in the buffer ratio. If the amount of carbon dioxide can be assumed constant in solutions with decreasing buffer concentration, a distinct curvature would be introduced into the extrapolation line. The absence of such curvature in the data obtained was taken as evidence that the precautions taken to keep out carbon dioxide were sufficient.

Some measurements were made at temperatures other than 25° to estimate the temperature coefficients of the dissociation constants and of the extinction constants. It was concluded that 0.1° regulation was satisfactory for an accuracy of 0.2% in the measured K_{A_iB}.

Comparison with Literature.—The dissociation constant of *m*-nitromesitol has not been measured previously. The values measured for the other nitrophenols are in reasonably good agreement with the values given in Table III except for the value given by Holleman and Wilhelmy for *m*-nitrophenol which is apparently in error. The visual colorimetric values of Kolthoff and of Michaelis seem also to be consistently lower than the values obtained in other ways. The values reported by Bader[27] for the mononitrophenols are not shown in Table III as they are entirely out of line with all later measurements.

The agreement for the chlorophenols is only fair. Abichandani and Jatkar[28] measured the complete set of chloro-, bromo- and iodophenols and reported that the dissociation constants of the bromo- and iodophenols were somewhat lower than those for the chlorophenols, particularly for the ortho compounds. The measurement of *o*-bromophenol in the present investigation was made to check this point, failing to show a difference comparable with the 0.28 log unit difference reported by Abichandani and Jatkar. Bennett, Brooks and Glasstone[29] also reported from measurements in ethanol–water mixtures that the fluorophenols were distinctly weaker than the chlorophenols, the largest difference being observed for the para isomer. The present measurement of *p*-fluorophenol verifies the marked difference between this compound and *p*-chlorophenol.

Summary

A photoelectric colorimeter has been constructed and used for precise measurements of the ratio K_{A_iB} between the dissociation constant in aqueous solution at 25° for a nitrophenol indicator and the constant for another substituted phenol. A detailed study has been given to the sources of error in measurements by this method. The thermodynamic dissociation constant and the ratio $K_{A_xB_0}$ between the dissociation constant of the substituted phenol and the constant for phenol have been calculated from these data for twelve substituted phenols. The values obtained have been compared with the results of previous measurements.

(29) Bennett, Brooks and Glasstone, *J. Chem. Soc.*, 1821 (1935).

(27) Bader, *Z. physik. Chem.*, **6**, 289 (1890).

(28) Abichandani and Jatkar, *J. Ind. Inst. Sci.*, **3**, 99 (1940).

STAMFORD, CONN.

CHICAGO, ILL.

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The Effects of Substituents on the Dissociation Constants of Substituted Phenols. II. Calculations from the Electrostatic Theory[1]

BY CHARLES M. JUDSON[2,3] AND MARTIN KILPATRICK[4]

Measurement of the dissociation constants of some substituted phenols have been described in the preceding paper.[5] The equation developed by Sarmousakis[6] using electrostatic theory to calculate the ratio $K_{A_xB_0}$ between the dissociation constant for a substituted acid and the constant for the unsubstituted acid has been applied in this paper to the substituted phenols. The conventions used to determine the variable parameters in the equation were changed slightly from those used by Sarmousakis. The calculated values have been compared with the observed values from the previous paper and from the literature. The test of the agreement between the calculated and observed values was made more rigorous by making the comparison for both the phenols and the benzoic acids using a consistent method of calculation.

The equation developed by Sarmousakis is a modification of the equation used by Kirkwood and Westheimer[7] for the electrostatic interaction between a substituent dipole and a dissociating proton. It can be readily shown from a simple treatment that this equation should have the general form

$$-2.3 \log K_{A_xB_0} = \frac{e\mu \cos \theta}{r^2 D_E kT} \qquad (1)$$

(1) Taken from the dissertation presented by Charles M. Judson to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1947. Presented before the 112th meeting of the American Chemical Society held in New York, N. Y., September, 1947.

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(5) Judson and Kilpatrick, THIS JOURNAL, **71**, 3110 (1949).

(6) Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

(7) Kirkwood and Westheimer, *ibid.*, **6**, 506 (1938); Westheimer and Kirkwood, *ibid.*, **6**, 513 (1938); Westheimer and Shookhoff, THIS JOURNAL, **61**, 555 (1939); Westheimer, *ibid.*, **61**, 1977 (1939).

where μ is the dipole moment of the substituent, r is the distance from the center of the dipole to the dissociating proton, θ is the angle between the vector representing the dipole and the vector corresponding to r, e is the charge on the electron, k is the Boltzmann constant, T is the absolute temperature and D_E is an effective dielectric constant. Kirkwood and Westheimer first showed how the term D_E could be estimated for certain cases. They calculated D_E for the para-substituted benzenoid acids by considering the molecule to be a prolate spheroidal cavity of low internal dielectric constant D_i embedded in a medium of higher dielectric constant D which is the dielectric constant of the solvent.

Sarmousakis set up as a model for the para-substituted acid an oblate rather than prolate spheroid with the proton and the center of the dipole located on the focal circle of the speroid, obtaining the equation

$$-\log K_{A_xB_0} = \frac{1}{2.3kT}\left[\frac{e\mu_\xi \cos(/\mu_\xi/i_1,r)}{r^2 D_\xi} + \frac{e\mu_\phi \cos(/\mu_\phi/i_2,r)}{r^2 D_\phi}\right] \quad (2)$$

The terms of this equation have been defined by Sarmousakis. It is sufficient to note that the equation is similar in form to equation (1) but is expressed in vector form with two quantities D_ξ and D_ϕ representing the effective dielectric constant. Sarmousakis showed how to calculate the quantities D_ξ and D_ϕ in terms of D and D_i and a parameter ξ_0 defining the shape of the molecule. The solution was expressed in terms of certain Legendre polynominals which were tabulated in Sarmousakis' paper. The quantity ξ_0 can be calculated in a simple manner from the molecular volume τ and the focal radius c which define the spheroidal cavity. It was possible using equation (2) to make calculations for the metasubstituted acids as well as the parasubstituted acids.

Sarmousakis recognized that there was a certain arbitrariness in the selection of numerical values for some of the parameters in equation (2). Instead of calculating the focal radius c from the distance between the dipole and the proton in the parasubstituted acid, he adjusted the focal radius c arbitrarily for each metasubstituted benzoic acid so as to give agreement between the calculated and observed values for the dissociation constant in aqueous solution. Using the same value for c in the parasubstituted acid, the difference between the calculated and observed values for the parasubstituted acid was then attributed to a resonance effect.

There are two possible positions which may be assumed for the proton in a substituted benzoic acid, a free rotation position permitting rotation about both the C–C bond and the C–O bond, and an extended position in which the C–O–H bond is frozen with the proton away from the dipole. The arbitrary values of c selected were found to

lie between the values of c calculated for these two positions.

Calculations of $K_{A_xB_0}$.—The conventions used in carrying out the calculations for the present paper were, with a few exceptions, the same as those used by Sarmousakis. An attempt was made, however, to carry out the calculations without any arbitrary adjustment of parameters such as was used by Sarmousakis. The focal radius c calculated from structural considerations was used instead of the arbitrarily adjusted focal radius used by Sarmousakis. In calculating the focal radius the position of the proton was taken for the phenols as an average position with free rotation about the C–O bond and the position for the benzoic acids was taken to be the average extended position described above. The distance r was calculated trigonometrically instead of using the value $\sqrt{3c}$ for the value of r. The location of the center of the dipole was taken for all cases at the mid-point of the line from the benzene ring to the projection of the outermost atom on the axis of the ring, instead of locating the dipole for polyatomic substituents at the position of the iodo group dipole.

The dipole moments for the halogenobenzenes were taken from Hurdis and Smyth,[8] for nitro-

TABLE I

log $K_{A_xB_0}$

	Obsd.	Calcd. 1[a]	Calcd. 2[b]
m-Phenols			
F	0.82	0.78	1.01
Cl	1.02	.80	1.03
Br	0.96	.77	0.99
I	.92	.71	.91
CH₃	− .07	− .18	− .14
NO₂	1.61	1.71	1.81
p-Phenols			
F	0.14	0.56	0.73
Cl	.64	.56	.72
Br	.59	.54	.70
I	.64	.50	.64
CH₃	− .23	− .13	− .10
NO₂	2.81	1.20	1.20
m-PhCOOH			
F	0.34	0.29	0.36
Cl	.38	.29	.37
Br	.39	.29	.36
I	.35	.26	.34
CH₃	− .06	− .06	− .05
NO₂	.72	.70	.63
p-PhCOOH			
F	.06	.21	.26
Cl	.22	.21	.26
Br	.23	.20	.25
I	c	.18	.23
CH₃	− .17	− .05	− .03
NO₂	.78	.53	.40

[a] Preliminary calculations. [b] Final calculations. [c] Not measured, low solubility.

(8) Hurdis and Smyth. THIS JOURNAL. **64**, 2212 (1942).

benzene from Smyth[9] and for toluene from Baker and Groves.[10] The bond distances and angles and the atomic radii were selected from the values given by Pauling,[11] Branch and Calvin[12] Maxwell.[13] The dielectric constant of water was taken as 78.5[14] and the value 2.00 used by Kirkwood and Westheimer and by Sarmousakis was again used for D_i. $K_{A_xB_0}$ values calculated in this way are shown in the third column of Table I.

Experimental Values of $K_{A_xB_0}$.—In order to compare the calculated and experimental values of log $K_{A_xB_0}$ it was necessary to select with as much consistency as possible a single set of values for the dissociation constants of the meta- and parasubstituted phenols and benzoic acids in aqueous solution. The values selected by Elliott and Kilpatrick[15] for comparison with their data in alcohol solution were used for the benzoic acids. The values reported in the previous paper were used for the nitrophenols, and the data given by Boyd[16] were used to calculate $K_{A_xB_0}$ for the cresols. The values for the chlorophenols were calculated from an average of the values in the previous paper and the values of Abichandani and Jatkar.[17] Except for p-fluorophenol, the values for the other halogenophenols, which differed only slightly from the values for the corresponding chlorophenols, were calculated from the average difference between the reported constants for the halogenophenols and the constants reported by the same investigator for the corresponding chlorophenol. The data of Hodgson and Smith[18] were used for the halogenophenols in addition to the sources cited for the chlorophenols. The measured value for p-fluorophenol, which was quite different from the value for p-chlorophenol, was taken directly from the previous paper. The accepted experimental values are listed in the second column of Table I.

Calculations with Adjusted Parameters.—The calculated values in the third column of Table I are consistently lower than the observed values. An arbitrary adjustment of parameters was therefore required. Instead of changing the focal radius c, the internal dielectric constant D_i was arbitrarily adjusted to provide the best possible agreement between the calculated and observed values for the metasubstituted halogenophenols and halogenobenzoic acids. The revised calculated values shown in the fourth column were obtained with D_i equal to 1.54. It was found that the same value of D_i selected to give agreement for

(9) Smyth, J. Phys. Chem., **41**, 209 (1937).
(10) Baker and Groves, J. Chem. Soc., 1147 (1939).
(11) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.
(12) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941.
(13) Maxwell, J. Optical Soc. Am., **30**, 374 (1940).
(14) Akerlof, THIS JOURNAL, **54**, 4125 (1932).
(15) Elliott and Kilpatrick, J. Phys. Chem., **45**, 472 (1941).
(16) Boyd, J. Chem. Soc., **107**, 1538 (1915).
(17) Abichandani and Jatkar, J. Ind. Inst. Sci., **3**, 99 (1940).
(18) Hodgson and Smith, J. Chem. Soc., 263 (1939).

the m-chloro, m-bromo and m-iodophenol also gave the best agreement for the corresponding m-halogenobenzoic acids.

The increase in the absolute value of $K_{A_xB_0}$ obtained by changing D_i from 2.00 to 1.54 clearly would not improve the agreement with the observed values for the metasubstituted nitro and methyl derivatives. Since the true location of the dipole in these polyatomic substituents was not known, it was possible to adjust this position so as to bring about better agreement between the observed and calculated values for the metasubstituted phenols and benzoic acids. In these cases it was not possible to bring about exact agreement for both the phenols and the benzoic acids so a compromise adjustment was made. The position selected for the dipole in the nitro group was at a distance of 1.26 Å. from the ring, compared to a distance of 1.46 Å. from the ring to the nitrogen atom and a distance of 1.99 Å. to the projection of the oxygen atom on the line of the C–N bond. For the methyl group the dipole was located 1.35 Å. from the ring, compared to a distance of 1.50 Å. to the methyl carbon atom and 1.83 Å. to the projection of the methyl hydrogen atom.

Resonance Contributions.—Sarmousakis calculated values of Δ log $K_{A_xB_0}$ for the parasubstituted benzoic acids from the difference between the observed and calculated values. This term Δ log $K_{A_xB_0}$ was considered to be a measure of the resonance contribution to the acid strength of the parasubstituted acid. In the present calculations the treatment is slightly more complicated because the calculated values have not been adjusted to bring exact agreement with the observed values for each individual acid. For this reason Δ log $K_{A_xB_0}$ was calculated by subtracting the difference between the observed and calculated values for the meta acid from the difference between the observed and calculated values for the para acid.

These methods of calculating resonance contributions are based on the assumption that there is no resonance in the metasubstituted acid. Actually it can be seen that in Table I there is a larger difference between the observed and calculated values for m-fluorophenol than for the other m-halogenophenols. This appears to be due to a resonance effect whose magnitude can be estimated by subtracting the average difference between the observed and calculated values for the remaining m-halogenophenols from the difference for m-fluorophenol. The resonance contributions estimated similarly for the other m-halogen acids were very small.

While the m-halogen acids can be considered from the point of view of the differences from one halogen to another, it is not so easy to tell from the measured $K_{A_xB_0}$ values whether there is any resonance in the acids with nitro and methyl substituents in the meta position. The differences

between the observed and calculated values for these metasubstituted acids may also be due in part to resonance effects.

The calculated values of the resonance contribution term are shown in Table II. While the general ideas involved in predicting the effects of resonance on the strength of acids have been presented in several places[19] and the effects for aromatic acids have been studied in particular detail,[19a] the resonance structures required to explain the effects in the acids considered here do not appear to have been formulated explicitly in any one place.

TABLE II
$\Delta \log K_{A_x B_0}$

	Phenols		Benzoic acids	
	m	p	m	p
F	−0.18	−0.40	−0.04	−0.18
Cl	.00	− .07	− .01	− .05
Br	− .02	− .08	.01	− .05
·I	.02	− .01	− .01	....
CH₃	....	− .20		− .13
NO₂	....	1.81		.29

The resonance in phenol between the aromatic ring and the anion of the acidic group (I) is more important than the resonance involving the corresponding form of the free acid. This leads to an acid strengthening resonance effect in phenol. The resonance between the ring and an alkyl or halogen group in the para position (II) tends to weaken the resonance of the acidic group (I) and thereby weaken the acid. The resonance between the ring and the para nitro group (III) enhances the resonance (I) and is acid strengthening.

The resonance between the carbonyl group and the ring in benzoic acid (IV) tends to weaken the resonance between the carbonyl group and the anion of the acidic group (V) and is acid weakening. The resonance of the para nitro group (III) with the ring decreases the resonance (IV) and is acid strengthening while the ·resonance of the methyl or halogen group (II) increases (IV) and is acid weakening.
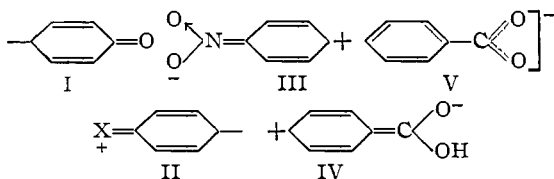
The resonance in the halogen-substituted acids is observed to increase in magnitude from the iodo to the fluoro group. The increase for the p-fluoro acid over the value for the p-chloro acid is particularly marked and shows that the magnitude of the resonance term cannot be predicted from the mesomeric moment[20] alone, since the

(19) (a) Ref. 12, Chapter VI; (b) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.
(20) Groves and Sugden, J. Chem. Soc., 1992 (1937).

mesomeric moments of the halogenobenzenes increase more or less uniformly from one halogen group to the next.

While resonance effects are not usually encountered in metasubstituted acids, the resonance effect in m-fluoro acids has been observed previously and explanations have been offered to account for it.[21]

Specific Ortho Effects.—The Legendre polynomials required for the calculation of D_ξ and D_ϕ for orthosubstituted acids have not been evaluated because the series converge too slowly. Some other method of treatment must be used to find out whether the experimental data can be interpreted to show the presence or absence of specific ortho effects.

Jenkins[22] has reported that for the halogeno- and nitrobenzoic acids the logarithm of the dissociation constant for three isomeric substituted benzoic acids and the unsubstituted acid is proportional to a function F which represents the field strength which would exist at the number one carbon atom of the ring due to the substituent dipole if the dielectric constant were unity. The function F is calculated from the equation

$$F = \mu\sqrt{1 + 3\cos^2\theta}/r^3 \qquad (3)$$

where r, μ and θ have the same meaning as in equation (1). According to this treatment log $K_{A_x B_0}$ should be a constant for the three isomeric acids if the effects are entirely inductive. The values of this ratio are shown in Table III for the substituted benzoic acids.

TABLE III
$\log K_{A_x B_0}/F$ FOR BENZOIC ACIDS

Subst.	Ortho	Meta	Para
F	2.2	3.2	0.8
Cl	3.3	3.7	3.1
Br	3.8	4.0	3.3
I	4.1	3.9	....
CH₃	6.0	−4	−15
NO₂	3.3	4.0	6.1

The dissociation constants were taken from the same sources as those used for Table I and the field strength was calculated using the same conventions and the same physical constants as were used to calculate log $K_{A_x B_0}$ from the Sarmousakis treatment. The function F was considered positive in all cases so that an increase in the algebraic value of the ratio in the table always corresponds to an acid strengthening.

The assumption involved in this treatment is that the acid group may be regarded more or less as a perfect conductor so that the ring carbon atom is the center determining the free energy of ionization. Since the resonance effect in the metasubstituted acids is relatively small, deviations of the ratios in Table III from the value for

(21) Dippy and Lewis, ibid., 644 (1936).
(22) Jenkins, ibid., 640 (1939).

the corresponding metasubstituted acid may be considered to indicate the presence of effects other than inductive.

The resonance effects of the parasubstituted acids indicated by the variations in Table III are in qualitative agreement with the resonance effects which were measured quantitatively by the Sarmousakis treatment. An acid strengthening resonance effect is shown for p-nitrobenzoic acid and an acid weakening resonance for p-toluic acid and the p-halogenobenzoic acids. The o-nitrobenzoic and o-toluic acids show deviations from the meta-substituted acids in the opposite direction from the deviations shown by the para-substituted acids. This may be considered evidence of a specific ortho effect, acid strengthening for o-toluic acid and acid weakening for o-nitrobenzoic acid. The o-halogenobenzoic acids have ratios between those of the meta- and the parasubstituted acids. In this case the presence or absence of specific ortho effects is not clearly demonstrated.

Jenkins had concluded that the absence of specific ortho effects was proven by the approximate agreement in these ratios for the three corresponding acids, except for the toluic acids in which case he admitted that a specific ortho effect was indicated. It must be admitted that if the values of log $K_{A_xB_0}$ are plotted against F, as was done by Jenkins, the discrepancies are not quite so obvious as when the ratios are calculated as in Table III. As an example the data for the nitrobenzoic acids are shown in Fig. 1. Since the theoretical basis of the treatment is not clearly established, there is certainly a question how large a deviation is required to be significant. Since the differences between the ratios in Table III for the meta- and parasubstituted acids can be interpreted satisfactorily in terms of resonance effects in the parasubstituted acid, the interpretation of the deviations for the orthosubstituted acids in terms of chelation or of resonance of a different type from that found in the parasubstituted acid seems justified.

Jenkins also plotted the logarithm of the dissociation constant against the electric potential at the number one carbon atom.[23] In a plot of the potential ψ against log $K_{A_xB_0}$ for a set of isomeric substituted benzoic acids, a line is obtained quite similar to that obtained in plotting against the field strength, but this line does not pass through the origin. In treating the phenols Jenkins plotted against the potential and found that the data for the ortho- and para-substituted halogenophenols in alcohol–water mixtures formed a line passing through the origin, that is, the point representing the unsubstituted acid. He then argued that the relative magnitude of resonance and inductive effects should be the same in the ortho- and para-substituted acids and that this linear relationship therefore indicated the

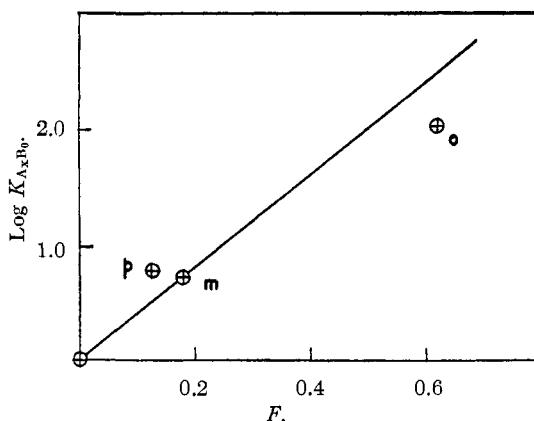(23) Jenkins, *J. Chem. Soc.*, 1137 (1939).

Fig. 1.—Dissociation constants of nitrobenzoic acids.

absence of specific ortho effects in the halogenophenols. There are three objections which can be taken to Jenkins' treatment of the halogenophenols. First, no reason was given to explain why the plot against potential should necessarily go through the origin when it had been shown that the plot for the halogenobenzoic acids did not go through the origin. Without the origin as a fixed point there is no obvious significance to a line through the points for two of the isomeric acids. Second, no proof has been given that the relative effects of resonance are the same in the ortho- and parasubstituted acids although this is probably acceptable as an approximation. Third, the value used in Jenkins' paper for p-fluorophenol in alcohol–water solution does not agree with the value in the paper of Bennett, Brooks and Glasstone[24] from which it was reported to have been taken. Using the value from the original paper the data for the fluorophenols does not fit the relationship proposed by Jenkins.

Abichandani and Jatkar[17] returned to the use of the field strength as a measure of the inductive effect in the phenols and used the method of Jenkins' first paper. They plotted the data for the halogenophenols in water and in alcohol–water mixtures against the field strength to show the existence of specific ortho effects in the halogenophenols. Using this same treatment, the ratio log $K_{A_xB_0}/F$ has been calculated for the halogen-, nitro- and methyl-substituted phenols in aqueous solutions using the same sources of data used in the application of the Sarmousakis treatment, with the

TABLE IV

log $K_{A_xB_0}/F$ OF PHENOLS

Subst.	Ortho	Meta	Para
F	2.7	7.7	1.8
Cl	4.2	10.0	8.9
Br	4.1	9.9	8.6
I	4.6	10.1	10.1
CH₃	-5.2	-5	-21
NO₂	4.4	8.9	22

(24) Bennett, Brooks and Glasstone, *ibid.*, 1821 (1935).

addition of the dissociation constant for o-fluoro-phenol from Bennett, Brooks and Glasstone. The large acid weakening effects in p-cresol and p-fluorophenol, the less marked weakening in the other p-halogenophenols and the large acid strengthening in p-nitrophenol are clearly shown just as for the comparable treatment of the benzoic acids and as for the more quantitative treatment by the Sarmousakis method. There is further a marked acid weakening effect in o-chloro-, o-bromo- and o-iodophenol. This effect is distinctly different from the resonance effect in the p-halogenophenol which is small except for the fluorophenol. There is also an acid weakening effect in o-nitrophenol shown and, in the case of o-cresol, there is an acid strengthening which at least compensates for the acid weakening resonance which appears in p-cresol.

The theoretical weakness of the treatment based on the field strength at the number one carbon atom is recognized. The basis for suggesting the further use of this treatment for the study of deviations from the normal inductive effects is that the effects indicated by this treatment for the phenols and benzoic acids can all be accounted for in terms of resonance forms which are reasonable in the light of our present knowledge.[19] Except for the effects in o-halogeno-phenols and in o-nitrobenzoic acid, these deviations from the inductive effect have been previously accepted. The effect in o-nitrobenzoic acid is small and therefore not definitely established. The effect in the o-halogenophenols is clearly established if this method of treatment is valid.

Summary

The Sarmousakis modification of the Kirkwood–Westheimer method of calculating the ratio of the dissociation constant of a substituted acid to that of the unsubstituted acid has been used to calculate values for the meta- and parasubstituted phenols and benzoic acids. Using a consistent set of assumptions it has been possible to adjust the parameters so that agreement could be obtained between the calculated and the observed values for aqueous solutions for both the meta-substituted phenols and the metasubstituted benzoic acids. The differences between the calculated and observed values for the parasubstituted acids have been calculated as a measure of resonance effects.

Following a suggestion made by Jenkins, values of log $K_{A_xB_0}/F$ were calculated relating the ratio between the dissociation constants to the field strength at the ring carbon atom due to the dipole. Differences in this ratio for the corresponding ortho-, meta- and parasubstituted acids have been interpreted qualitatively in terms of resonance and chelation effects.

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Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds[1,2]

BY GEORGE B. BUTLER AND ROBERT L. BUNCH

The absence of information in the literature concerning the polymerization of unsaturated quaternary ammonium compounds prompted us to study the preparation and polymerization of compounds of this type as a possible source of water insoluble polymers containing strongly basic groups. Products of this nature should be capable of absorbing negative ions from neutral salt solutions.

Since the presence of nitrogen in organic compounds quite often exhibits an inhibitory effect on peroxide catalyzed polymerization, there was some doubt that polymerization of these compounds could be accomplished. However, since quaternary ammonium halides are salts of strong bases and strong acids, it appeared likely that polymerization of these neutral salts would occur under the proper conditions. This was found to be the case as described in detail below.

In order for a cross-linked polymer to result from vinyl type polymerization of a pure unsaturated quaternary ammonium salt, the presence of at least two unsaturated groups in the molecule is essential. Therefore, all of the compounds studied have contained at least two unsaturated groups, while some have contained three or four. The compounds were prepared by reaction of unsaturated tertiary amines, several of which had not been prepared previously with the appropriate alkyl halides. The majority of the compounds were prepared as the bromides, and were found to have rather high melting points. Introduction, however, of relatively high molecular weight radicals such as benzyl usually lowered the melting point. Most of the salts were found to be rather hygroscopic and are very soluble in water, low molecular weight alcohols, and formamide, fairly soluble in hot ketones, but insoluble in most other organic solvents.