than one temperature, we are in a position to calculate the heat of solution of nitrogen in these solvents by the aid of the relation

$$\left(\frac{\partial \ln x_2}{\partial T}\right)_{p_2} = -\left(\frac{\partial \ln x_2}{\partial \ln p_2}\right)_T \left(\frac{\partial \ln p_2}{\partial T}\right)_{x_2} = \frac{-\bar{H}_2}{RT^2}$$

since the nitrogen obeys Henry's law in these very dilute solutions and therefore $(\partial \ln x_2/\partial \ln p_2)_T = 1$. The values in Table I yield $\bar{H}_2 = -140$ cal. in perfluoro-*n*-heptane and -260 cal. in perfluorodimethylcyclohexane. These values are small and obviously subject to considerable percentage error.

A few remarks may be added concerning the point mentioned above, that of stretching a theory based upon mixing liquids to cover the solubility of a gas above its critical temperature. First it would be quite possible to go back to an early step in the derivation of Eqn. 1 where the potential energy of a liquid mixture relative to its two gaseous components is expressed in terms of the liquid structure, and to subtract therefrom only the potential energy of the pure liquid solvent, which would give an expression for the partial molal energy of the solution of the gas. Its free energy of solution at the equilibrium pressure and composition is of course zero. If we had a satisfactory expression for the entropy of solution of the gaseous component, the problem would be solved, but unfortunately we have not been able to express the entropy of this process as satisfactorily as we have the entropy of mixing two liquids to form a regular solution.

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Summary

1. Values for the solubility of nitrogen have been determined, expressed as Bunsen coefficient. In *n*-perfluoroheptane, 0°, 0.411; 25°, 0.385; 50°, 0.360; perfluoromethylcyclohexane, 25°, 0.375; perfluorodimethylcyclohexane, 25°, 0.328; 50°, 0.317; *n*-hexane, 25°, 0.239; cyclohexane, 25°, 0.156; benzene, 25°, 0.124; carbon disulfide, 25°, 0.0823.

The above data are tabulated with existing data for six other solvents and it is shown that the order of solubility, expressed as mole fraction, closely parallels the order of the "solubility parameters," defined as the square roots of their energies of vaporization per cc.

3. The solubility equation for regular solutions, with a semiempirical adjustment of its parameters, yields calculated values in fair agreement with the experimental ones, except in the case of the fluorocarbons, where the experimental values are larger. This discrepancy is attributed to the unusually large molal volumes of these solvents because it is considerably reduced by introducing a correction of the Flory–Huggins type.

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[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY, PITTSBURGH, PENNSYLVANIA]

Ultraviolet Absorption Study of the Ionization of Substituted Phenols in Ethanol

BY NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR.

It is well known that the ultraviolet absorption spectra for the anions or cations of many polar substituted aromatic materials are markedly different from the spectra obtained for the compounds themselves. The spectra of the ions generally exhibit a large bathochromic shift of the absorption ascribed to the phenyl ring chromophore. In addition the intensity of absorption is increased. Since the spectral shift is large, often of the order of 20 mμ or larger, it provides a method whereby dissociation constants may be determined. Ordinarily these cannot be calculated from the spectrophotometric data alone but depend also on separately determined values of *p*H or on previously determined equilibrium constants which are pertinent to the processes involved.

In this manner Stendstrom and co-workers[1,2] demonstrated that the shift of the phenol spectrum induced by the addition of sodium hydroxide is due to the creation of the phenolate ions. From their data they obtained a value of the dissociation constant for phenol. Using the same procedure, Flexser, Hammett and Dingwall[3] calculated the ionization constants for benzoic acid, 2,4-dinitrophenol and acetophenone. More recently Ewing and Steck[4] have utilized this phenomenon in studies of the acidic and basic properties of quinolinols and isoquinolinols. Similar studies were made of various 4-aminoquinolines by Irvin and Irvin.[5]

The present studies are of the substituted phenols. The substituted phenols may be divided into three classes according to their steric hindrance to inter-molecular hydrogen bonding.[6] Phenols with the ortho positions either unsubsti-

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(1) W. Stendstrom and M. Reinhard, *J. Phys. Chem.*, **29**, 1477 (1925).

(2) W. Stendstrom and N. Goldsmith, *ibid.*, **30**, 1683 (1926).

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

(4) G. W. Ewing and E. A. Steck, *ibid.*, **68**, 2181 (1946).

(5) J. L. Irvin and E. M. Irvin, *ibid.*, **69**, 1091 (1947).

(6) N. D. Coggeshall, *ibid.*, **69**, 1620 (1947).

tuted or occupied by a small group such as a methyl are known as unhindered phenols. Those with one ortho position occupied by a large group such as a *t*-butyl and the other either unsubstituted or occupied by a small group are known as partially hindered phenols. Those with both ortho positions occupied by large groups are known as the hindered phenols. It is well known that the same type of hindrance that influences intermolecular hydrogen bonding is effective in hindering intermolecular association effects which influence the ultraviolet absorption spectra of the phenols.[7] The hindered phenols, for example, exhibit quite small spectral changes between examination in paraffin and in polar solvents such as ethanol whereas large changes are observed for the unhindered and partially hindered phenols. The differences have been interpreted as due to the different degrees of proximity possible between the hydroxyl groups of the phenols and the polar groups of the solvent.

In view of the above results it is to be expected that the behavior of the various phenols in a solvent containing a strong base such as sodium hydroxide will vary in accordance with the steric hindrance of the above type. Since the formation of a phenolate ion involves the removal of the hydrogen nucleus from the hydroxyl group any shielding such as offered by large groups on the ortho positions would be expected to be effective in reducing the ionization. It is important to evaluate such effects not only as a method of determining the relative acidity of the various phenols, but also in order to provide information pertinent to a detailed consideration of the ionization processes in the liquid phase. The present report is of a study of the ultraviolet absorption spectra of a series of substituted phenols in ethanol and in ethanol containing sodium hydroxide. The data are interpreted in terms of the influence of steric hindrance on the ionization.

Experimental

All of the absorption spectra were obtained with the use of a Beckman Quartz Spectrophotometer equipped for work in the ultraviolet. In some of the preliminary investigations a study was made of the dependence of spectral changes on temperature. For this the temperature controlled absorption cell compartment previously described[7] was used. A Precision Scientific Company constant temperature bath was employed to provide the water used to regulate the temperature of this compartment.

With the exception of the simpler ones, the substituted phenols studied were prepared in this Laboratory.[8,9] There was evidence that each compound used was at least 99% pure. Such other chemicals as were used were the best available commercially and were, when necessary, further purified by recrystallization. Absolute ethanol was used as the solvent in all cases. Effects due to benzene in the ethanol were eliminated by using the same solvent in the comparison cell as used in the sample cell.

In these studies the ethanol solutions containing hydroxyl ions were prepared by the use of aqueous solutions containing one mole/liter or more of sodium hydroxide or of other bases. Solutions containing other inorganic materials were prepared in the same general manner. In every case the reference cell was filled with the same combination solvent as used for the particular phenol being investigated. In this manner any errors or discrepancies which might have been introduced through impurities in the sodium hydroxide or other inorganic material were avoided.

Data and Discussion

Preliminary Experiments.—In examining the literature on the subject of changes of ultraviolet absorption spectra of polar substituted aromatics induced by addition of specific types of ions in the solvent, it was apparent that sufficient proof that the shifted spectra are due to ionized solute was lacking. It was desirable to obtain further data to verify that this explanation is correct and the effect is not due to intermolecular effects such as hydrogen bonding or the formation of transient complexes between neutral molecules and ions. For that reason a number of experiments were performed on phenols in ethanol containing various inorganic materials. The fact that the present work was done with ethanol as the solvent instead of water, as was the case for most of the previous work, made it further desirable that such experiments be done. This was to verify that the processes were the same for the two solvents.

p-Cresol was examined in solutions containing the bases sodium hydroxide, lithium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, and ammonium hydroxide. The same spectral shift was observed in every case although with differences in degree of ionization. For a concentration of 3×10^{-4} mole/liter of *p*-cresol in solution a concentration of about 12 moles/liter of the weak base ammonium hydroxide was required for complete ionization whereas for lithium, sodium and potassium hydroxides, concentrations of less than one tenth mole/liter were sufficient. These data confirm previous work, but do not rule out the possibilities of complexes being responsible for the shift. Hence to determine if the phenomenon depended specifically upon the addition of hydroxyl ions data were obtained for *p*-cresol in solutions containing sodium chloride and hydrogen chloride. The resulting spectra were virtually indistinguishable from the spectrum obtained with pure ethanol as the solvent. Next a reversal procedure was tested on several phenols. In this the spectra were shifted by the addition of sodium hydroxide and then brought back to that observed

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[7] N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

[8] D. R. Stevens, *Ind. Eng. Chem.*, **35**, 655 (1943).

[9] G. H. Stillson, D. W. Sawyer and C. K. Hunt, THIS JOURNAL, **67**, 303 (1945).

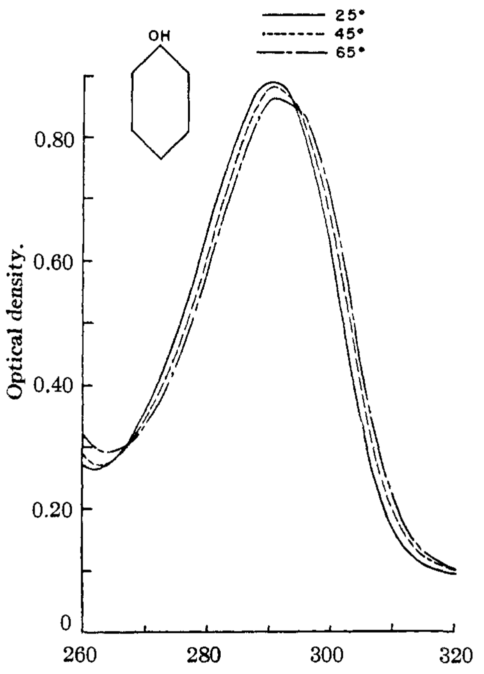

Fig. 1.—Ultraviolet absorption spectra of 2.8 × 10^{-4} mole/liter of phenol at various temperatures in ethanol containing 1.0 × 10^{-1} mole/liter of sodium hydroxide.

for pure ethanol solvent by the addition of hydrogen chloride to the same solutions. A complete reversal was achieved for each of the phenols tested, namely, *p*-cresol, 2-methyl-4,6-di-*t*-butylphenol and 2,4,6-tri-*t*-butylphenol.

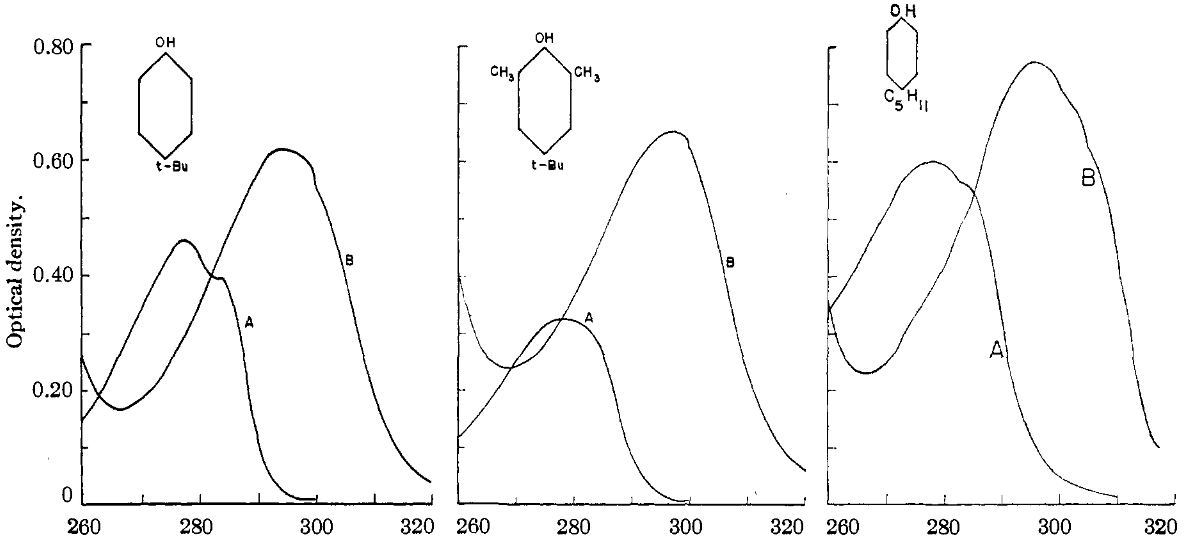

Fig. 2.—Ultraviolet absorption spectra of three unhindered phenols in: A, pure ethanol; B, ethanol containing 1.0 × 10^{-1} mole/liter of sodium hydroxide.

Errera and Sack[10] have shown that the population of intermolecular complexes between ethanol and dioxane in a carbon tetrachloride solution is very strongly reduced by an increase of temperature from 20 to 55°. It would be expected that the energy per intermolecular hydrogen bond or complex between a phenol molecule and an ion would be of the same order of magnitude as for the complexes studied by Errera and Sack. Therefore, if the spectral shift considered here were due to such effects we would get at least a partial reversion to that observed for the ethanol solution when the temperature was elevated. In Fig. 1 may be seen the results for such a test on 2.8 × 10^{-4} mole/liter of phenol in an ethanol solution containing one-tenth mole/liter of sodium hydroxide. Here the optical density is plotted *versus* wave length. The optical density D is defined by $D = \log I_0/I$, where I_0 and I are the incident and transmitted energies, respectively. It may be seen that the rise in temperature to 65° produces only a very minor change and it is in the opposite direction to that which would be expected if the spectral changes were due to intermolecular effects. The same results were also obtained for 2-methyl-4,6-di-*t*-butylphenol and for 2,6-di-*t*-butyl-4-ethyl phenol. The preliminary experiments therefore all definitely confirm the ionization explanation for the spectral shift observed for the phenols.

Unhindered Phenols.—In Fig. 2 may be seen the data for three of the unhindered phenols examined. Here are given the spectra for the materials in pure ethanol and in ethanol containing one-tenth mole/liter of sodium hydroxide. The concentration of absorbing material is about the same in each case being 2.5 × 10^{-4} mole/liter for the *p*-*t*-butylphenol, 2.0 × 10^{-4} mole/liter for the 2,6-dimethyl-4-*t*-butylphenol, and 2.0 × 10^{-4} mole/liter for the *p*-*t*-amylphenol. It is to be noted that in each case there is a complete spectral

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(10) J. Errera and H. Sack, *Trans. Faraday Soc.*, **34**, 728 (1938).

shift. By this is meant that the spectra observed for the solutions containing sodium hydroxide show no evidence for any un-ionized phenol molecules, *i. e.*, no maxima at the wave lengths at which the maxima occur for the compounds in pure ethanol solutions.

For solutions containing lower concentrations of sodium hydroxide two absorption maxima are observed, one representing the un-ionized phenol molecules, and one representing the phenolate ions. For the unhindered phenols a sodium hydroxide concentration of less than 1.0×10^{-1} mole/liter is sufficient to produce the complete spectral shift. However, as will be discussed below, the concentrations of sodium hydroxide at which the shifts become apparently complete were not determined as there are difficulties in utilizing these data in a quantitative manner. The sodium hydroxide concentration of 1.0×10^{-1} mole/liter was chosen as a convenient reference for comparison between the different classes of phenols. In Table I may be seen the wave lengths of maximum absorption for the various unhindered phenols in pure ethanol and in ethanol plus 1.0×10^{-1} mole/liter of sodium hydroxide. The spectral shift $\Delta(1/\lambda)$, calculated from these wave lengths, is also given. As the absorption bands are broad the maxima are only given to the nearest mμ. The values of $\Delta(1/\lambda)$ are therefore only reliable to two significant figures.

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION FOR UNHINDERED PHENOLS IN ETHANOL AND ETHANOL PLUS SODIUM HYDROXIDE AND $\Delta(1/\lambda)$ VALUES

Compound	λ max. (mμ) (ethanol)	λ max. (mμ) (ethanol plus NaOH)	$\Delta(1/\lambda)$ cm.$^{-1}$
p-Cresol	280	299	2200
p-*t*-Butylphenol	278	294	2000
p-*t*-Amylphenol	278	295	2100
m-Cresol	274	291	2100
o-Cresol	274	291	2100
2,6-Di-methyl-4-*t*-butylphenol	278	297	2300
Average value of $\Delta(1/\lambda)$ = 2100			

Partially Hindered Phenols.—In Fig. 3 may be seen the behavior of three partially hindered phenols. The concentrations were: 1.5×10^{-4} mole/liter of 2-methyl-4,6-di-*t*-butylphenol, 1.7×10^{-4} mole/liter of 2,4-di-*t*-butylphenol, and 2.0×10^{-4} mole/liter of 2-*t*-butyl-4-methylphenol. It is immediately evident that a concentration of 1.0×10^{-1} mole/liter of sodium hydroxide which produced a complete spectral shift for the unhindered phenols, produces only a partial shift in the present cases. This is evident from the fact that the B curves all show maxima representative of the un-ionized material. In each case it is seen that these maxima are shifted to the red as compared to the maxima for the A curves. This is believed to be the result of an actual change in the absorption frequencies of the un-ionized material and of the geometrical superposition of the independent effects of the ionized and un-ionized materials. The latter effect was confirmed in a number of cases by the numerical construction of such intermediate curves. This was done by making suitable combinations of the data for the case of ethanol alone and the data for the 5.0×10^{-1} mole/liter of sodium hydroxide solutions wherein complete shifts were exhibited. The concentration of 5.0×10^{-1} mole/liter was somewhat more than necessary to produce the complete spectral shift, but was chosen as a convenient reference for comparisons between the various classes of phenols. In Table II are the values of the absorption maxima and of the $\Delta(1/\lambda)$'s.

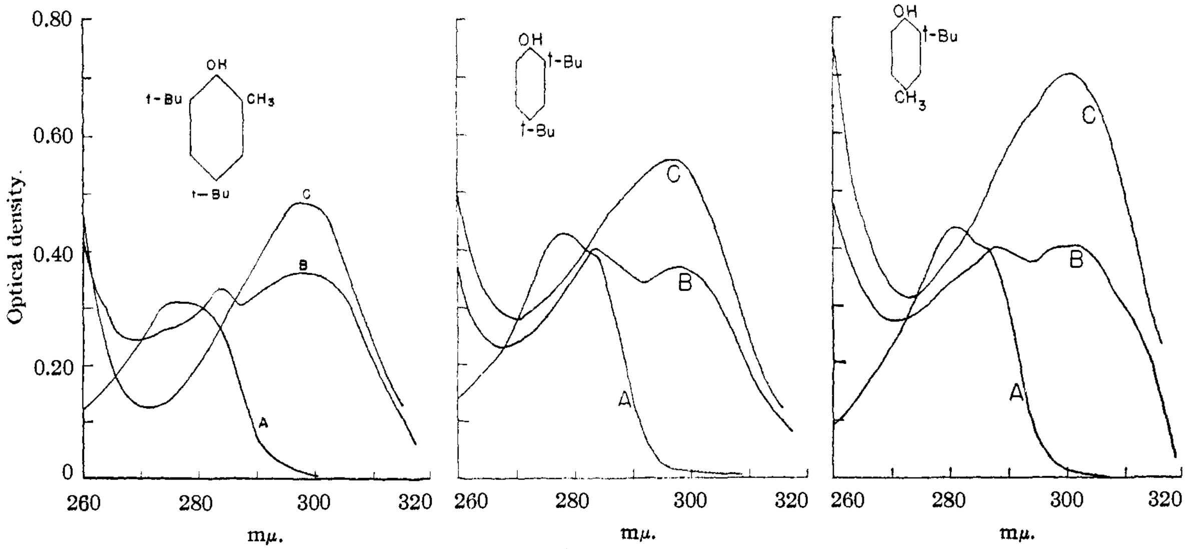

Fig. 3.—Ultraviolet absorption spectra of three partially hindered phenols in: A, pure ethanol: B, ethanol plus 1.0×10^{-1} mole/liter of sodium hydroxide, and C, ethanol plus 5.0×10^{-1} mole/liter of sodium hydroxide.

TABLE II

WAVE LENGTHS OF MAXIMUM ABSORPTION FOR PARTIALLY HINDERED PHENOLS IN ETHANOL AND ETHANOL PLUS SODIUM HYDROXIDE AND $\Delta(1/\lambda)$ VALUES

Compound	λ max. (mμ) (ethanol)	λ max. (mμ) (ethanol + NaOH)	$\Delta(1/\lambda)$ cm.$^{-1}$
2-Methyl-4,6-di-*t*-butylphenol	277	298	2500
2-*t*-Butyl-4-methylphenol	281	301	2300
2,4-Di-*t*-butylphenol	278	297	2300
3-Methyl-6-*t*-butylphenol	276	294	2200
Average value of $\Delta(1/\lambda)$ = 2300			

Hindered Phenols.—In Fig. 4 may be seen the data for three hindered phenols. In each case the concentration of the phenol is approximately 1.7 × 10^{-4} mole/liter. It may be seen that a sodium hydroxide concentration of 1.0 × 10^{-1} mole/liter produces only minor spectral changes and that a concentration of 5.0 × 10^{-1} mole/liter which produces a complete shift for the partially hindered phenols is responsible here for only a partial shift. In the D curves are given the spectra for the phenols in the presence of 5.0 mole/liter of sodium hydroxide. Even this concentration does not produce a complete ionization.

With the dilution scheme used it was impossible to go over about 5.0 mole/liter of sodium hydroxide due to the precipitation of sodium hydroxide. Hence the complete ionization of the unhindered phenols cannot be achieved in this manner. In Table III may be seen the wave lengths of maximum absorption and the $\Delta(1/\lambda)$ values.

TABLE III

WAVE LENGTHS OF MAXIMUM ABSORPTION FOR HINDERED PHENOLS IN ETHANOL AND ETHANOL PLUS SODIUM HYDROXIDE AND $\Delta(1/\lambda)$ VALUES

Compound	λ max. (mμ) (ethanol)	λ max. (mμ) (ethanol + NaOH)	$\Delta(1/\lambda)$ cm.$^{-1}$
2,6-Di-*t*-butyl-4-methylphenol	277	303	3100
2,6-Di-*t*-butyl-4-cyclohexylphenol	275	300	3100
2,4,6-Tri-*t*-butylphenol	275	302	3300
2,6-Di-*t*-butyl-4-ethylphenol	276	303	3200
2,6-Di-*t*-butyl-4-phenylphenol	266	302	4500
Average value of $\Delta(1/\lambda)$ = 3400			

Discussion.—It is obvious from the data given in the figures that great differences exist between the three classes of phenols as regards their ease of ionization in ethanol solution. These differences are ascribed to the steric hindering effects of the large ortho substituents. Although one-tenth mole/liter of sodium hydroxide was sufficient to achieve complete ionization for the unhindered phenols it resulted in only partial ionization of the partially hindered phenols. A sodium hydroxide concentration of 5.0 × 10^{-1} mole/liter was sufficient to produce complete ionization for the latter compounds but definitely only produced a partial ionization of the hindered phenols. In addition the hindered phenols were not completely ionized by as much as 5.0 mole/liter of sodium hydroxide. This positively establishes the role of the large ortho groups in hindering the ionization.

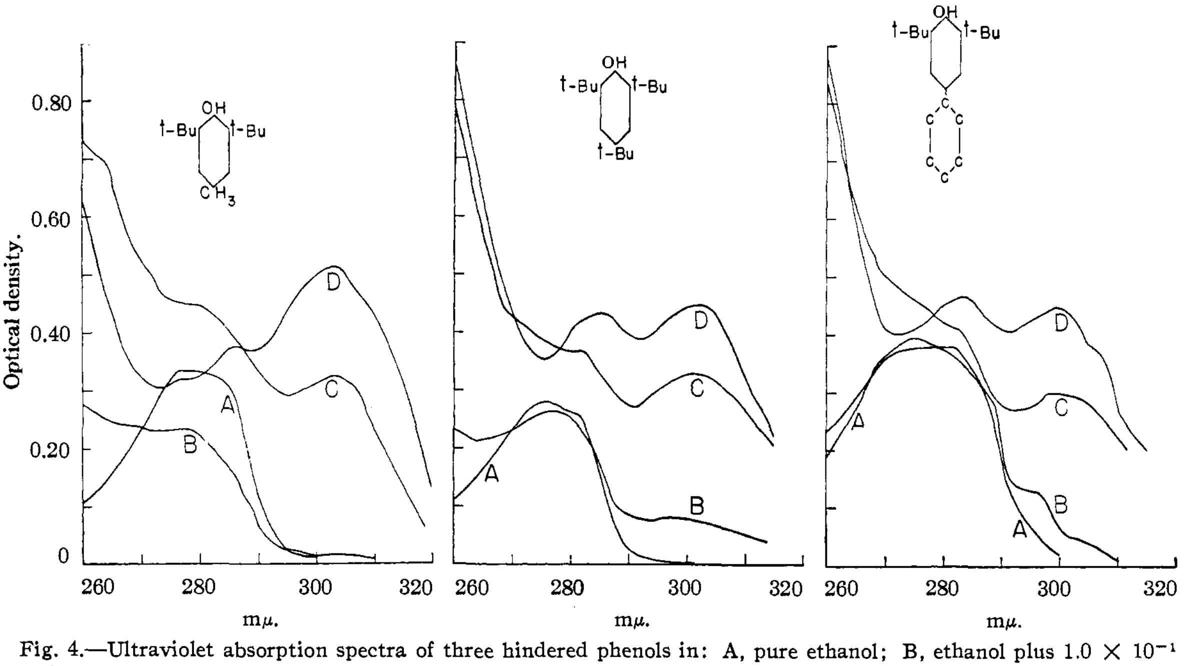

Fig. 4.—Ultraviolet absorption spectra of three hindered phenols in: A, pure ethanol; B, ethanol plus 1.0 × 10^{-1} mole/liter of sodium hydroxide; C, ethanol plus 5.0 × 10^{-1} mole/liter of sodium hydroxide, and D, ethanol plus 5.0 mole/liter of sodium hydroxide.

There is a very interesting implication in the above data regarding the processes of ionization. The data show that the large groups on the ortho position sterically hinder the ionization. They are large in spatial extension and therefore shield the phenolic hydroxyl group from close approach by other molecules or ions. Since they also hinder the ionization, we may therefore assume that the ionization process is a result of a close approach or collision between a phenolic hydroxyl group and other molecules or ions. With this assumption the primary factors affecting ionization are the details of geometry and electric fields of the molecules and ions involved rather than gross dielectric properties.

It is evident from the data in the tables that there is a further difference between the spectral behavior of the phenols. The difference in frequency of maximum absorption $\Delta(1/\lambda)$ between the molecules and the phenolate ion is in each case expressed in wave numbers. This provides a measure of the differences of transition energies between the ground and first excited electronic states. As was stated above the wave lengths of maximum absorption are only reliable to about 1 mμ. Hence the $\Delta(1/\lambda)$ values are reliable to only two significant figures. Despite this limitation it is clear that a definite difference exists between the unhindered and partially hindered phenols. For the former the average value of $\Delta(1/\lambda)$ was 2100 cm.$^{-1}$, whereas it was 2300 cm.$^{-1}$ for the latter. This implies that the size of the ortho substituent affects the transition energy for the phenolate ion. This implication is further confirmed by a comparison between the partially hindered and the hindered phenols. The average value of $\Delta(1/\lambda)$ for the latter was 3200 cm.$^{-1}$, excluding a consideration of 2,6-di-*t*-butyl-4-phenylphenol. This compound has an anomalously high $\Delta(1/\lambda)$ value presumably due to some effect of the conjugation of the phenyl rings.

The data then show that the large groups on the ortho positions affect the energy of transition between the ground and the first excited electronic states of the phenolate ions. This may be explained as the result of the energy of polarization of the *t*-butyl groups by the electric fields resulting from the polar resonance forms of the first excited state. This carries a further implication that in the polar resonance forms which contribute the most to the first excited state there is an accumulation of electric charge on the number one position of the phenyl ring. This is necessary since it is the ortho substituents that affect the energy. Such an accumulation of charge would create large fields which would polarize the ortho substituents.

The above results make another tool available for the determination of molecular structure of phenols of unknown composition. Since the behavior of the three classes is different for each, a phenol of unknown composition may be examined under the various conditions and thereby assigned to one of the classes. Another application has been made to analytical problems. Ordinarily it is impossible to quantitatively analyze a mixture of mononuclear aromatic hydrocarbons and phenols by ultraviolet absorption. This is because the absorption is approximately the same for each class, being due to the phenyl ring chromophore. The addition of sodium hydroxide however results in the ionization of the phenols with the resultant spectral shift. This allows data to be obtained independently for the aromatics and for the phenols. Similar considerations apply to other polar substituted aromatics. If the material in question is basic the addition of an acid will result in ionization and the same type of spectral shift.

Acknowledgment is gratefully made to Dr. Donald R. Stevens and Dr. G. Stillson for furnishing some of the substituted phenols examined. Appreciation is also due Dr. Paul D. Foote, Executive Vice-President of Gulf Research & Development Company, for permission to publish this material.

Summary

A study has been made of the ultraviolet absorption spectra of substituted phenols in ethanol solutions containing sodium hydroxide. Preliminary work was done to verify that the spectral shift which occurs when sodium hydroxide is added is due to the formation of phenolate ions. This comprised tests with different bases, acids and salts; the reversal of the effect by the addition of acid to a basic solution; and a study of the temperature dependence of the spectral shift. The unhindered phenols gave evidence of complete ionization in solutions containing 1.0×10^{-1} mole/liter of sodium hydroxide. The partially hindered phenols were only partially ionized at this concentration of sodium hydroxide, but demonstrated complete ionization for a concentration of 5.0×10^{-1} mole/liter of sodium hydroxide. The hindered phenols were neither completely ionized with the latter concentration of sodium hydroxide nor for the much larger concentration of 5.0 mole/liter. These results demonstrate the great differences in acidity between the different classes of phenols and show that ionization is hindered by the presence of large ortho substituents. This leads to the conclusion that the process of ionization is the result of a collision or of a small distance of approach between the phenolic hydroxyl and other molecules or ions. The difference of energy of transition between the ground and first excited state for the neutral molecule and for the phenolate ion depends upon the type of phenol. An explanation is given which is based on the energy of polarization of the large ortho groups. Applications of the phenomenon to analytical and molecular structure problems are given.

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