plotted as ordinate against the reduced height $z = x/2\sqrt{Dt}$ as abscissa. On such a plot the values of z for a constant ordinate increment represent the positions of the Rayleigh fringes. The ratio of the separation of the pair indicated in column 1 of Table II to that of the same pair from a normal plot (*i.e.*, one of which $D_1/D_2 = (dn/dc)_1/(dn/dc)_2 = 1$) is tablulated in the subsequent columns of that table. As is indicated in the first column an increment of 0.04 in N was selected, thus duplicating the conditions used in this research. In order that the uncertainty in the graphical interpolations would not obscure trends in the computed fringe spacings, the assumed variations in D and dn/dc, given at the head of each column, are greater than those usually encountered in practice.

With dn/dc constant and $dD/dc < 0$, column 3, the ratio increases with dilution, but the mean value does not differ significantly from unity. Since the diffusion coefficient is proportional to the square of this ratio it appears that the method of computation used by the author yields a mean value when D varies linearly with C and the specific refraction is constant. On the other hand if D is constant and dn/dc varies sufficiently, column 2, an incorrect value for the coefficient is obtained although in the absence of independent data this fact would not be recognized experimentally. Comparison of the figures in column 4 with those in columns 3 and 5 indicates that the ratio is more nearly constant if the concentration dependence of D and dn/dc has the same sign, a result suggested above in connection with the diffusion of butanol.

When dn/dc is constant the approximate linearity of the ratio with concentration, *e.g.*, column 3 of Table II, provides a simple method for the evaluation of D_1/D_2. If a ratio in this column is plotted against the corresponding mean concentration the slope, m, of the resulting line is characteristic for the assumed value of D_1/D_2. On preparing such graphs for $D_1/D_2 = 0.8806, 0.7228, 0.5506, 0.3270$ and 0.1407 the corresponding values found for $-m$ were 0.109, 0.264, 0.468, 0.836 and 1.250. A plot of these *versus* D_1/D_2 appears to be linear in the neighborhood of $D_1/D_2 = 1$ where $D_1/D_2 = 1 + 1.09m$. If, now, the reduced fringe separations of an actual photograph are normalized, through division by their average value, they may be plotted just as the ratios of Table II and D_1/D_2 evaluated from the slope of the resulting line. Figure 2 is such a plot for the butanol fringes. Here the small circles represent individual values from each of the last five photographs, whereas a large one is the average at a given mean concentration. The slope of the line through these points, as determined by least squares, is -0.0530 from which $D_1/D_2 = 0.942$. The results summarized in Table II suggest that
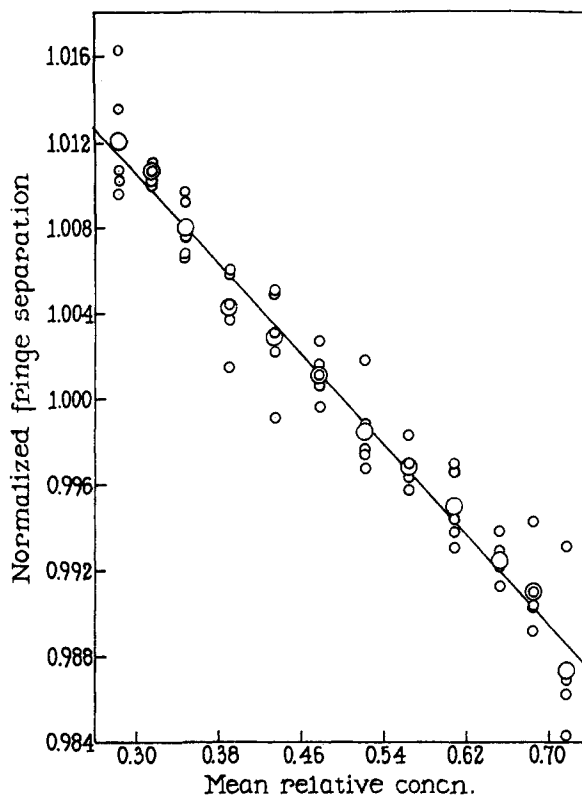

Fig. 2.—Effect on the fringe separation of a variation of the diffusion coefficient with the concentration in the boundary.

correction for the concentration dependence of the specific refraction might raise this somewhat closer to the value of 0.954 predicted by the results of Lyons and Sandquist. The graphical methods used here are inadequate, however, when $(dn/dc)_1/(dn/dc)_2$ is as near unity, namely, 1.03, as in this experiment. As mentioned above, the question must be left open as to whether or not the usual variations in the specific refraction are a source of detectable skewness.

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Dissociation Constants of Some Phenols and Methylol Phenols

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The acidities of phenol and of its methylol derivatives as well as of further methyl and methylol substituted phenols have been determined by the ultraviolet spectroscopic method. The relative values of pK thus obtained are estimated to be accurate within ± 0.03. A calculated correction to obtain the thermodynamic values is given. A discussion of the effect of acidity of substituted phenols on their relative reactivities is given.

The various phenols charged and methylol phenols engendered in the process of making phenolic resins differ quite largely in their speed of reaction with formaldehyde.[1] This reactivity can be expected to bear some relation to their acidity, since the anion of a phenol is more reactive toward electrophilic substitution than the undissociated molecule.[2]

The effect of substituents is not simple, partic-

(1) M. M. Sprung, THIS JOURNAL, **63**, 334 (1941).
(2) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 149-150, 204-205.

ularly when the substituent varies widely in nature. A knowledge of the relative acidities may, however, give some insight into the relative rate of reaction of phenols with formaldehyde in buffered solutions when the directing substituents are comparatively simple and slightly active, such as the methyl or methylol groups.

For the measurement of these acidities, a method operating at very low concentration is preferred for two reasons: low solubility of many phenols does not permit higher concentrations; and calculation of the correction needed to obtain the thermo-

dynamic values of pK is impractical at higher ionic strengths. The ultraviolet absorption spectra were therefore used to determine the percentage of the anion form of a phenol present in buffered, aqueous solutions of known pH.[3] From these data the pK easily can be calculated. Spectra were taken of solutions 0.0002 M in phenol and 0.02 M in a carbonate-bicarbonate buffer. The values obtained are therefore subject to a correction to adjust them to the thermodynamic scale.

At 25° the Debye-Hückel relation for the ionic activity coefficient is given by

$$-\log f = \frac{0.5056z^2\sqrt{\mu}}{1 + 0.3286 \times 108a\sqrt{\mu}}$$

where f, z and a refer, respectively, to the activity coefficient, valency and radius of the particular ionic species involved, and μ to the ionic strength. For polyatomic ions this quantity is somewhat artificial, since the formula was developed for charged, spherical ions. However, a trial shows that assumption of any value for a from 1 Å. to 6 Å. yields values for $-\log f$ that do not deviate from the mean of -0.09 by more than ± 0.01. The correction to be applied to the values found for pK may therefore be taken to be 0.09 without exceeding the experimental errors.

The pK values obtained for various phenols and their derivatives are shown in Table I. The values given in parentheses were determined in buffers other than the one at the most favorable pH normally used and are not quite as accurate as the other values given. They may nevertheless serve as a general check on the accuracy of the method. It will be noted that the thermodynamic value for phenol corresponds very well with other recent determinations of this constant at 9.94 and 9.95.[4]

TABLE I

| | pK | |
	Found	Thermo-dynamic
Phenol	9.85	9.94
o-Methylolphenol	9.83	9.92
p-Methylolphenol	9.73	9.82
m-Methylolphenol	9.74	9.83
2,4-Dimethylolphenol	9.68	9.77
2,6-Dimethylolphenol	9.57 (9.59)	9.66
2,4,6-Trimethylolphenol	9.47 (9.49)	9.56
o-Methylphenol	10.19	10.28
p-Methylphenol	10.10 (10.08)	10.19
2,4-Dimethylphenol	10.49	10.58
2,4,6-Trimethylphenol	10.80	10.88
2-Methylol-4-methylphenol	10.06	10.15
2,6-Dimethylol-4-methylphenol	9.83	9.92

Though carbon is more electronegative than hydrogen, the methyl group is electron-donating and ortho-para directing.[2] It would thus be expected to lower the acidity of phenol, which it does. Replacement of an o-hydrogen atom in phenol by methyl thus causes an increase of 0.34-0.35 in pK. Replacement of the second o-hydrogen by methyl causes a further, equal rise in pK. Replacement of the p-hydrogen atom in phenol or a

(3) L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, 57, 2103 (1935).

(4) W. H. Fletcher, ibid., 68, 2726 (1946); C. M. Judson and M. Kilpatrick, ibid., 71, 3110 (1949).

derivative of phenol by methyl causes a rise of only 0.23-0.26 in pK.

The methylol group should have a mild electron-withdrawing effect on the nucleus, in analogy to the chloromethyl group.[5] This is borne out by the fact that replacement of a p-hydrogen in phenols by the methylol group increases the acidity, lowering pK by 0.10-0.15. The same effect is noted when a methylol group replaces the m-hydrogen. Since the effect is largely inductive, it might be expected to be at least as great in the ortho position as in meta or para. However, replacement of the o-hydrogen in a phenol by methylol causes only 0.02-0.05 decrease in pK, instead of 0.15. The difference lies in the fact that in an o-methylolphenol the two hydroxyls approach each other sufficiently closely to permit formation of a hydrogen bond. Since the effect is to decrease acidity, this bond must form with the bridging proton being supplied by the phenolic hydroxyl, this proton being thus more firmly bound.[6] The effect of this bond is to increase pK by about $0.15 - 0.03 = 0.12$.

When the second o-hydrogen on an o-methylolphenol is replaced by a methylol group, the pK decreases by 0.21-0.26, or more than the straight inductive effect would seem to provide. The total
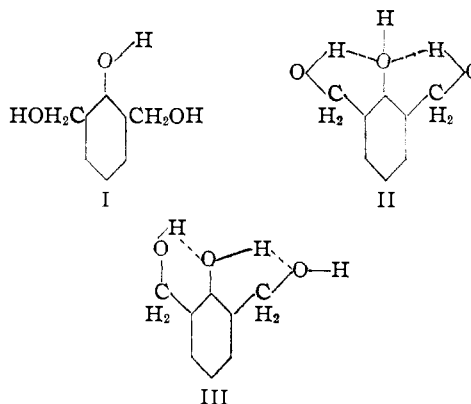
decrease in pK for two o-methylol groups averages about 0.27. This is approximately double what the inductive effect of a single methylol would be. Nevertheless, structure I hardly seems probable as there is no reason why hydrogen bonds should not form here since they form in other o-methylol compounds. Symmetry considerations might recommend structure II, but this would lead one to expect a decrease in pK of $2 \times 0.15 = 0.30$ inductively plus a further decrease caused by two hydrogen bonds partially saturating the affinity of the phenolic hydroxyl for its own proton. Moreover, the phenolic hydroxyl, being planar with the ring as a result of resonance, can hold only one other hydrogen atom through a hydrogen bond. Structure III seems most probable. Such a structure would call for an inductive effect on pK of -0.15 and a hydrogen bond effect of $+0.12$ for the first methylol, and an inductive effect of -0.15 and a hydrogen bond effect of -0.09 for the second methylol, which seems entirely plausible.

As to the effect of such methylol substituents on further electrophilic attack on the ring in open ortho

(5) L. N. Ferguson, Chem. Revs., 50, 47 (1952).

(6) R. T. Arnold and J. Sprung, THIS JOURNAL, 61, 2475 (1939).

or para positions: The amount of any phenol present in the reactive anion formed in a buffered, alkaline solution will depend on its pK by the obvious equation. Insofar as other factors do not alter the picture, a phenol will, in such a solution, be more reactive the lower its pK. Some of these other factors may be previsioned. Calculations (from their pK values) will show that in the same solution more p-methylolphenol will be present as anions than saligenin, while the cresols will furnish considerably less anions. On this basis, considering the methyl group in o- and p-cresol to have rather little effect on substitution meta to itself, o-cresol (pK 10.19) should be somewhat less reactive than p-cresol (pK 10.10). This agrees with the reaction rates found by Sprung.[1] p-Methylolphenol should be more reactive than either cresol or saligenin on the basis of its acidity, but this is probably more than balanced by the fact that the whole ring is deactivated by the methylol group. This is true also of saligenin, but here (and possibly in the 2,6-dimethylolphenols) another factor enters into the picture. A hydrogen bond involving the phenolic proton will tend to keep the phenolic hydroxyl group turned into the plane of the ring in which position it must be for formation of the ring-oxygen pseudo double bond postulated for the resonance forms of undissociated phenol. The hydrogen bond will therefore tend to favor the resonance transfer of negative charge to the ring in the undissociated form, increasing its reactivity, especially in the para position. This resonance stabilization would not extend to the anion. Finally, the 2,6-dimethylolphenol, being both the most acid and having its phenolic hydroxyl held to the plane of the ring, should be the most reactive of the methylol derivatives of phenol toward formaldehyde.

Experimental Section

All ultraviolet spectra were obtained with the Beckman DU spectrometer equipped with thermoplates to stabilize the temperature of the cell holder at $25.0 \pm 0.1°$. Spectra were taken against a blank consisting of the aqueous buffer, acid or alkali used as solvent for the phenol in the other cell. The same, matched pair of quartz, 1-cm. cells was used in the same order throughout. Concentrations were chosen so that the transmissions read ranged between 20 and 80% of the blank, and usually 30–70%. All transmission readings were checked and rechecked if they did not agree within 0.3% in transmission. Finally, the absorption curves for any phenol were considered usable only if all passed through the isosbestic point within 0.5% in transmission. This requirement was easily met by all the curves provided certain precautions concerning the solutions were met.

The spectrum of the acid (un-ionized) form of all of the phenols was measured in 0.1 N H_2SO_4. In the case of the methylolphenols, care was taken to dilute the 1.0 N acid used to make up the spectroscopic solutions before adding the sample in order to prevent resinification. In several cases suspected of being critical, thus 2,4,6-trimethylolphenol, another sample was measured in pH 4.67 acetate buffer. Comparison of these curves with those in strong acid showed no differences, the curves coinciding perfectly. Apparently even trimethylolphenol in such dilute solution is not affected by 0.1 N H_2SO_4, at least with 4–5 hours. Spectra of the anion were taken in 0.1 N NaOH. In some cases up to 0.5 N NaOH was used to determine whether any further change in the spectrum resulted on further addition of alkali. No change was found, but 0.15 N NaOH was used for mesitol to make sure the system was sufficiently alkaline. The absorption of these alkaline solutions tended to change unpredictably on standing, apparently due to air oxidation. The water used in making them up was therefore boiled for 15 minutes, then cooled and stored under nitrogen. This eliminated the difficulty. The buffers were also made with boiled, distilled water and similarly stored. Most of the phenols were measured in the same buffer of pH 10.28, but in some cases in which this pH was too far from the 50% ionization point most favorable for measurement another buffer also was used. All buffers consisted of mixtures in various proportions of 0.02 M Na_2CO_3 and 0.02 M $NaHCO_3$. The pH of the buffers was measured with a Beckman G pH meter using the pinhole calomel and Beckman No. 1190–80 glass electrode, standardized before and after measurement against the pH 4.00, 6.85 and 9.18 National Bureau of Standards pH standards at 25°. As an independent check the carbonate buffers as well as the pH standards were checked against the calculated voltage developed by a standard hydrogen electrode. These various cross-checks all agreed among themselves to at least ± 0.01 pH unit.

Evaluation of the results was carried out in analogy to the procedures of the reference 3.

Of the phenols used for the measurements, phenol, o-cresol, p-cresol, 2,4-xylenol and 2,6-xylenol were highest purity commercial samples once redistilled. Further purification was considered unnecessary, since any slight, residual impurity would be very unlikely to have a pK differing much from that of the phenol in question. Mesitol was obtained from 2,6-dimethylol-4-methylphenol by treating with gaseous HCl in glacial acetic acid to obtain 2,6-dichloromethyl-4-methylphenol, which was acetylated on the phenolic hydroxyl with Ac_2O and H_2SO_4, reduced with Zn and HCl and saponified with KOH in MeOH to yield mesitol in 38% over-all yield. Product was recrystallized from C_6H_6 + petroleum ether, yielding long white needles, m.p. 72.2–72.5° cor. The 2,6-dimethylol-4-methylphenol was synthesized by reaction of p-cresol with formaldehyde in alkali according to Ullmann and Brittner,[7] m.p. 128.5–129.0° cor. The 2-methylol-4-methylphenol was synthesized from p-cresol and formaldehyde according to v. Auwers,[8] m.p. 104.3–105.0° cor. p-Methylolphenol was prepared by hydrogenation of p-hydroxybenzaldehyde, using a commercial Pd catalyst (American Platinum Works), m.p. 108–109° by the usual method or 118–123° by dip method. This substance resinifies so easily on heating that the melting point depends to an extreme degree on the rate of heating. However, chromatographic analysis shows no impurities. O-Methylolphenol was prepared by recrystallization of the commercial product from ester and from CCl_4, m.p. 86° cor. The m-methylolphenol, 2,4-dimethylolphenol, 2,6-dimethylolphenol and 2,4,6-trimethylolphenol were placed at our disposal by Dr. J. H. Freeman of this Laboratory, who has described their synthesis previously.[9]

(7) F. Ullmann and K. Brittner, *Ber.*, **42**, 2539 (1909).

(8) K. von Auwers, *ibid.*, **40**, 2524 (1907).

(9) J. H. Freeman, THIS JOURNAL, **74**, 6257 (1952).