[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Dissociation Constants of Some Chlorophenols

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The purpose of this investigation was to obtain data on the dissociation of phenol derivatives, with particular emphasis on the dichlorophenols, in order to study the effect of the number and position of substituted chlorine atoms on the dissociation of the phenolic hydrogen. Data recorded by various workers using diverse methods are available in the literature concerning the dissociation of: phenol, the monochlorophenols, 2,4-dichlorophenol, and all of the tri- and tetrachlorophenols and pentachlorophenol. It has been the aim of the present investigation to obtain the data necessary to complete the series of chlorophenol dissociation constants and check the previous work on the lower members of the series.

Experimental and Materials

The method used in this investigation was the determination of the *p*H numbers of solutions of the respective phenol derivatives in the presence of their sodium salts. Because of the slight solubilities of the chlorophenols in water, the solutions were made up with 50% methanol. The measurements were carried out by means of the hydrogen electrode using a saturated calomel half-cell as a reference electrode. Measurements were made on two sets of solutions for each of the chlorophenols studied. In all of these solutions, the concentration of the phenol was 0.1 molal in a water–methanol solvent containing 50% of methanol by volume. In the first set of solutions (A), the concentration of sodium hydroxide was 0.05 molal and in the second set (B), 0.01 molal. In the case of phenol, measurements were also made on a set of corresponding solutions containing no methanol in order to estimate the effect of the solvent upon the dissociation constant. Pure chlorophenols were prepared for this work by Dr. John R. Ruhoff in this Laboratory and will be described elsewhere by him. All other materials used were of the highest purity.

Results

The *p*H values are collected together with the corresponding temperatures and dissociation constants, in Table I. The potential of the saturated calomel electrode is a function of temperature and a graph of Clark's values was used.[1] The dissociation constants were calculated on the basis of concentrations without correction to activities using the equation

$$K = [H^+] \times [A^-]/[HA] = [H^+] \times [NaOH]/([HA] - [NaOH])$$

assuming that the phenolate-ion concentration is equal to that of the sodium hydroxide. Thus the dissociation constant is equal to the apparent hydrogen-ion concentration for the A series of solutions, as the phenol is half neutralized with sodium hydroxide. The last column of Table I contains the results for the aqueous solutions of phenol and estimated values of the dissociation constants of aqueous solutions of the chlorophenols obtained by assuming that the effect of the change from water to 50% methanol upon the *p*H of the solution is the same for these compounds as for phenol. This point will be discussed further below.

TABLE I

		A			B		Aqueous	
Substance	*p*H	*T*	$K' \times 10^{10}$	*p*H	*T*	$K' \times 10^{10}$	*p*H	$K' \times 10^{10}$
Phenol	10.63	29.0	0.23	9.65	29.1	0.244	9.78	1.7
o-Chlorophenol	9.34	29.0	4.6	8.28	29.0	5.8	8.49	32
m-Chlorophenol	9.71	29.0	1.9	8.71	29.0	2.2	8.86	14
p-Chlorophenol	10.04	28.4	0.91	9.05	28.5	0.99	9.18	6.6
2,3-Dichlorophenol	8.30	29.0	50	..	..	..	7.45	360
2,4-Dichlorophenol	8.60	29.4	25	7.58	29.8	29	7.75	180
2,5-Dichlorophenol	8.20	29.7	63	7.21	29.7	68	7.35	450
2,6-Dichlorophenol	7.64	29.0	230	6.68	29.0	230	6.79	1600
3,4-Dichlorophenol	9.24	29.0	5.8	8.20	29.0	7.0	8.39	41
3,5-Dichlorophenol	8.78	29.0	17	7.68	29.0	23	7.93	120

A, Phenol: NaOH = 2:1. B, Phenol: NaOH = 10:1.

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[1] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1928, p. 672.

Discussion of Results

The results obtained in this investigation are in fairly good agreement with those obtained by Kuhn and Wassermann[2] for phenol and the monochlorophenols working under similar conditions. The values obtained by other workers[3] using various methods exhibit great variety.

The early work of Bader gives values far higher than those of any of the later investigators. The later work is in agreement as to the order of magnitude but the variations are rather large. The data now available are probably of sufficient accuracy to establish definitely the order in which the dissociation constants of the series are arranged.

In Table II, we have listed the estimated values for the dissociation constants for the mono- and dichlorophenols in aqueous solution and the values measured by Tiessens[4] for the higher members of the series. The estimated values for the mono- and di-substitution products are those given in the last column of Table II and are derived by assuming that the change from water to 50% methanol affects the pK' of all of these compounds to the same extent. That this is approximately so is suggested by the work of Mizutani,[3] who has studied phenol and *p*-chlorophenol in various mixtures of methanol and water. Bright and Briscoe,[5] who have studied the chlorobenzoic acids, find that the effect of the alcohol is proportional to the strength of the acid. It seems probable, however, that the estimated values are of the correct order of magnitude and that the values will retain the same order in the series. The errors to be anticipated are small compared to the differences shown between the members of the series.

TABLE II

DISSOCIATION CONSTANTS OF THE CHLOROPHENOLS IN AQUEOUS SOLUTION (*VALUES BY TIESSENS[4])

Phenol	Monochloro		Dichloro		Trichloro		Tetrachloro		Pentachloro
$K' \times 10^7$	Isomer	$K' \times 10^{10}$	Isomer	$K' \times 10^{10}$	Isomer	$K' \times 10^{10}$	Isomer	$K' \times 10^{10}$	$K' \times 10^{10}$
1.7	*o*	32	2,3	360	2,3,4	260*	2,3,4,5	1100*	55,000*
	m	14	2,4	180	2,3,5	540*	2,3,4,6	69,000*	
	p	6.6	2,5	450	2,3,6	7600*	2,3,5,6	36,000*	
			2,6	1600	2,4,6	3800*			
			3,4	41	2,4,5	180*			
			3,5	120	3,4,5	470*			

Hixon and Johns[6] have summarized the available data on the dissociation constants of substituted phenols, amines and benzoic acids and find that the values can be correlated with the relative electronegativities of the substituent and its distance from the ionizing group, that is, whether it is ortho, meta or para. Our results are in accord with the findings of Hixon.

Comparison of the data presented in Table II shows several factors operating in the effect of substitution. The effect is proportional to the number of substituents in the ring. It is also proportional to the proximity of the substituents to the hydroxyl group. A comparison of the values for 2,3- and 2,5-dichlorophenol shows that when there are two chlorine atoms attached to the ring in the ortho and meta positions, respectively, the effect produced is greater when they are para to each other than when they are adjacent. This indicates that there is some interaction between the effects of the two substituents. This effect is also shown by Tiessens' values for the 2,3,4- and 2,4,5-trichlorophenols. Comparison of the values for the tetrachlorophenols and pentachlorophenol presents a deviation from the order to be expected from the above conclusions drawn from the lower members of the series in that the 2,3,4,6-tetrachlorophenol has a value higher than that of the 2,3,5,6-compound which has its substituents closer to the hydroxyl group and also higher than that of pentachlorophenol which has one more chlorine atom. This suggests the possibility that the value of this compound is in error.

Summary

The dissociation constants of phenol, the monochlorophenols and the dichlorophenols have been measured electrometrically in 50% methanol solution. A complete set of values for the series of chlorophenols is thus rendered available. The relation of these values to the problem of the effect of substitution upon the electronegativity of radicals is mentioned.

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(2) Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 3 (1928).

(3) (a) Roller, *J. Phys. Chem.*, **34**, 367 (1930); (b) Stenström and Goldsmith, *ibid.*, **30**, 1683 (1926); (c) Lundén, *Z. physik. Chem.*, **70**, 249 (1910); (d) Hahn and Klockmann, *ibid.*, **A146**, 373 (1930); (e) Michaelis and Rona, *Biochem. Z.*, **49**, 232 (1913); (f) Treadwell and Schwarzenbach, *Helv. Chim. Acta*, **11**, 386 (1928); and references mentioned therein.

(4) Tiessens, *Rec. trav. chim.*, **48**, 1066 (1929); **50**, 112 (1931).

(5) Bright and Briscoe, *J. Phys. Chem.*, **37**, 787 (1933).

(6) Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927).