted from average.

Average $k = 117.0 \pm 1.40 \times 10^{-4}$ min.$^{-1}$

Not used in summary

TABLE IX

HYDROLYSIS OF $C_6H_5CCl_3$ at 30°C

5 ml. of an acetone solution of $C_6H_5CCl_3$ (1.9758 gm. per 100 ml.) was used, giving an original concentration of 0.1011 M.

Calculated infinity point = 45.84 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	5	2.71	5.9	123.7*
2	14	6.69	14.6	112.7
3	21	9.70	21.2	113.2
4	35	16.51	36.0	127.6*
5	60	28.70	62.6	164.0*
6	112.5	32.70	71.3	111.1

*Omitted from average.

Average $k = 112.3 \pm 0.83 \times 10^{-4}$ min.$^{-1}$

Not used in summary

TABLE X

HYDROLYSIS OF $C_6H_5CCl_3$ at 30°C

5 ml. of an acetone solution of $C_6H_5CCl_3$ (0.9744 gm. per 100 ml.) was used, giving an original concentration of 0.04985 M.

Calculated infinity point = 19.86 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$	Observed infinity
1	15	3.09	15.5	112.8	20.00
2	30	5.62	28.3	110.9	20.00
3	60	9.74	49.1	112.4	20.00
4	105.25	13.63	68.6	110.2	19.95
5	130	15.10	76.0	109.9	19.87

Average $k = 111.2 \pm 1.1 \times 10^{-4}$ min.$^{-1}$

TABLE XI

HYDROLYSIS OF $C_6H_5CH_2Br$ at 30°C

5 ml. of an acetone solution of $C_6H_5CH_2Br$ (1.6934 gm. per 100 ml.) was used, giving an original concentration of 0.09901 M.

Calculated infinity point = 11.23 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	232	1.38	12.3	5.652
2	462	2.58	23.0	5.650
3	852	4.34	38.7	5.734
4	1304	5.78	51.5	5.545
5	1803	7.08	63.1	5.522

Average $k = 5.621 \pm 0.07 \times 10^{-4}$ min.$^{-1}$

Not used in summary

TABLE XII

HYDROLYSIS OF $C_6H_5CH_2Br$ at 30°C

5 ml. of an acetone solution of $C_6H_5CH_2Br$ (1.6934 gm. per 100 ml.) was used, giving an original concentration of 0.0990 M.

Calculated infinity point = 11.23 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	240	1.31	13.3	5.937
2	356	1.84	18.7	5.798
3	502	2.46	24.9	5.713
4	1342	5.26	53.3	5.676
5	1538	5.71	57.9	5.621
6	1755	6.18	62.6	5.610
7	1912	6.56	66.5	5.719
8	1951	6.66	67.5	5.762

Average $k = 5.730 \pm 0.077 \times 10^{-4}$ min.$^{-1}$

Not used in summary

TABLE XIII

HYDROLYSIS OF $C_6H_5CH_2Br$ at 30°C

5 ml. of an acetone solution of $C_6H_5CH_2Br$ (1.729 gm. per 100 ml.) was used, giving an original concentration of 0.1011 M.

Calculated infinity point = 11.46 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	k x 10^4
1	310	1.80	15.7	5.512
2	470	2.66	23.2	5.619
3	567	3.14	27.4	5.648
4	997	4.99	43.5	5.735
5	1224	5.78	50.4	5.736
6	2547	8.85	77.2	5.810

Average k = 5.677 ± 0.084 x 10^{-4} min.$^{-1}$

TABLE XIV

HYDROLYSIS OF $C_6H_5CH_2Br$ at 45°C

5 ml. of an acetone solution of $C_6H_5CH_2Br$ (1.729 gm. per 100 ml.) was used, giving an original concentration of 0.1011 M.

Calculated infinity point = 11.46 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	48	1.28	11.2	24.67
2	110	2.78	24.3	25.26
3	201	4.50	39.3	24.81
4	330	6.47	56.5	25.20
5	600	8.94	78.0	25.25

Average $k = 25.04 \pm 0.24 \times 10^{-4}$ min.$^{-1}$

TABLE XV

HYDROLYSIS OF $C_6H_5CHBr_2$ at 30°C

5 ml. of an acetone solution of $C_6H_5CHBr_2$ (3.1128 gm. per 100 ml.) was used, giving an original concentration of 0.1245 M.

Calculated infinity point = 28.24 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	k x 10^4
1	60	1.15	4.1	6.940*
2	342	5.95	21.1	6.919
3	587	9.35	33.1	6.852
4	1312	16.65	59.0	6.790
5	1800	19.95	70.7	6.811
6	2571	23.30	82.5	6.782
7	2821	24.15	85.5	6.851*

*Omitted from average.

Average k = 6.831 ± 0.044 x 10^{-4} min.$^{-1}$

TABLE XVI

HYDROLYSIS OF $C_6H_5CHBr_2$ at 45°C

For points 1, 2, 3, and 4. 5 ml. of an acetone solution of $C_6H_5CHBr_2$ (3.1128 gm. per 100 ml.) was used, giving an original concentration of 0.1245 M.

Calculated infinity point = 28.24 ml. 0.0441 N NaOH.

For points 5 and 6. 5 ml. of an acetone solution of $C_6H_5CHBr_2$ (2.5320 gm. per 100 ml.) was used, giving an original concentration of 0.1013 M.

Calculated infinity point = 22.97 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	61	6.60	23.4	43.65
2	135	12.75	45.2	44.49
3	249	18.80	66.6	44.02
4	399	22.90	81.1	41.75*
5	492	20.35	88.6	44.13*
6	611	20.95	91.2	39.80*

*Omitted from average.

Average $k = 44.05 \pm 0.36 \times 10^{-4}$ min.$^{-1}$

TABLE XVII

HYDROLYSIS OF $C_6H_5CHBr_2$ at 45°C

5 ml. of an acetone solution of $C_6H_5CHBr_2$ (2.5320 gm. per 100 ml.) was used, giving an original concentration of 0.1013 M.

Calculated infinity point = 22.97 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	60	5.60	24.4	46.58
2	120	9.50	41.4	45.24
3	244	15.35	66.8	45.23
4	360	18.20	79.2	43.67
5	480	19.75	86.0	40.94
6	589	21.00	91.4	41.71

Not used in summary

TABLE XVIII

HYDROLYSIS OF $C_6H_5CHBr_2$ at 45°C

5 ml. of an acetone solution of $C_6H_5CHBr_2$ (2.5320 gm. per 100 ml.) was used, giving an original concentration of 0.1013 M.

Calculated infinity point = 20.18 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4
1	61	5.08	25.1	47.55*
2	120	8.60	42.6	46.30
3	259	14.03	69.5	45.89
4	364	16.38	81.2	45.88
5	477	17.83	88.3	45.09*
6	623	18.77	93.0	42.72*

*Omitted from average.

Average k = 46.02 ± 0.18 x 10^{-4} min.$^{-1}$

TABLE XIX

HYDROLYSIS OF $C_6H_5CBr_3$ at 20°C

5 ml. of an acetone solution of $C_6H_5CBr_3$ (2.7738 gm. per 100 ml.) was used, giving an original concentration of 0.08434 M.

Calculated infinity point = 33.60 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$	Observed infinity
1	7	8.05	24.0	391.4	34.37
2	16.33	15.62	46.5	383.0	34.50
3	25	20.30	60.4	370.8	34.36
4	40	25.45	75.8	354.2	34.18

Average $k = 374.9 \pm 12.4 \times 10^{-4}$ min.$^{-1}$

TABLE XX

HYDROLYSIS OF $C_6H_5CBr_3$ at 30°C

5 ml. of an acetone solution of $C_6H_5CBr_3$ (2.7738 gm. per 100 ml.) was used, giving an original concentration of 0.08434 M.

Calculated infinity point = 33.60 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4	Observed infinity
1	3	9.64	28.7	1127	33.80
2	5	14.93	44.4	1176	33.75
3	7	18.71	55.7	1163	34.12
4	9.333	21.82	65.0	1123	33.94
5	24	30.82	91.8	1039*	34.18

*Omitted from average.

Average k = 1147 ± 22 x 10^{-4} min.$^{-1}$

TABLE XXI

HYDROLYSIS OF $C_6H_5CHClBr$ at 20°C

5 ml. of an acetone solution of $C_6H_5CHClBr$ (1.9200 gm. per 100 ml.) was used, giving an original concentration of 0.09343 M.

Calculated infinity point = 21.19 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	110	1.93	9.1	8.682*
2	250	4.06	19.2	8.509
3	400	6.11	28.8	8.506
4	685	9.44	44.6	8.610
5	1283	14.24	67.2	8.691
6	1325	14.42	68.1	8.613

*Omitted from average.

Average $k = 8.586 \pm 0.062 \times 10^{-4}$ min.$^{-1}$

TABLE XXII

HYDROLYSIS OF $C_6H_5CHClBr$ at 30°C

5 ml. of an acetone solution of $C_6H_5CHClBr$ (1.920 gm. per 100 ml.) was used, giving an original concentration of 0.09343 M.

Calculated infinity point = 21.29 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	103	5.79	27.3	30.99
2	212	10.16	47.9	30.81
3	254	11.62	54.9	31.30
4	302	12.94	61.1	31.24
5	973	20.09	94.8	30.41*

*Omitted from average.

Average $k = 31.09 \pm 0.19 \times 10^{-4}$ min.$^{-1}$

TABLE XXIII

HYDROLYSIS OF $C_6H_5CHClBr$ at 45°C

5 ml. of an acetone solution of $C_6H_5CHClBr$ (1.920 gm. per 100 ml.) was used, giving an original concentration of 0.09343 M.

Calculated infinity point = 21.19 ml. 0.0441 N NaOH.

Soln.	Time (min.)	Ml. 0.0441 N NaOH	Per cent complete	$k \times 10^4$
1	15	4.47	21.1	158.0
2	30	8.12	38.3	161.1
3	45	10.93	51.6	161.2
4	65	13.82	65.2	162.5
5	100	17.09	80.6	164.3
6	160	19.42	91.7	155.2*

*Omitted from average.

Average $k = 161.4 \pm 1.6 \times 10^{-4}$ min.$^{-1}$

TABLE XXIV

HYDROLYSIS OF $C_6H_5CCl_2Br$ at 20°C

5 ml. of an acetone solution of $C_6H_5CCl_2Br$ (1.3450 gm. per 100 ml.) was used, giving an original concentration of 0.05606 M.

Calculated infinity point = 22.33 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$	Observed infinity
1	5	6.35	28.4	669.3	21.90
2	10	11.11	49.8	688.3	22.03
3	15	14.85	66.5	729.2	22.10
4	20	17.03	76.2	719.2	22.13
5	25	18.45	82.6	700.2	22.03
6	30	19.35	86.7	671.5*	21.87

*Omitted from average.

Average $k = 701.2 \pm 18.4 \times 10^{-4}$ min.$^{-1}$

TABLE XXV

HYDROLYSIS OF $C_6H_5CCl_2Br$ at 20°C

5 ml. of an acetone solution of $C_6H_5CCl_2Br$ (1.3450 gm. per 100 ml.) was used, giving an original concentration of 0.05606 M.

Calculated infinity point = 22.33 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$	Observed infinity
1	5	6.00	26.9	626.0	22.07*
2	10	11.10	49.6	687.5	22.30
3	15	14.80	66.3	724.8	22.33
4	20	17.00	76.1	716.4	22.18
5	25	18.58	83.2	713.8	22.28
6	30	19.49	87.2	687.5*	22.09

*Omitted from average.

Average $k = 710.6 \pm 11.6 \times 10^{-4}$ min.$^{-1}$

Not used in summary

TABLE XXVI

HYDROLYSIS OF $C_6H_5CCl_2Br$ at 30°C

5 ml. of an acetone solution of $C_6H_5CCl_2Br$ (1.3341 gm. per 100 ml.) was used, giving an original concentration of 0.05560 M.

Calculated infinity point = 22.15 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4
1	2	10.22	46.1	3095
2	3	10.47	47.3	2134
3	5	14.67	66.2	2172
4	8	18.00	81.3	2094
5	10	20.27	91.5	2467

Not used in summary

TABLE XXVII

HYDROLYSIS OF $C_6H_5CCl_2Br$ at 30°C

5 ml. of an acetone solution of $C_6H_5CCl_2Br$ (1.3341 gm. per 100 ml.) was used, giving an original concentration of 0.05560 M.

Calculated infinity point = 22.15 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$
1	2	6.92	31.2	1873*
2	3	10.32	46.6	2091
3	4	15.32	69.2	2942*
4	5	14.85	67.1	2220
5	6	15.92	71.9	2115
6	7	19.17	86.5	2866*
7	7	17.07	77.0	2104
8	8	18.05	81.5	2109
9	9	19.02	85.9	2175*
10	10	19.32	87.2	2058*

*Omitted from average.

Average $k = 2128 \pm 37 \times 10^{-4}$ min.$^{-1}$

TABLE XXVIII

HYDROLYSIS OF $C_6H_5CClBr_2$ at 20°C

5 ml. of an acetone solution of $C_6H_5CClBr_2$ (1.4098 gm. per 100 ml.) was used, giving an original concentration of 0.04957 M.

Calculated infinity point = 19.75 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	k x 10^4
1	5.5	5.23	26.5	559.4*
2	10	9.45	47.8	651.2
3	10	11.55	58.5	879.2*
4	15	12.29	62.2	649.2
5	20.5	14.69	74.4	664.4
6	30	16.78	85.0	631.6

*Omitted from average.

Average k = 649.1 ± 8.8 x 10^{-4} $min.^{-1}$

TABLE XXIX

HYDROLYSIS OF $C_6H_5CClBr_2$ at 30°C

5 ml. of an acetone solution of $C_6H_5CClBr_2$ (1.7832 gm. per 100 ml.) was used, giving an original concentration of 0.06270 M.

Calculated infinity point = 24.98 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$	Observed infinity
1	2	4.07	16.3	889.2	
2	5	8.19	32.8	794.7	
3	10	10.64	42.6	555.1	
4	30	12.76	51.1	237.8	20.66
5	92	13.19	52.8	81.62	20.47
6	115	13.39	53.6	66.79	
7					20.67
8					20.16

Not used in summary

TABLE XXX

HYDROLYSIS OF $C_6H_5CClBr_2$ at 30°C

5 ml. of an acetone solution of $C_6H_5CClBr_2$ (1.4098 gm. per 100 ml.) was used, giving an original concentration of 0.04957 M.

Calculated infinity point = 19.75 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$
1	4.42	10.71	54.2	1770
2	5	11.39	57.7	1720
3	7	14.33	72.6	1848
4	10	16.77	84.9	1892

Average $k = 1808 \pm 63 \times 10^{-4}$ min.$^{-1}$

TABLE XXXI

HYDROLYSIS OF $C_6H_5CF_2Cl$ at 36°C

5 ml. of an acetone solution of $C_6H_5CF_2Cl$ (0.7305 gm. per 100 ml.) was used, giving an original concentration of 0.04493 M.

Calculated infinity point = 17.90 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$
1	8917	1.55	8.7	0.10178*
2	24346	3.39	19.0	0.08649
3	46116	5.67	31.7	0.08283
4	66503	7.35	41.2	0.07974

*Omitted from average.

Average $k = 0.08302 \pm 0.0023 \times 10^{-4}$ min.$^{-1}$

TABLE XXXII

HYDROLYSIS OF $C_6H_5CF_2Cl$ at 45°C

5 ml. of an acetone solution of $C_6H_5CF_2Cl$ (0.7287 gm. per 100 ml.) was used, giving an original concentration of 0.04482 M.

Calculated infinity point = 17.86 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$
1	1574	0.74	4.1	0.2686*
2	1592	0.62	3.5	0.2218
3	1594	0.57	3.2	0.2037*
4	1597	0.62	3.5	0.2215
5	4040	1.53	8.6	0.2218
6	4069	1.58	8.9	0.2278

*Omitted from average.

Average $k = 0.2232 \pm 0.0023 \times 10^{-4}$ min.$^{-1}$

TABLE XXXIII

HYDROLYSIS OF $C_6H_5CF_2Cl$ at 60°C

For points 1, 2, and 3. 5 ml. of an acetone solution of $C_6H_5CF_2Cl$ (0.7287 gm. per 100 ml.) was used, giving an original concentration of 0.04482 M.

Calculated infinity point = 17.86 ml. 0.0502 N NaOH.

For points 4, 5, 6, 7, and 8. 5 ml. of an acetone solution of $C_6H_5CF_2Cl$ (0.7305 gm. per 100 ml.) was used, giving an original concentration of 0.04493 M.

Calculated infinity point = 17.90 ml. 0.0502 N NaOH.

Soln.	Time (min.)	Ml. 0.0502 N NaOH	Per cent complete	$k \times 10^4$
1	1151	1.91	10.7	0.9848
2	4198	6.02	33.7	0.9795
3	8721	10.39	58.2	0.9997
4	11370	12.08	67.5	0.9883
5	11526	11.64	65.0	0.9117*
6	15354	13.97	78.1	0.9877
7	18398	15.35	85.7	1.0594*
8	20207	15.92	89.0	1.0898*

*Omitted from average.

Average $k = 0.9880 \pm 0.0048 \times 10^{-4}$ min.$^{-1}$

B. SUMMARY OF RESULTS

In the following tables is presented a summary of the experimental results obtained from the hydrolysis reactions of the alpha-halogenated toluenes.

Table XXXIV presents a summary of the rates of hydrolysis at 20, 30, and 45°C. Since only those rate constants are used that were considered most representative of the reaction under consideration, the number of the table from which the constant was obtained has been indicated.

It is to be noted that in the calculation of these rate constants, the calculated infinity point is used for the value of ml_∞ (page 23).

Table XXXV shows the results of dividing the rate constants, at 30°C, by the number of halogen atoms thought responsible for the reaction. This is an indication of the reactivity of the individual halogen atoms in the particular halide.

In Table XXXVI is found the results of calculating the rate constants, using the observed infinity point for the value of ml_∞ (page 23). Only those constants are listed that correspond to the rate constants given in Table XXXIV. These are the constants used in the original publication of this investigation.[1]

In Table XXXVII are presented the energies of activation, as

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[1]Hine and Lee, loc. cit.

Calculated by means of a modification of the van't Hoff equation,[2]

$$\log \frac{k_2}{k_1} = \frac{E}{4.576} \frac{T_2 - T_1}{T_2 T_1}.$$

[2] Remick, op. cit., p. 185.

TABLE XXXIV

SUMMARY OF RATES OF HYDROLYSIS

OF ALPHA-HALOGENATED TOLUENES

$k \times 10^4$ min.$^{-1}$

	20°C	30°C	45°C
$C_6H_5CH_2Cl$		0.2236(I)	1.174 (II)
$C_6H_5CHCl_2$		2.233 (V)	13.74 (VI)
$C_6H_5CCl_3$	35.72 (VII)	111.2 (X)	
$C_6H_5CH_2Br$		5.677 (XIII)	25.04 (XIV)
$C_6H_5CHBr_2$		6.831 (XV)	46.02 (XVIII)
$C_6H_5CBr_3$	374.9 (XIX)	1147 (XX)	
$C_6H_5CHClBr$	8.586(XXI)	31.09 (XXII)	161.4 (XXIII)
$C_6H_5CCl_2Br$	701.2 (XXIV)	2128 (XXVII)	
$C_6H_5CClBr_2$	649.1 (XXVIII)	1808 (XXX)	
$C_6H_5CF_2Cl$*		0.0436**	0.2232(XXXII)

*For the rate of hydrolysis at 60°C, see Table XXXIII.

**Calculated from the rates of hydrolysis at higher temperatures.

TABLE XXXV

RATES OF HYDROLYSIS

PER HALOGEN ATOM

	$k \times 10^4$ min.$^{-1}$ at 30°C	
	per Cl	per Br
$C_6H_5CH_2Cl$	0.2236	
$C_6H_5CHCl_2$	1.107	
$C_6H_5CCl_3$	37.1	
$C_6H_5CH_2Br$		5.677
$C_6H_5CHBr_2$		3.416
$C_6H_5CBr_3$		382
$C_6H_5CHClBr$		31.09
$C_6H_5CCl_2Br$		2128
$C_6H_5CClBr_2$		904
$C_6H_5CF_2Cl$	0.0436	

TABLE XXXVI

RATES OF HYDROLYSIS, CALCULATED

FROM OBSERVED INFINITY POINTS

	$k \times 10^4$ min.$^{-1}$	
	20°C	30°C
$C_6H_5CCl_3$	34.55 (VII)	110.4 (X)
$C_6H_5CBr_3$	362.3 (XIX)	1148 (XX)
$C_6H_5CCl_2Br$	718.2 (XXIV)	

TABLE XXXVII

ENERGIES OF ACTIVATION

	Energy of Activation in kcal.
$C_6H_5CH_2Cl$	21.2
$C_6H_5CHCl_2$	23.3
$C_6H_5CCl_3$	20.1
$C_6H_5CH_2Br$	19.0
$C_6H_5CHBr_2$	24.4
$C_6H_5CBr_3$	20.4
$C_6H_5CHClBr$	21.9*
$C_6H_5CCl_2Br$	19.2
$C_6H_5CClBr_2$	18.1
$C_6H_5CF_2Cl$	20.8*

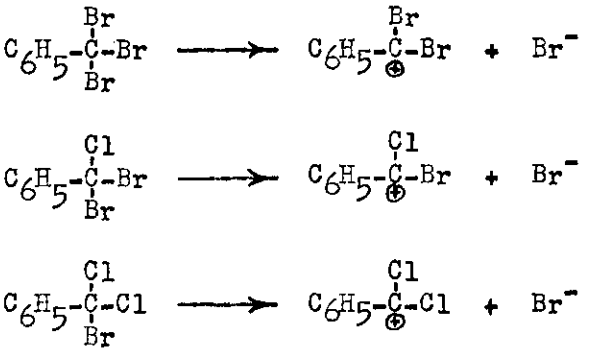
*This value is an average obtained from the rates at three temperatures.

C. CONCLUSIONS

In all cases of substitution of alpha-hydrogen by chlorine, the rate constants show increased reactivity. However, it is to be noted that the increase in rate, per chlorine atom, between $C_6H_5CHCl_2$ and $C_6H_5CCl_3$ is 30-fold, while the increase in rate, per chlorine atom, between $C_6H_5CH_2Cl$ and $C_6H_5CHCl_2$ is only 5-fold. This is probably due to the $C_6H_5CH_2Cl$ hydrolyzing largely by an S_N2 mechanism, giving, therefore, a much larger rate constant than for an S_N1 hydrolysis.

In the bromine substitutions of alpha-hydrogen, the same general effect is noted, except that in this case, $C_6H_5CH_2Br$ is actually more reactive, per bromine atom, than is $C_6H_5CHBr_2$. This makes even more likely the probability that the benzyl halides hydrolyze by an S_N2 mechanism.

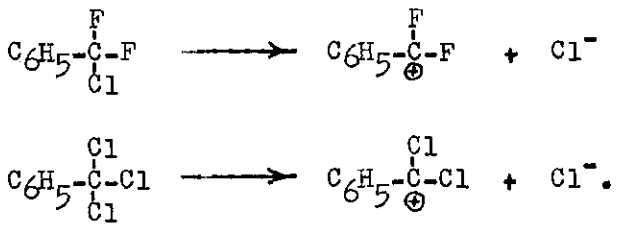
In the series, $C_6H_5CBr_3$, $C_6H_5CClBr_2$, and $C_6H_5CCl_2Br$, the effects of chlorine atoms on the reactivity of bromine atoms attached to the same carbon atom is easily noticeable. In this series, if our original assumption of initial replacement of bromine holds true, the following reactions should take place,



Since the environments of the three sets of reaction products are identical, the difference in reaction rates should be due solely to the nature of the carbonium ion formed.

In the series illustrated above, the reaction rates follow the order, 382, 904, and 2128, indicating that the effect of a chlorine atom on the reactivity of a bromine atom attached to the same carbon atom is to increase the rate of reaction. This order of reactivity may be attributed to resonance stabilization of the carbonium ion by the directly attached halogen atom. Since chlorine, an element in an earlier period of the periodic table, has a greater tendency for double bond formation than has bromine, it is not surprising that it would cause greater stabilization than would bromine, thus causing greater reactivity.

A comparison of $C_6H_5CF_2Cl$ and $C_6H_5CCl_3$ shows a different type of effect than was apparent in the chloro-bromo series. If our assumption holds true that, in the molecule $C_6H_5CF_2Cl$, the chlorine is replaced initially, the following reactions should take place,



As was true with the chloro-bromo series, the difference in reaction rates should be due solely to the nature of the carbonium ion formed.

However, in the fluoro-chloro series, above, the reaction rates follow the order, 0.0436 and 111.2, indicating that the effect of a fluorine atom on a chlorine atom attached to the same carbon atom is to decrease the rate of reaction.

Thus, since fluorine, being an element in an earlier period of the periodic table, should have a greater tendency for double bond formation than has chlorine, the order of reactivity cannot be attributed to resonance stabilization of the carbonium ion. Instead, the inductive effect of the highly electronegative fluorine atom apparently greatly predominates over the tendency of fluorine for double bond formation.

Other information obtained from the summary of experimental results concerns the table of values for the energies of activation. The only generalization drawn from this information is that the values for the benzal halides are higher.

In summary, it appears that in the case of chlorine and bromine, alpha-halogenation of toluene increases the S_N1 reactivity, as compared to hydrogen, by resonance stabilization of the carbonium ion. Also, chlorine apparently has a greater tendency for resonance stabilization

than has bromine, due to the greater ease of double bond formation.

In both alpha-chlorination and alpha-bromination, the resonance stabilization is probably opposed by the inductive effect of the electronegative halogen atoms, as compared to the central carbon atom. However, due to the small differences in electronegativity[1] between carbon and chlorine (0.5), as well as between carbon and bromine (0.3), the effect of resonance stabilization predominates.

In the case of fluorine, which has a high electronegativity as compared to carbon (the difference being 1.5), any tendency for resonance stabilization is evidently over-shadowed by the inductive effect. Thus, alpha-fluorination tends to decrease the S_N1 reactivity.

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[1] L. Pauling, The Nature of the Chemical Bond (Ithaca, N. Y.: Cornell University Press, 1948), p. 64.

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