our Laboratory who will report his conclusions at an early date.

Acknowledgment.—We wish to thank Dr. F. J. Norton, Mr. L. B. Bronk, and the Misses M. L. Caldwell and M. Clark for analytical assistance, and Dr. W. F. Gilliam for supplying us with the phenylchlorosilanes.

Summary

1. Thermal rearrangement of the methylchlorosilanes has been studied between 250 and 450° and at vapor concentrations of about 2.3 moles per liter.

2. The equilibrium concentrations of the redistribution products have been established at methyl-to-silicon ratios of 2 and 3 and have been found to deviate very considerably from the predictions of random distribution. This discrepancy is possibly related to the non-ideal gaseous behavior of these substances under the conditions employed to effect rearrangement. At $CH_3/Si = 1$ rearrangement was very slow and complicated by side reactions; for this reason accurate equilibrium values have not been obtained.

3. Demethylation occurs to an appreciable extent at 375° and above, resulting in the establishment of methylene bridges between silicon atoms. This reaction is illustrated by the formation of bis-(dimethylchlorosilyl)-methane from trimethylchlorosilane.

4. Methylphenyldichlorosilane and methylethyldichlorosilane have been prepared by heating phenyltrichlorosilane and ethyltrichlorosilane, respectively, with certain methylchlorosilanes.

5. The following new compounds have been prepared and characterized: methylphenyldiethoxysilane, methylphenyldifluorosilane, methylethyldiethoxysilane, and methylethyldibromosilane.

SCHENECTADY, N. Y. RECEIVED MAY 3, 1948

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reaction of Ferrous and Ferric Ions with 1,10-Phenanthroline. II. Kinetics of Formation and Dissociation of Ferrous Phenanthroline

BY T. S. LEE, I. M. KOLTHOFF AND D. L. LEUSSING

The equilibrium constants for the dissociation of ferroin (ferrous phenanthroline) and ferriin (ferric phenanthroline) have been determined and were reported in a previous paper.[1] The present paper deals with kinetics of the dissociation and of the formation of ferroin. Data are also given from which the rate of dissociation of ferriin can be calculated. However, the mechanism of this reaction is not understood.

Experimental

Materials.—Preparation of reagent solutions was described in a previous paper.[1]

Rate of Dissociation of Ferroin.—Five ml. of 0.00997 M phenanthroline solution was added to 5.00 ml. of 0.0104 M ferrous sulfate solution. Under these conditions the formation of ferroin is rapid and quantitative. The mixture was diluted in a volumetric flask to nearly 500 ml. and the desired amount of standard 2 M sulfuric acid was added. The mixture was then diluted quickly to 500 ml. with water. The final sulfuric acid concentration was 0.005, 0.05 or 0.5 M. The temperature of all solutions was maintained at 25 ± 0.1° before and after mixing. After various reaction periods portions of the reaction mixture were removed and the amount of ferroin determined with the Model DU Beckman spectrophotometer at a wave length of 500 mμ.

Rate of Formation of Ferroin.—Reaction mixtures were prepared by mixing together sulfuric acid, ferrous sulfate, and phenanthroline–sulfuric acid solutions. The final concentrations of the reactants are given in Table I. The temperature of the reagent solutions and reaction mixtures was 25 ± 0.1°. After various reaction periods portions of the mixtures were analyzed spectrophotometrically for ferroin.

Rate of Dissociation of Ferriin.—The experiments were described in the experimental part of a previous paper[1] under "Measurement of E. m. f. of the Cell Au | Fe^{++}, Fe^{+++}, H_2SO_4 | $FePh_3^{++}$, $FePh_3^{+++}$, H_2SO_4 | Au."

Rate of Dissociation of Ferroin

Figure 1 shows the rate of dissociation of ferroin in solutions of different acidities. The function $\log c_0/c$ is plotted against time, where c_0 is the initial concentration of ferroin and c is the concentration of ferroin at a given time. It is seen that the experimental points for the reaction mixtures which are 0.5 and 0.05 M in sulfuric acid fall on a straight line, indicating that the dissociation of ferroin is a first order reaction and that the rate is the same in 0.5 and 0.05 M. The curve for the reaction mixture which is 0.005 M in sulfuric acid is coincident with the straight line during the initial stages of reaction. After a reaction period of one hour the experimental curve approaches asymptotically a horizontal line. The horizontal line corresponds to the equilibrium concentration of ferroin in the reaction mixture. At the two higher acidities the rate of formation of ferroin is negligible as compared to the rate of dissociation.

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[1] T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).

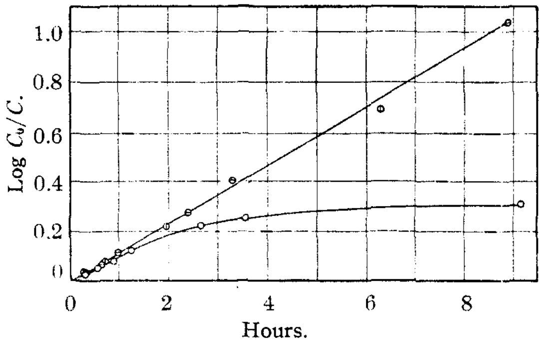

Fig. 1.—Rate of dissociation of ferroin at 25°: ○, 0.005 M sulfuric acid; ◒, 0.05 M; ⦶, 0.5 M.

However, in the reaction mixture which is 0.005 M in acid the rate of formation of ferroin is not negligible after the initial stages of reaction and the experimental curve deviates from the straight line.

From Fig. 1 it is concluded that the dissociation of ferroin is a first order reaction independent of acid concentration in 0.005 to 0.5 M sulfuric acid. The value of the rate constant at 25° is 0.0045 min.$^{-1}$. This value corresponds to a half life period of about two and one-half hours.

An approximate value of the rate of dissociation of ferroin in acid solutions can also be calculated from the data of Ruben, *et al.*[2] These investigators determined the extent of exchange of radioactive iron between ferrous ion and ferroin in 0.05 N sulfuric acid solution after reaction periods of four minutes and sixty minutes. The values of the rate constant are calculated from the two experiments to be 0.01 ± 0.006 and 0.0047 ± 0.0008 min.$^{-1}$, respectively, at 25°. Within the limits of error stated by Ruben, *et al.*, these values are in agreement with the value given above.

Rate of Formation of Ferroin

In the determination of the rate of formation of ferroin the concentrations of phenanthroline, ferrous sulfate and acid were large relative to the amount of ferroin formed. In consequence the concentrations of reactants may be considered constant throughout the reaction period. If the rate of formation of ferroin is determined by one reaction step only, the formation would be expected to be a zero order reaction under the experimental conditions. The equation representing the rate of change of concentration of a substance being formed by a zero order reaction and dissociating by a first order reaction is

$$dc/dt = A - k_{\text{diss.}}c \qquad (1)$$

where A is a constant. Integration of equation (1) gives

$$c = A\,\frac{(1 - e^{-k_{\text{diss.}}t})}{k_{\text{diss.}}} \qquad (2)$$

In Fig. 2 the experimental values of the concentration of ferroin are plotted against calculated

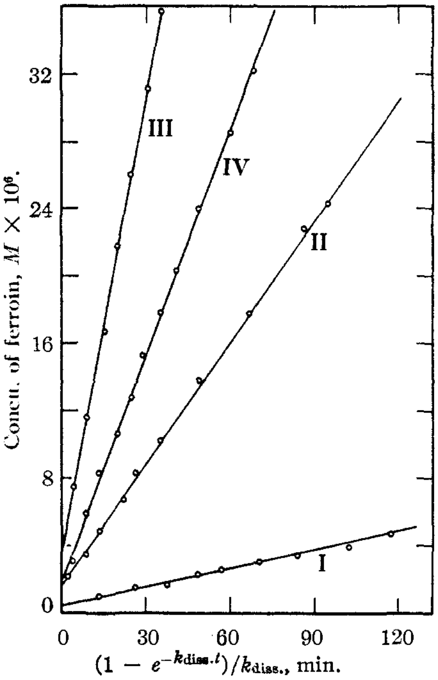

Fig. 2.—Rate of formation of ferroin in 0.5 M sulfuric acid at 25° (see Table I).

values of $(1 - e^{-k_{\text{diss}}t})/k_{\text{diss.}}$. It is seen that the points lie on straight lines, indicating that the formation of ferroin is indeed a zero order reaction under the conditions of the experiments. It will be noted that the concentration of ferroin obtained by extrapolating the lines to zero time is not zero. This is discussed below.

The slopes of the lines in Fig. 2 are equal to A of equation (2) and represent the rates of formation of ferroin in the various reaction mixtures. In Table I the values of A, obtained from Fig. 2, are compared with the concentrations of phenanthrolium ion and ferrous sulfate. From expts. I, II and III it is found that the value of A varies as the third power of the phenanthrolium ion concentration. The relative values of A in the three experiments were found to be 1.2, 8.0, and 26, respectively, whereas values of 1, 8, and 27 would be expected from a third power relationship. The data of Table I also indicate that A is directly proportional to the ferrous ion concentration.

TABLE I

RATE OF FORMATION OF FERROIN IN 0.50 M SULFURIC ACID AT 25°

Expt.	Concn. of $FeSO_4$ $M \times 10^3$	Concn. of phenanthrolium ion, $M \times 10^3$	A min.$^{-1}$ $\times 10^6$	Concn. of phenanthroline, $M \times 10^9$	$k_{\text{form.}}$ min.$^{-1}$ $\times 10^{-19}$
I	2.53	1.00	3.5	9.7	1.5
II	2.53	2.00	23.5	19	1.3
III	2.53	3.00	77.5	29	1.2
IV	4.96	2.00	44.1	19	1.4

The equation (3) can therefore be written

$$A = C(\text{Fe}^{++})(\text{PhH}^{+})^3 \qquad (3)$$

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[2] Ruben, Kamen, Allen and Nahinsky, THIS JOURNAL, **64**, 2297 (1942).

where C is a constant and parentheses represent concentrations. It should be mentioned here that A should also be proportional to $a_{Fe^{++}}a^3_{PhH^+}$, where a represents activity, since the ionic strength of all of the reaction mixtures in expts. I–IV was essentially the same.

Inasmuch as the hydrogen activity in each of the reaction mixtures was the same, the concentration of free phenanthroline was proportional to the phenanthrolium ion concentration. It is reasonable to assume that the equilibrium

$$Ph + H^+ = PhH^+ \qquad (4)$$

is established rapidly. Equation (3) then becomes

$$A = C'(Fe^{++})(Ph)^3 \qquad (5)$$

Equation (5) may be interpreted most simply by the step-wise formation of $FePh_3^{++}$

$Fe^{++} + Ph = FePh^{++}$ rapidly established equilibrium
$FePh^{++} + Ph = FePh_2^{++}$ rapidly established equilibrium
$FePh_2^{++} + Ph \longrightarrow FePh_3^{++}$ rate-determining step

Accordingly the equation representing the rate of formation of ferroin should be

$$A = k'(FePh_2^{++})(Ph) \qquad (6)$$

Since

$$(FePh_2^{++})/(Fe^{++})(Ph)^2 = K''' \qquad (7)$$

equation (6) can be written as

$$A = k'K'''(Fe^{++})(Ph)^3 = k_{formation}\,(Fe^{++})(Ph)^3 \qquad (8)$$

Equation (8) is in agreement with the experimental data (equation 5).

There is experimental evidence that the $FePh^{++}$ and $FePh_2^{++}$ complexes hypothesized in the above scheme are present in appreciable concentrations in solutions of suitable composition. The lines of Fig. 2 indicate that a colored substance was present in the reaction mixtures (Table I) immediately after mixing. The colored substance was yellow and could be observed visually until the red color of the ferroin which was forming obscured it. The intercepts of the lines I, II and III are in the approximate ratio 1:4:9 indicating that the color is due chiefly to a complex containing two phenanthroline molecules probably $FePh_2^{++}$. In a series of experiments not described above solutions were also prepared which were 0.5 M in ferrous sulfate, 4.4×10^{-4} M in phenanthroline, and 0.5 M in sulfuric acid. The high concentrations of iron and acid in these solutions were favorable for the formation of iron complexes containing less than three molecules of phenanthroline. A colored substance was formed which was yellow (maximum absorption at 440 mμ). The intensity of color was found to be proportional to the phenanthroline concentration and approximately proportional to the iron concentration. The results indicate that the complex formed under these conditions was $FePh^{++}$. Therefore it appears that both complexes $FePh^{++}$ and $FePh_2^{++}$ may be formed under favorable conditions.

In order to simplify the discussion mention of activity coefficients has previously been omitted. It would be expected that the effect of ionic strength on the rate of formation of ferroin would be relatively small since one of the reactants is uncharged.[3] As an approximation activity coefficients need not be included in equation (8).

In order to evaluate $k_{formation}$ the concentration of free phenanthroline in reaction mixtures I–IV was calculated from the reaction

$$(Ph) = a_{Ph} = \frac{a_{PhH^+}}{a_{H^+}} K_A \qquad (9)$$

where a represents activity and K_A is the acid dissociation constant of phenanthrolium ion (1.1×10^{-5}).[1] Values of activities of the phenanthrolium ion and of hydrogen ion were calculated from the concentrations of phenanthrolium ion and of sulfuric acid, respectively, as described previously.[1] The results of the calculations are given in Table I. It is seen that the value of $k_{formation}$ is about 1.3×10^{19} min.$^{-1}$ at 25°.

According to the mass action law

$$k_{diss.}/k_{form.} = K_{diss.} \qquad (10)$$

where $K_{diss.}$ is the equilibrium constant for the dissociation of ferroin. Equation (10) involves the assumption that the activities of ferrous ion and of ferroin are equal. The value of the left-hand side of equation (10) is 3×10^{-22}. The value of $K_{diss.}$ obtained by an entirely independent method[1] is 5×10^{-22}. The agreement between the value of $K_{diss.}$ calculated from equation (10) and that determined by direct experiment is gratifying. The agreement constitutes an experimental proof of the validity of the mass action law.

Our interpretation of the kinetics of the rate of formation of ferroin and our value for the specific rate constant are quite different from the interpretation and value given by Thiel and Logemann.[4] The data of Thiel and Logemann are only semi-quantitative and their interpretation is based on incorrect assumptions.

Rate of Dissociation of Ferriin

The rate of dissociation of ferriin was determined by measuring the rate of decrease of e. m. f. of the cell

$$Au \mid Fe^{++},\ Fe^{+++},\ H_2SO_4\ (cM) \mid FePh_3^{++},\ FePh_3^{+++},\ H_2SO_4\ (cM) \mid Au$$

The initial concentration of Fe^{++}, Fe^{+++}, $FePh_3^{++}$, and $FePh_3^{+++}$ was 0.0025 M each. The concentration, c, of sulfuric acid used in different experiments was 0.05, 0.5, 1 and 2 M. The experimental results are shown in Fig. 3.

In interpreting the results it must be remembered that any ferrous iron which is formed by dissociation of ferroin reacts with ferriin to form ferric iron and ferroin. Consequently the concentration of ferroin does not change from its initial value as long as any ferriin remains. The concen-

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[3] J. N. Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[4] Thiel and Logemann, *Sitzber. Ges. Beförder. ges. Naturw. Marsburg*, **69**, 60 (1934).

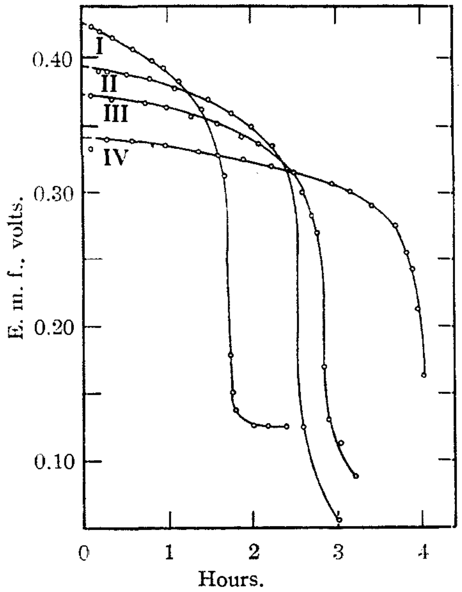

Fig. 3.—Rate of decrease of potential of the ferrous–ferric, ferroin–ferriin cell at 25°: I, 0.05 *M* sulfuric acid; II, 0.5 *M*; III, 1 *M*; IV, 2 *M*.

tration of ferriin in the ferroin–ferriin half cell at any time was calculated from the relation

$$E - E_0 = \frac{RT}{nF} \ln \frac{(\mathrm{FePh_3}^{+++})}{(\mathrm{FePh_3}^{+++})_0} \qquad (11)$$

where the subscript zero indicates an initial value (*i. e.*, value at zero time) and parentheses indicate concentrations. Activity coefficients do not appear in equation (11) because the ionic strength of the solution was essentially constant throughout the reaction period.

If the rate of dissociation of ferriin is a first order reaction, the disappearance of ferriin from the reaction mixture would be given by equation (12)

$$-\,d(\mathrm{FePh_3}^{+++})/dt = k''(\mathrm{FePh_3}^{+++}) + b \qquad (12)$$

where k'' is the constant for the rate of dissociation of ferriin and b is the product of the rate constant for the dissociation of ferroin and the initial concentration of ferroin. Integration of equation (12) gives

$$2.303 \log \frac{(\mathrm{FePh_3}^{+++})_0 k'' + b}{(\mathrm{FePh_3}^{+++})k'' + b} = k''t \qquad (13)$$

Values of k'' were calculated from the inflection points of the curves of Fig. 3. (An inflection point corresponds to the time at which all of the ferriin had disappeared from the reaction mixture.) The equation used for the calculation was derived from equation (13)

$$2.303 \log \frac{(\mathrm{FePh_3}^{+++})_0 k'' + b}{b} = k''t_i \qquad (14)$$

where t_i represents the time corresponding to an inflection point. The specific rate constants of the dissociation of ferriin, k'', were found to be 0.0137 min.$^{-1}$ in 0.05 *M* sulfuric acid, 0.0047 in 0.5 *M*, 0.0031 in 1 *M*, and less than 0.002 in 2 *M*.

In order to show that the decomposition of ferriin is a first order reaction the experimental data for the 0.5 *M* sulfuric acid experiment (Curve II, Fig. 3) and the value of k'' given above (0.0047) were used to calculate the points plotted in Fig. 4. It is seen that the points lie on a straight line indicating that equation (13) is valid and that the decomposition of ferriin is indeed a first order reaction.

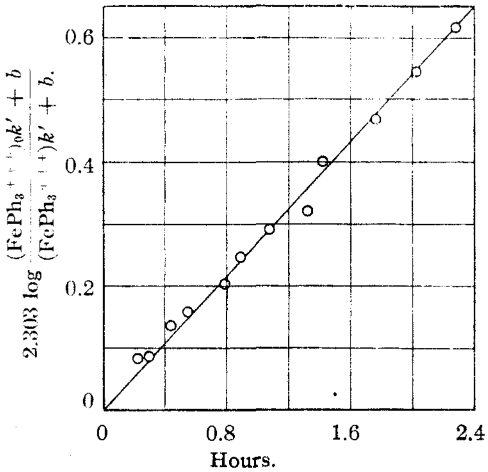

Fig. 4.—Rate of dissociation of ferriin in the presence of ferroin in 0.5 *M* sulfuric acid at 25°.

The rate of dissociation of ferriin decreases with increasing sulfuric acid concentration. This may be due to a kinetic salt effect or to the formation of $\mathrm{FeHPh_3}^{++++}$ in solutions of high acidity. As mentioned in the previous paper[1] the dissociation constant of ferriin also decreases with increasing acidity. The increased stability of ferriin in solutions of high acidity may result from the following equilibrium.

$$\mathrm{FePh_3}^{+++} + \mathrm{H}^+ \rightleftharpoons \mathrm{FeHPh_3}^{++++}$$

(It must be further assumed that the rate of dissociation of $\mathrm{FeHPh_3}^{++++}$ into ferric ion and phenanthroline is slow compared to the rate of dissociation of $\mathrm{FePh_3}^{+++}$.) The existence of $\mathrm{FeHPh_3}^{++++}$ is not established conclusively by the present experimental evidence and should be tested by further experiments.

Acknowledgment.—Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled us to carry out this investigation.

Summary

The dissociation of ferroin has been found to be a first order reaction with a rate constant of 0.0045 min.$^{-1}$ at 25°. The rate is independent of acidity in the solutions studied (0.005 to 0.5 *M* sulfuric acid).

The rate A of formation of ferroin has been found to obey the expression: $A = k_{\mathrm{form.}}(\mathrm{Fe}^{++})(\mathrm{Ph})^3$. Evidence is given that the rate determin-

ing step is the reaction $FePh_2^{++} + Ph \rightarrow FePh_3^{++}$. Within experimental error the ratio of $k_{\text{diss.}}/k_{\text{form.}}$ was found to be equal to the experimentally determined value of the dissociation constant $K_{\text{diss.}}$ of ferroin.

The dissociation of ferriin was found to be a first order reaction in sulfuric acid solutions. The rate of reaction decreases with increasing sulfuric acid concentration.

MINNEAPOLIS, MINN. RECEIVED JUNE 14, 1948

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Relative Reactivities of Some Substituted Benzyl Fluorides[1]

BY WILLIAM T. MILLER, JR., AND JACK BERNSTEIN[2]

The development of a general method of preparation for the substituted benzyl fluorides[3] made possible the measurement of their relative reactivities. It was considered that such a study would furnish a worthwhile comparison of the replacement reactions of fluorine with those of the other halogens since the reactivity of the benzyl chlorides and bromides have been studied from this point of view by a number of workers. No systematic quantitative measurements on the reactivity of alkyl fluorides have previously appeared in the literature.

The basic reaction pattern for side-chain halides has been elucidated by Ingold[4] on the basis of two general type reaction mechanisms usually termed S_N1 and S_N2 for unimolecular and bimolecular reactions with nucleophilic reagents. Ordinarily hydrolysis or alcoholysis reactions occur by both mechanisms but one or the other may be made predominant by the choice of suitable reactants and the effect of substituents then becomes diagnostic of reaction mechanism.

In the present work the rates of reaction of various substituted benzyl fluorides with sodium ethoxide in 95% alcohol were determined and satisfactory second order rate constants were obtained as shown in Table I. The order found for the effect of the substituent in increasing the reactivity of the side chain fluorine was in general *m*-NO_2 > *p*-X > *m*-X > *p*-CH_3 > H > *m*-CH_3 > *o*-X in agreement with the order for electron attraction by a substituent,[5] and hence indicated a predominately bimolecular or S_N2 reaction mechanism favored by the withdrawal of electrons. Franzen,[6] who studied the reaction of several substituted benzyl chlorides with sodium ethoxide in absolute alcohol, also observed this reaction to be a second order reaction in which the effect of substituents in increasing the reactivity was *o*-CH_3 > *p*-X > *p*-CH_3 > *m*-X > *m*-CH_3 > H > *o*-X. The effect of halogen substitution is of especial interest since the order for electron release is the resultant of opposing inductive and mesomeric or resonance effects as defined by Ingold.[5] The net result of these effects for benzenoid halogen has been indicated to be in the order F > Cl > Br > I on the basis of evidence from a number of sources.[7] In the meta substituted benzyl fluorides the order of reactivity was found to be exactly as expected, I > Br > Cl > F. In the para series the order was I > Cl > Br > F, the position of the chloro and bromo isomers being reversed due presumably to polarization effects.

The relative reactivities of the substituted benzyl fluorides were also found by determining the per cent. reaction of the fluorides after refluxing in various reagents for a definite length of time. The solvents were alcohol and 1.0 *N* hydrochloric acid, alcohol and 0.1 *N* hydrochloric acid, aqueous alcohol, and alcohol and 1.0 *N* sodium hydroxide. The initial molar concentrations of the benzyl fluorides were maintained approximately the same in all cases to insure comparable results. When acidic solvents were used, there was some loss of hydrogen fluoride, but the loss could not change the order of reactivity since corresponding losses would occur in all cases.

In the reaction with alcohol and 1.0 *N* sodium hydroxide solution, the observed order of reactivity was *m*-NO_2 > *p*-X > *p*-CH_3 > *m*-CH_3 > H > *m*-X > *o*-X. This order does not follow either the order for electron release or electron withdrawal for the substituents, although it agrees with the order for the effect of substituents determined by Olivier[8] for the reaction of substituted benzyl chlorides with dilute alkali in aqueous acetone. Apparently in this case, reaction was occurring concurrently by both S_N2 and S_N1 mechanisms. This seemed further to be indicated since the reaction of *p*-chlorobenzyl fluoride with dilute aqueous alcoholic sodium hydroxide yielded

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[1] Presented in part before the Division of Organic Chemistry of the American Chemical Society at Atlantic City, N. J., September 10, 1941. Based on the thesis submitted by Jack Bernstein to the Graduate School of Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1941.

[2] Present address: Squibb Institute for Medical Research, New Brunswick, N. J.

[3] Bernstein, Roth and Miller, THIS JOURNAL, **70**, 2310 (1948).

[4] Ingold and Rothstein, *J. Chem. Soc.*, 1217 (1928); Hughes and Ingold, *ibid.*, 244 (1935). For general type mechanisms for halide replacement reactions see Hughes, *ibid.*, 968 (1946), and references cited.

[5] Ingold, *Chem. Revs.*, **15**, 225 (1934).

[6] Franzen, *J. prakt. Chem.*, [2] **97**, 82 (1919); Franzen and Rosenberg, *ibid.*, **101**, 333 (1920).

[7] Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, London, 1941, p. 101.

[8] Olivier and Weber, *Rec. trav. chim.*, **53**, 869 (1934).