

424. *The Dissociation Constants of the Monohalogenated Anilines and Phenols.*

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ALTHOUGH several determinations are on record of the dissociation constants of *p*-chloro- and *p*-bromo-aniline (Farmer and Warth, J., 1904, **85**, 1726; Flürscheim, J., 1910, **97**, 88; Williams and Soper, J., 1930, 2469), such data have not been found for the complete series of halogenated amines, and in particular, no values have been reported for the fluoro-anilines. A few observations are available for chloro- and bromo-phenols, but complete data for the monohalogenophenols are lacking. These constants are of considerable importance in connexion with any discussion of aromatic chemistry in which halogenated nuclei are involved, and they are, moreover, of direct interest in connexion with the problem of the influence of the various halogens on side-chain reactivity of various kinds (Bennett, J., 1933, 1112). We have therefore prepared a complete set of monohalogenated anilines and phenols and have determined their dissociation constants under comparable conditions by observations of p_{H} , using the glass electrode.

Since the majority of phenols and amines studied in the present work are sparingly soluble in water, aqueous alcohol (30% of ethyl alcohol by vol., 24.7% by weight) was used as solvent throughout; certain measurements were also made in water for purposes of comparison. The use of aqueous alcohol as solvent raises the question of the justification of regarding the dissociation constant as a measure of the intrinsic strength of an acid (or base), *i.e.*, of its tendency to lose (or gain) a proton. According to Wynne-Jones (*Proc. Roy. Soc.*, 1933, **140**, A, 440; see also *Chem. and Ind.*, 1933, **52**, 273; Burkhardt, *ibid.*, p. 330), this concept is invalid, since the order of the strengths of a series of acids may vary from solvent to solvent, and both theoretical and experimental evidence is quoted to support this contention. From an examination of the theoretical considerations (Bjerrum and Larsson, *Z. physikal. chem.*, 1927, **127**, 358; Brönsted, *Chem. Reviews*, 1928, **5**, 231; *Z. physikal. chem.*, 1934, **169**, 52; Wynne-Jones, *loc. cit.*), it appears, however, that the strengths of a series of acids (or bases) of the same type should be in the same order in all solvents, provided there be no complicating side reactions of a purely chemical nature. This should justify the use of the dissociation constant, as measured in any convenient solvent, in order to compare amongst themselves the strengths of a number of phenols or amines. It is true that in certain instances organic acids do not show the same order of dissociation constants in all solvents, but in view of the overwhelmingly large number of cases in which the order is the same for acids (or bases) of the same type in water and in

various organic solvents (Michaelis and Mizutani, *Z. physikal. Chem.*, 1925, **116**, 135; Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 3; Halford, *J. Amer. Chem. Soc.*, 1931, **53**, 2944; Hall, *ibid.*, 1930, **52**, 5115; Hall and Sprinkle, *ibid.*, 1932, **54**, 3469; LaMer and Downes, *ibid.*, 1933, **55**, 1840; Goodhue and Hixon, *ibid.*, 1934, **56**, 1329; Kilpatrick and Kilpatrick, *Chem. Reviews*, 1933, **13**, 131), the former may be regarded as exceptions due either to chemical interaction or to experimental error. Results obtained in the course of the present work with chloro- and fluoro-phenols and -amines, when compared amongst themselves and with those of others (Kuhn and Wassermann, *loc. cit.*; Williams and Soper, *loc. cit.*), show that the ratio of the dissociation constants of the phenols, or of the amines, in water are almost identical with the ratios in various mixtures of water and ethyl or methyl alcohol. Further evidence that the order of the strengths of acids is the same, at least in water and in 30% alcohol, is obtained from the measurements of p_H made during the titration with sodium hydroxide of a mixture of citric acid, potassium dihydrogen phosphate, boric acid, and veronal (Table I); the values in the aqueous alcohol are systematically 0.3—0.5 unit higher than for the corresponding system in aqueous solution, showing that the dissociation constants of the seven acids present are in the same order in both solvents.

EXPERIMENTAL.

Preparation and Purification of Materials.—*Isomeric fluoronitrobenzenes.* The nitroanilines were converted into the fluoronitrobenzenes by Balz and Schiemann's method (*Ber.*, 1927, **60**, 1186). The diazonium borofluoride, precipitated by adding sodium borofluoride as solid or concentrated solution to the diazonium solution, was obtained in 80—90% yield. The derivative of the *o*-isomeride is more soluble in water, and the bulk of the solution must be kept at a minimum. The decomposition of the salt was carried out as follows: Small portions of the salt were mixed with an equal bulk of sand in a large distilling flask and heated on an oil-bath; a stream of air was passed through the flask to which an air condenser and a large bottle were connected, the whole being evacuated. The temperature of the oil-bath was slowly raised to 170°, and the product was collected in ether, washed with dilute alkali, dried, and distilled. The yield of fluoronitrobenzene was 40—50% for the *m*- and *p*- but 10% for the *o*-isomeride.

Amines. The three fluoroanilines were prepared from the pure fluoronitrobenzenes. *o*-Fluoroaniline had b. p. 72°/17 mm. *m*-Fluoroaniline, b. p. 184—185°, yielded with phenyl isocyanate *m*-fluorodiphenylcarbamide, crystallising in colourless monoclinic needles, m. p. 200° (Found: C, 67.8; H, 4.8. $C_{13}H_{11}ON_2F$ requires C, 67.8; H, 4.8%); and *p*-fluoroaniline, b. p. 184—186°, similarly yielded *p*-fluorodiphenylcarbamide in colourless flat needles with straight extinction, m. p. 236° (Found: C, 68.0; H, 4.8%).

Of the remaining amines, the chloro- and *o*- and *m*-bromo-anilines were purchased from British Drug Houses, and the others were prepared from the nitroaniline through the halogenonitrobenzenes. Chloroanilines: *o*-, b. p. 209°; *m*-, b. p. 229—230°; *p*-, m. p. 69°; bromoanilines: *o*-, b. p. 229°, m. p. 30°; *m*-, b. p. 247°; *p*-, m. p. 62°; iodoanilines: *o*-, m. p. 59°; *m*-, m. p. 25°; *p*-, m. p. 62°.

Phenols. Of the fluorophenols, the *m*-isomeride was obtained in 50% yield by decomposition of the diazonium salt from pure *m*-fluoroaniline. It had b. p. 178° and yielded a *p*-nitrobenzoate which crystallised from acetic acid in flat needles or elongated plates, m. p. 93°, with high double refraction, each an association twin with composition plane forming a central line down its length (Found: C, 60.0; H, 3.3. $C_{13}H_8O_4NF$ requires C, 59.8; H, 3.1%).

Repeated attempts to prepare the *o*- and *p*-fluorophenols from the amines by the same process were unsuccessful, large amounts of brown material (presumably azo-compounds) being produced. These substances were therefore prepared through the fluoroanisoles (compare Swartz, *Bull. Acad. roy. Belg.*, 1913, 255, who prepared *p*-fluorophenol from *p*-fluorophenetole).

The *o*-anisyl diazonium borofluoride (82 g. from 50 g. of anisidine) yielded *o*-fluoroanisole (18 g.), b. p. 157—159°. This was added to anhydrous aluminium chloride (15 g.), and the mixture heated to 110° in an oil-bath for 3 hours under reflux. Dilute hydrochloric acid was added to the cooled mixture, and the phenol removed in ether, extracted from it by 10% sodium hydroxide, and finally liberated by acid, taken up in ether again, the solution dried, and distilled. The fluorophenol had b. p. 151—152° (6 g.), and its *p*-nitrobenzoate crystallised from acetic acid in large plates, m. p. 98°, with high double refraction and oblique extinction, sometimes showing similar twinning to that of the *m*-isomeride (Found: C, 59.9; H, 3.2%).

p-Fluoroanisole, b. p. 174—175° (23 g. from 50 g. of *p*-anisidine), in the same way yielded

p-fluorophenol, b. p. 81.5°/13 mm. (15 g.), which solidified, m. p. 28°. Its *p*-nitrobenzoate crystallises from acetic acid in large orthorhombic plates with high double refraction, m. p. 100° (Found : C, 60.0; H, 3.3%).

Of the remaining phenols, *p*-chloro- (m. p. 37°) and *p*-bromo-phenol (m. p. 63°) were purified specimens of purchased material, and *m*-chlorophenol (b. p. 214°, m. p. 28°) was kindly provided by Dr. H. H. Hodgson. The *m*-bromophenol (b. p. 236°, m. p. 32°) and iodophenols (*o*-, m. p. 42°; *m*-, m. p. 40°; *p*-, m. p. 93°) were prepared from the pure amines. In order to ensure the purity of *o*-chloro- and *o*-bromo-phenols, the purchased materials were converted into the *p*-toluenesulphonates, which were respectively large colourless monoclinic crystals, m. p. 74° (Found : C, 55.1; H, 4.1. C₁₃H₁₁O₃ClS requires C, 55.3; H, 3.9%), and massive monoclinic prisms, m. p. 76° (Found : C, 47.9; H, 3.6. C₁₃H₁₁O₃BrS requires C, 47.7; H, 3.4%). The phenols were recovered from these : *o*-chlorophenol, b. p. 174—175°; *o*-bromophenol, b. p. 193—194°.

All the substances examined were freshly redistilled or recrystallised at least twice immediately before use.

Method of Measurement.—According to Brönsted (*loc. cit.*), the strengths of acids (or bases) are best compared in a given solvent by the use of the acidity (or basicity) “constant,” defined for the acid HA by the expression $k = a_{\text{H}} \cdot [\text{A}^-] / [\text{HA}]$, where a_{H} represents the activity of the hydrogen ion, and square brackets indicate concentration terms. The function varies with concentration and the true (sometimes called “thermodynamic”) constant (K) for a given solvent should be obtained at infinite dilution by extrapolation or by use of the expression $a_{\text{H}} \cdot a_{\text{A}^-} / a_{\text{HA}}$, with the standard state defined so as to make the activity and stoichiometric concentration identical at infinite dilution. On introduction of activity coefficients (f), it is seen that $K = \{a_{\text{H}} \cdot [\text{A}^-] / [\text{HA}]\} \cdot f_{\text{A}^-} / f_{\text{HA}}$. For the solvent used in the present work (dielectric constant 64.4; Wyman, *J. Amer. Chem. Soc.*, 1931, 53, 3292) the extended Debye–Hückel equation giving the variation of the activity coefficient of the A⁻ ions with concentration at 25° may be written in the form $-\log f_{\text{A}^-} = 0.683\sqrt{\mu} - C\mu$, where μ is the ionic strength of the medium and C is a constant, which is greater the larger the “mean effective diameter” of the ions present. Since all the phenols and anilines yield relatively large ions, it is not unreasonable to suppose that C will have a value of at least 2. On the basis of this assumption it can be calculated that the maximum variation of f_{A^-} in the course of the measurements described in this paper was from 0.96 to 0.92 when using a 0.01*N*-solution of phenol or aniline, or from 0.92 to 0.88 in the few cases in which a 0.05*N*-solution was used. As a general rule, the activity coefficient of an undissociated substance increases with increasing ionic strength, as is shown by the “salting-out” effect of ions, but with phenols or amines in the presence of their respective salts this is probably not the case. The solubility of aniline in water is increased by the presence of its salts (Sidgwick, Pickford, and Wilsdon, *J.*, 1911, 99, 1222; von Euler and Svanberg, *Z. Elektrochem.*, 1917, 23, 192; Pedersen, *J. Amer. Chem. Soc.*, 1934, 56, 2615), and the critical solution temperature of phenol is lowered by the presence of phenoxide; consequently, in each case the activity coefficient of the undissociated species decreases with increasing ionic strength, and this is probably true in general for anilines and phenols in the presence of their salts. In view of the relatively small deviation of f_{A^-} from unity, it appears, therefore, that no considerable error will be involved in the present circumstances by assuming that $f_{\text{A}^-} / f_{\text{HA}}$ is unity; similarly for a base it may be supposed that f_{B^+} is equal to f_{BOH} . The thermodynamic dissociation constant under these conditions will then be equal to the acidity (or basicity) constant defined above. This assumption has been made by other workers, sometimes without justification, and it is virtually equivalent to the use of the “acidity potentials” as defined by Schwarzenbach (*Helv. Chim. Acta*, 1930, 13, 870).

The most convenient method for determining the acidity (or basicity) constant is to titrate a solution of the phenol (or amine) of known concentration with a standard solution of a strong alkali (or acid), and to find the p_{H} of the system at different stages of neutralisation. Since the latter gives a direct measure of a_{H^+} in a given mixture, and the ratio $[\text{A}^-] / [\text{HA}]$ can be determined from the amounts of acid (or alkali) added, the dissociation constant can be calculated. For acid–base mixtures of p_{H} 4—10, the simple Henderson equation may be used, but outside these limits the more accurate forms must be employed (cf. Glasstone, “The Electrochemistry of Solutions,” pp. 189—194). The constancy of the values of K obtained in this work justify the assumptions made concerning the ratio of the activity coefficients of the ions and undissociated molecules.

The accurate determination of p_{H} involves some form of the hydrogen electrode: it is well known that the gas electrode is unsatisfactory in the presence of amines or of phenols, although it has been used, e.g., by Branch, Yabroff, and Bettman (*J. Amer. Chem. Soc.*, 1934, 56, 937), in

aqueous-alcoholic solutions of chlorophenols; these authors state, however, that the final potentials were only attained very slowly and often large drifts were observed. The quinhydrone electrode has been employed in some cases for phenols and amines (*e.g.*, Kuhn and Wassermann, *loc. cit.*), but poisoning may occur and the electrode is evidently unsatisfactory in these solutions. Two obvious objections to the use of quinhydrone are, first, with phenols the p_H values often exceed 9, which is beyond the limit of reliability of the electrode, and secondly, there is always a danger of interaction between an amine and the quinol. The antimony electrode has been employed with aqueous-alcoholic solutions by Halford (*ibid.*, 1931, 53, 2944), although this is known to give only approximate p_H values over a relatively limited range. The glass electrode suffers from none of the disadvantages of the other hydrogen electrodes; it is said to be unsatisfactory in alcohol-rich aqueous mixtures (Dole, *ibid.*, 1932, 54, 3095), but it appeared likely to be reliable in the mixture we were using. This expectation was borne out in the course of the present work, and satisfactorily reproducible results were obtained when difficulties due to the resistance of the glass had been overcome.

Measurements of p_H .—The glass electrodes were made of the special glass supplied by Messrs. Dixon of Devonshire Street, London, W.C.1 (see Harrison, J., 1930, 1522); a number of both the MacInnes and Dole type (*Ind. Eng. Chem., Anal.*, 1929, 1, 57) and of the bulb type were tried, but, in agreement with the findings of Harrison (*loc. cit.*) and contrary to those of Greville and MacLagan (*Trans. Faraday Soc.*, 1931, 27, 210), the latter were found to be much more satisfactory, especially if the valve in the potentiometer was not of the "electrometer triode" type. The bulbs were blown on 3-mm. tubing and had a diameter of about 2.5–3 cm.; they contained an acetate-acetic acid buffer and a little quinhydrone into which a clean platinum wire was inserted, and their resistance was about 20 megohms, or less. The potentiometer circuit was similar to that described by Morton (J., 1931, 2938), modified so as to operate directly from the A.C. mains; the valve was an Osram ML 4, and its sensitivity was varied by means of a rheostat in the cathode circuit which provided "automatic" grid bias. In order to maintain stability, the negative side of the valve system was connected to earth. The circuit can be recommended as a simple and efficient one for use with electrodes of not too high resistance, although precautions must be taken that the double-pole switch has good insulation and that the impedance of the potentiometer system is high (*cf.* Morton, J., 1934, 256).

A saturated potassium chloride-calomel electrode was used as the comparison electrode, and this was connected to the beaker, containing the glass electrode supported on a well-insulated stand, by means of a syphon tube filled with saturated potassium chloride solution. There is, no doubt, a liquid-junction potential of uncertain magnitude between the aqueous alcohol in the beaker and the potassium chloride solution, but since the same (or similar) junction appears in the measurements made to standardise the glass electrode, the error resulting from its presence is probably negligible. The combined cell was supported on a well-insulated porcelain plate inside an aluminium thermostat filled with liquid paraffin kept at 25°; to avoid the interference of stray potentials, the thermostat was connected to earth. When using the glass electrode, it was found advisable to immerse the bulb so that the liquid inside it was at the same level as that in the titration vessel; this necessitated occasional adjustment of the electrode during the course of measurement. The glass electrode acquired its equilibrium potential with reasonable rapidity, 5 minutes being generally sufficient if the change of p_H did not exceed 2 units.

The electrodes were calibrated by means of a form of Britton and Robinson's universal buffer solution (J., 1931, 1456); it consists of citric acid, potassium dihydrogen phosphate, boric acid, diethylbarbituric acid, and sodium chloride, being 0.0286*M* with respect to each. This solution in water was first titrated with 0.2*N*-sodium hydroxide, and the p_H values determined by means of a hydrogen-gas electrode; the experiment was then repeated with the buffer mixture and the alkali dissolved in the 30% alcohol. The results are shown in Table I: the close proximity, at least up to p_H 10, of the curves, which are readily reproducible, suggests that the results are reliable in the alcoholic solution. The potential of the glass electrode was then determined in a number of solutions of known p_H made from the buffer mixture and sodium hydroxide in water and also in the aqueous alcohol. The plot of p_H against electrode potential was very close to a straight line over the p_H range 2–10, and the slope was 98–100% of the theoretical value; the potentials in the alcoholic solution were about 0.020 below those in water. The glass electrodes were generally calibrated in this way before each titration of phenol or amine; the potential of an efficient electrode in a given solution varied only slightly over a period of weeks.

For determination of the dissociation constants, 50 c.c. of a 0.01*N*-solution (in some cases 0.05*N*) of phenol or amine in the 30% alcohol were titrated with a 0.01*N* (or 0.05*N*)-solution of sodium hydroxide free from carbon dioxide, or of hydrochloric acid, made up in the same

solvent; the p_H values of the solution were determined after each addition of titrant. With the fluoro-phenols and -amines, the measurements were also made in aqueous solution with glass electrodes calibrated in the same solvents.

TABLE I.
Calibration of Universal Buffer.

50 C.c. of buffer solution titrated by 0.2N-NaOH.

C.c.	p_H (H ₂ O).	p_H (30% EtOH).	C.c.	p_H (H ₂ O).	p_H (30% EtOH).	C.c.	p_H (H ₂ O).	p_H (30% EtOH).
0	2.39	2.73	14	5.05	5.38	28	7.46	7.76
2	2.71	2.99	16	5.36	5.73	30	7.76	8.09
4	3.13	3.51	18	5.69	6.01	32	8.12	8.47
6	3.60	3.95	20	6.10	6.43	34	8.56	8.92
8	3.98	4.34	22	6.44	6.81	36	8.98	9.47
10	4.39	4.65	24	6.75	7.15	38	9.43	9.93
12	4.70	5.03	26	7.10	7.44	40	9.90	10.41

In Table II full details are given for *o*-fluoroaniline and *o*-fluorophenol. In Tables III and IV the data for the complete series of anilines and phenols respectively are summarised, the most trustworthy values for aniline and phenol (in water) being added from the literature.

TABLE II.
Dissociation Constant of *o*-Fluoroaniline.

I. In 30% ethyl alcohol at 25.0°.

50 C.c. of 0.05N-amine titrated with 0.05N-HCl.

Acid, c.c.	10	15	20	25	30	40	
p_H	3.18	2.90	2.71	2.57	2.47	2.29	
p_{K_b}	11.47	11.54	11.57	11.57	11.54	11.51	Mean 11.53; $K_b = 2.95 \times 10^{-12}$.

II. In water at 25.0°.

50 C.c. of 0.01N-amine titrated with 0.01N-HCl.

Acid, c.c.	5	10	15	20	25	
p_H	3.98	3.63	3.44	3.27	3.15	
p_{K_b}	11.03	11.05	11.01	11.05	11.04	Mean 11.04; $K_b = 9.20 \times 10^{-12}$.

Dissociation Constant of *o*-Fluorophenol.

50 C.c. of 0.01N-phenol titrated with 0.01N-NaOH.

I. In 30% ethyl alcohol at 25.0°.

NaOH, c.c. ...	10	15	20	25	30	40	
p_H	8.73	9.01	9.20	9.37	9.56	10.00	
p_{K_a}	9.33	9.38	9.38	9.37	9.39	9.39	Mean 9.37; $K_a = 4.27 \times 10^{-10}$.

II. In water at 25.0°.

NaOH, c.c. ...	10	15	20	25	30	40	
p_H	8.20	8.43	8.63	8.82	8.99	9.42	
p_{K_a}	8.80	8.80	8.81	8.82	8.81	8.82	Mean 8.81; $K_a = 15.5 \times 10^{-10}$.

TABLE III.
Dissociation Constants of Anilines at 25.0°.

Substance.	Mean p_{K_b} .	Limits of p_{K_b} .	K_b $\times 10^{12}$.	Substance.	Mean p_{K_b} .	Limits of p_{K_b} .	K_b $\times 10^{12}$.
I. In 30% ethyl alcohol.							
Aniline	9.90	9.85—9.92	126	<i>o</i> -Bromoaniline	12.00	11.96—12.01	1.00
<i>o</i> -Fluoroaniline	11.53	11.47—11.57	2.95	<i>m</i> -Bromoaniline	11.10	11.04—11.13	7.94
<i>m</i> -Fluoroaniline	10.98	10.90—11.01	10.5	<i>p</i> -Bromoaniline	10.66	10.62—10.70	21.9
<i>p</i> -Fluoroaniline	9.92	9.92—9.93	120	<i>o</i> -Iodoaniline ...	12.45	12.35—12.54	0.36
<i>o</i> -Chloroaniline	11.87	11.82—11.89	1.35	<i>m</i> -Iodoaniline...	11.12	11.09—11.17	7.59
<i>m</i> -Chloroaniline	11.07	11.02—11.11	8.51	<i>p</i> -Iodoaniline ...	10.82	10.77—10.85	15.1
<i>p</i> -Chloroaniline	10.54	10.51—10.55	28.8				
II. In water.							
<i>o</i> -Fluoroaniline	11.04	11.01—11.05	9.20	<i>p</i> -Fluoroaniline	9.36	9.33—9.38	441
<i>m</i> -Fluoroaniline	10.59	10.55—10.68	25.7	Aniline *			400

* Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

TABLE IV.

Dissociation Constants of Phenols at 25.0°.

Substance.	Mean pK_a .	Limits of pK_a .	$K_a \times 10^{10}$.	Substance.	Mean pK_a .	Limits of pK_a .	$K_a \times 10^{10}$.
I. In 30% ethyl alcohol.							
Phenol	10.49	10.43—10.52	0.32	<i>o</i> -Bromophenol	9.01	8.98—9.04	9.78
<i>o</i> -Fluorophenol	9.37	9.33—9.39	4.27	<i>m</i> -Bromophenol	9.36	9.34—9.39	4.37
<i>m</i> -Fluorophenol	9.82	9.80—9.83	1.51	<i>p</i> -Bromophenol	9.81	9.77—9.85	1.55
<i>p</i> -Fluorophenol	10.59	10.58—10.61	0.26	<i>o</i> -Iodophenol ...	9.04	9.01—9.05	9.12
<i>o</i> -Chlorophenol	8.99	8.97—9.01	10.2	<i>m</i> -Iodophenol...	9.41	9.30—9.43	3.89
<i>m</i> -Chlorophenol	9.31	9.28—9.34	4.90	<i>p</i> -Iodophenol ...	9.66	9.64—9.70	2.19
<i>p</i> -Chlorophenol	9.88	9.85—9.92	1.32				
II. In water.							
<i>o</i> -Fluorophenol	8.81	8.80—8.82	15.5	<i>p</i> -Fluorophenol	9.95	9.95—9.95	1.12
<i>m</i> -Fluorophenol	9.28	9.26—9.29	5.25	Phenol *			1.20

* Mizutani, *Z. physikal. Chem.*, 1925, **118**, 318; compare Walker and Cormack, *J.*, 1900, **77**, 5.

DISCUSSION OF THE RESULTS.

These results are in general agreement with other comparable values on record. For instance, the three monochloroanilines have been compared by de Rohden (*J. Chim. physique*, 1915, **13**, 207) by conductometric titration in water; by Brønsted and Duus (*Z. physikal. Chem.*, 1925, **117**, 299) by a potentiometric method and by observations of the catalysis of the decomposition of diazoacetic ester in water; by Kuhn and Wassermann (*loc. cit.*) by potentiometric observations in 50% methyl alcohol; by Williams and Soper (*loc. cit.*) by a partition method in water; and by Goodhue and Hixon (*loc. cit.*) by calculation from the solvolysis constants of Goldschmidt and Mathiesen (*Z. physikal. Chem.*, 1926, **119**, 439) in ethyl and methyl alcohols, the bromoanilines being included. The three monochlorophenols have also been compared by Kuhn and Wassermann (*loc. cit.*) in 50% methyl alcohol; by Branch, Yabroff, and Bettmann (*loc. cit.*) in 25% ethyl alcohol; and by Murray and Gordon (*J. Amer. Chem. Soc.*, 1935, **57**, 110) in 50% methyl alcohol.

The figures now recorded confirm the difference between the strengths of *p*-chloro- and *p*-bromo-aniline which had originally attracted attention, and the inclusion of the other halogens shows that the underlying tendency is general and much more pronounced than had been apparent from the scanty data previously available.

As regards both *m*-halogenoanilines and *m*-halogenophenols, the strengths are almost the same for the various halogens with the exception of the fluoro-compounds—the fluoro-amine being definitely stronger and the fluorophenol weaker than the others. It may be recalled that the strengths of the *m*-halogenobenzoic acids are all approximately equal (Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 31). In the *o*- and *p*-series of anilines the strengths fall definitely from fluorine to iodine, the variation being largest with the *p*-isomerides. In the *o*- and *p*-series of phenols there is less variation, but once again the fluoro-compounds are outstanding, the fluoro-phenols being all weaker than the other analogous halogenophenols. The most striking fact which emerges is that although *m*-fluoroaniline and *m*-fluorophenol differ in strength markedly from aniline and phenol, in the expected directions, *p*-fluoroaniline and *p*-fluorophenol are each approximately equal in strength to the parent substances.

The significance of these comparisons will be referred to in a subsequent paper.