

55. *The Dissociation Constants of m-Halogenated Phenols and of some of their Mononitro-derivatives.*

By HERBERT H. HODGSON and REGGIE SMITH.

The dissociation constants of the *m*-halogenated phenols have been measured in aqueous and in 30% aqueous-alcoholic solutions, and the data of Bennett, Brooks, and Glasstone (J., 1935, 1821) confirmed. The dissociation constants of 2-, 4-, and 6-nitro-3-fluorophenol, 2- and 4-nitro-3-chloro- and 2- and 4-nitro-3-bromo-phenol have also been obtained in 30% aqueous alcohol to ascertain the combined effect of the nitro-group and the halogen atom.

BENNETT, BROOKS, and GLASSTONE (J., 1935, 1821) have recorded the dissociation constants of all the monohalogenated phenols in solution in aqueous alcohol (30% of ethyl alcohol by vol., 24.7% by weight), in connexion with a study of the polar influences of halogens in substituted aromatic compounds (*ibid.*, p. 1827). Since one of the present authors was in possession of the complete set of 2-, 4-, and 6-nitro-*m*-halogenophenols (Hodgson and Moore, J., 1925, 127, 1599; 1926, 155; 1927, 630; Hodgson and Nixon, J., 1928, 1879), it appeared of interest to find the combined effect of the halogen atom and the nitro-group on the dissociation constants of the phenols in which they were substituents.

The nitro-*m*-halogenophenols are only sparingly soluble in 30% alcohol and of necessity 0.005*N*-solutions had to be used; even at this dilution, solutions of 6-nitro-3-chloro-, -3-bromo-, and -3-iodo-phenols could not be made. The paper therefore records data for all the 2- and 4-nitro-3-halogenophenols and for 3-fluoro-6-nitrophenol. Bennett, Brooks, and Glasstone (*loc. cit.*, p. 1822) state that the order of the strengths of acids is the same at least in water and in 30% alcohol. Dissociation constants in water, however, are considerable multiples of those in aqueous alcohol, *e.g.*, $K_a \times 10^{10}$ for *m*-fluorophenol is 5.25 in water and 1.51 in 30% alcohol, and therefore we considered that measurements in aqueous 90% alcohol (the composition required to bring 3-iodo-6-nitrophenol into 0.005*N*-solution) would not be justified. Measurements of the four *m*-halogenophenols have been made in 0.005*N*-solutions in water, and the orders of the magnitudes of the dissociation constants found to be the same as for 30% aqueous alcohol. The data of Bennett, Brooks, and Glasstone for 30% aqueous alcohol, therefore, have been confirmed, though our results are slightly lower (see Table).

The dissociation constants of the *m*-halogenophenols, except *m*-fluorophenol (< *m*-iodophenol), show uniformity, whether in water or in 30% alcohol, in the anticipated order of their inductive ($-I$) effects, *viz.*, Cl > Br > I. The anomalous minimum value exhibited by *m*-fluorophenol is completely reversed when the powerful effect of the nitro-group is combined with it whether in the 2-, 4-, or 6-position. The dissociation constants of all the halogenonitrophenols now measured not only exhibit entire uniformity

and in the order 6-nitro-*m*-Hal. > 2-nitro-*m*-Hal. > 4-nitro-*m*-Hal., but they are all greater than the dissociation constants of the *o*-, *m*-, and *p*-nitrophenols. Further, in all cases the dissociation constant of the fluoronitro-member of the series is greater than that of its chloro-, bromo-, or iodo-analogue, the order being F > Cl > Br > I. It would appear, therefore, that, whatever may be the cause of the exceptional minimum value for fluorine in *m*-fluorophenol, it has been removed in the fluoronitrophenols, since the data clearly indicate addition and not subtraction of the nitro- and the halogeno-effect.

EXPERIMENTAL.

The substances were prepared according to the directions given in the papers cited; they were distilled under reduced pressure several times (where possible), and recrystallised immediately before use.

The dissociation constants were evaluated from measurements of the p_H values of 0.005N-solutions (50 c.c.) at various stages of neutralisation by 0.005N-sodium hydroxide. Accurate determinations of the p_H values were made by means of a glass electrode of the bulb type, used in conjunction with a direct p_H -reading electrometer valve potentiometer. The glass electrode was trustworthy and gave reproducible results. The bulb electrode contained N-hydrochloric acid saturated with quinhydrone, into which dipped a platinum wire connected to a gold-plated terminal, and was totally immersed in the solution whose p_H value was required; this solution was connected by means of a bridge tube (with tap), containing saturated potassium chloride, to a standard electrode of the saturated calomel type. The entire apparatus was supported inside a copper thermostat maintained at $25.0^\circ \pm 0.05^\circ$. The potentiometer was of the electrometer triode type operated from a 12-volt battery, and was calibrated to read directly in p_H units. Potassium hydrogen phthalate and borax were used throughout for buffer solutions to standardise the electrode and the meter; the calibrations were checked before each titration. In all the measurements, the glass electrode was left for 10 minutes before the p_H value of the titrated solution was read. The potential of uncertain magnitude which occurs at the liquid junction between the saturated potassium chloride solution and the solution to be measured was neglected throughout (cf. Bennett, Brooks, and Glasstone, *loc. cit.*, p. 1824).

Dissociation Constants of Phenols at 25.0°.—The actual titrations are not included, since our experimental details are identical with those of Bennett, Brooks, and Glasstone (*loc. cit.*).

In 30% ethyl alcohol.

Phenol.	Mean p_{Ka} .	Limits of p_{Ka} .	K_a .	Phenol.	Mean p_{Ka} .	Limits of p_{Ka} .	K_a .
<i>m</i> -Fluoro-	9.82	9.81—9.84	1.51×10^{-10}	<i>m</i> -Bromo-	9.48	9.46—9.50	3.31×10^{-10}
3-Fluoro-6-nitro-	6.63	6.62—6.65	2.34×10^{-7}	3-Bromo-2-nitro-	6.78	6.76—6.79	1.66×10^{-7}
3-Fluoro-2-nitro-	6.70	6.67—6.73	1.99×10^{-7}	3-Bromo-4-nitro-	6.84	6.83—6.85	1.45×10^{-7}
3-Fluoro-4-nitro ...	6.78	6.76—6.80	1.66×10^{-7}	<i>m</i> -Iodo-	9.51	9.50—9.53	3.09×10^{-10}
<i>m</i> -Chloro-.....	9.44	9.43—9.46	3.63×10^{-10}	3-Iodo-2-nitro- ...	6.89	6.88—6.90	1.29×10^{-7}
3-Chloro-2-nitro-...	6.75	6.73—6.76	1.78×10^{-7}	3-Iodo-4-nitro- ...	6.94	6.92—6.96	1.15×10^{-7}
3-Chloro-4-nitro-...	6.80	6.78—6.81	1.58×10^{-7}				

In water.

<i>m</i> -Fluoro-	9.27	9.26—9.28	5.37×10^{-10}	<i>m</i> -Bromo-	9.11	9.09—9.12	7.76×10^{-10}
<i>m</i> -Chloro-.....	9.07	9.05—9.08	8.51×10^{-10}	<i>m</i> -Iodo-	9.17	9.15—9.18	6.76×10^{-10}

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TECHNICAL COLLEGE, HUDDERSFIELD.

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