unreacted ester was then determined by titration of the acid liberated during its solvolysis. The method was found to give quantitative results in several control experiments. Values of $k_1°$ obtained by this method were highly precise and showed no drifts during more than three half-lives, but inexplicably were 10% higher than values of $k_1°$ obtained by following the progress of the solvolysis by direct titration for acid. Although this discrepancy has disturbed us, we believe that the error, if any, will cancel out in the ratio $k_1/k_1°$. Typical kinetic data are shown in Table VI.

Measurement of Optical Rotations.—Rotations were measured with a Bellingham and Stanley polarimeter at the wave length of the sodium D line (589 mμ), or at the 546 mμ mercury line, the latter giving a 20% larger rotation.

Due to the limited solubility, the concentration of III could not be made higher than 0.01 *M*, and in a 4-dm. tube the initial rotations were of the order of 0.25°. Before each measurement, the zero point of the polarimeter was checked by taking a set of 8 readings without the polarimeter tube. Next, a set of 8 readings was taken with the polarimeter tube in place; to eliminate errors from polarization of the end plates, the tube was then reversed and another set of 8 readings was taken. The difference between the mean of the 16-tube readings and the mean of the 8 air readings was taken as the rotation of the solution.

The standard deviation in each set of 8 readings was about 0.003°, and the difference between the means of the 2 sets of tube readings was of the order of 0.005°.

Rate Measurements.—The half-lives of all reactions were sufficiently long so that accurate timing presented no problem. The solvolysis of neophyl *p*-toluenesulfonate was followed by a standard sealed-ampoule technique, the ampoules having been flushed with pure nitrogen prior to filling. The racemization of L-(+)-*threo*-3-phenyl-2-butyl *p*-toluenesulfonate was measured as follows: Reaction mixtures were prepared in 50-ml. volumetric flasks, and the volumetric flasks were then immersed in a water thermostat maintained at 25.00°. Optical rotations were measured immediately after attainment of temperature equilibrium, and then once a day for 4 days thereafter. The measurements of the optical rotations required approximately 30 minutes each, and were carried out in a 4-dm. polarimeter tube thermostated at 25.00°. The mid-points of the periods of measurement were recorded as the effective time. After each measurement the reaction mixture was returned to the volumetric flask and replaced in the thermostat.

Least-squares Treatment of the Data.—For a first-order solvolysis or racemization, $\ln|(y_\infty - y_t)| = a - k_1t$, where y denotes the acid titer or the optical rotation, and a and k_1 are adjustable constants. Since the error in $|(y_\infty - y_t)|$ is constant throughout the kinetic run, the error in $\ln|(y_\infty - y_t)|$ is inversely proportional to $|(y_\infty - y_t)|$, and the statistical weight of the corresponding point may be equated to $|(y_\infty - y_t)|$. Thus

$$\Sigma[(y_\infty - y_t)^2 \ln|(y_\infty - y_t)|] = a\,\Sigma(y_\infty - y_t)^2 - k_1\Sigma[(y_\infty - y_t)^2 t]$$

$$\Sigma[(y_\infty - y_t)^2 t \ln|(y_\infty - y_t)|] = a\,\Sigma(y_\infty - y_t)^2 t - k_1\,\Sigma(y_\infty - y_t)^2 t^2$$

[CONTRIBUTION NO. 1066 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNA.]

Stereoelectronic Effects on Organic Bases. II.[1] Base Strengths of the Phenolic Ethers[2]

BY EDWARD McCOLLIN ARNETT AND CHING YONG WU

RECEIVED MARCH 23, 1960

The pK_a's of the oxonium ions of phenol and the phenyl ethers of the following alkyl groups have been studied: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *n*-amyl and also 5,5-dimethylhomochroman. Several others were too insoluble or too unstable to investigate. Decomposition of the ethers by the aqueous sulfuric acid medium was controlled by working at 0° and a special treatment of the data was developed to deal with sulfonation and solvent effects. The technique gives highly precise pK_a's by the Hammett method, but discrepancies in the H_0 scale at strong acidities are noted. The results show that these phenolic compounds are protonated on the oxygen rather than the ring and are in general more sensitive to stereoelectronic effects than are their nitrogen analogs.

Much of the theoretical foundation of modern organic chemistry is based upon observations of the effects of changing molecular structure upon acid-base equilibria[3,4] of carboxylic acids, phenols and amines, all of which may be readily investigated in the *p*H range of acidity. Also a few types of weak bases[5–9] have been studied by means of the Hammett H_0 indicator method which serves, in effect, to extend the *p*H scale to the solutions of high acidity required for the protonation of weak bases. There remains to be answered the question of how analogous compounds of nitrogen, oxygen, phosphorus and sulfur compare in their abilities to accept a proton under similar conditions. Such comparisons should yield fundamental knowledge about the relative importance of electronic and steric effects as they operate on the central atom and be of considerable use in predicting the point of attack by protons in polyfunctional molecules and the best conditions for separating weak bases by extraction. A good point of entry to this field should be a comparison of alcohols and ethers with primary and secondary amines. Although the literature contains numerous attempts to measure basicities of simple aliphatic alcohols and ethers, most of the methods involve techniques that make it risky to refer the results to the standard state of infinite dilution in aqueous solution on which the pK_a scale is based. Comparison of the results shows disagreement not only between the magnitudes of these base strengths but often even differences in order. The difficulty is mainly an analytical one since the simple aliphatic compounds do not have the spectral absorption characteristics that allow them to be treated as Hammett indicators.

We have approached this problem through the

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(1) Part I, E. M. Arnett and C. Y. Wu, *Chemistry & Industry*, 1488 (1959).

(2) We are grateful to the Research Corporation and the National Science Foundation for supporting this work.

(3) H. C. Brown, D. H. McDaniel and O. Häfliger, "Determination of Organic Structures by Physical Methods," edited by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955, Chapter 14.

(4) H. K. Hall, Jr., THIS JOURNAL, **79**, 5441 (1957).

(5) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(6) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

(7) R. Stewart and K. Yates, *ibid.*, **80**, 6355 (1958).

(8) K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959).

(9) K. Yates, Thesis, University of British Columbia, 1959.

phenolic compounds since the similarity of their electronic structures and spectra to those of the anilines[10] suggests that they should undergo a large decrease in absorption of light in the region of 270 mμ upon protonation of the oxygen. They should therefore behave as ordinary Hammett indicators (like the anilines) and show the usual type of titration curve which permits estimation of the pK_a of their conjugate acids.[11] These expectations have been realized and our results may be compared with the data[3,4] for analogous anilines.

Probably one reason why phenolic compounds have not been studied previously as weak bases is their extreme sensitivity to sulfonation,[7] oxidation[12] and other decomposition reactions. Fortunately, we were able to decrease the decomposition rates greatly by conducting the spectral measurements at 0° using a specially built thermostated jacket for the spectrophotometer cells. We have confirmed a recent report[13] that the H_0 scale is relatively insensitive to temperature changes thereby justifying its use at 0°.

Experimental

Most of the phenyl ethers were commercially available. Isopropyl phenyl ether, *n*-amyl phenyl ether, *sec*-butyl phenyl and isobutyl phenyl ether were prepared by the reaction of phenol with the corresponding alkyl chloride in aqueous ethanolic alkali according to standard procedures.[14] *t*-Butyl phenyl ether was donated by Dr. D. R. Stevens of Mellon Institute. In all cases solutions of the ethers in diethyl ether were washed with 10% aqueous sodium hydroxide to remove traces of phenol; the solutions were then washed repeatedly with distilled water, the solvent removed by evaporation and the phenolic ether distilled under reduced pressure. Boiling points and refractive indices agreed closely with literature values and the compounds were further checked for purity by infrared spectrum and homogeneity to gas chromatography.

A large series of aqueous sulfuric acid solutions was prepared using Baker and Adamson C.P. grade concentrated sulfuric acid and distilled water. The H_0 values of these solutions were determined routinely by measuring the density with a pycnometer and estimation of the weight per cent. sulfuric acid from density tables in the "International Critical Tables." The H_0 of the solution was then read from a large plot of H_0 *versus* weight per cent. sulfuric acid prepared from the tables of Paul and Long.[5] In many cases these values were then checked by titration of the solution with standard base and frequently tested further by direct H_0 determination using Hammett indicators purchased from the Aldrich Chemical Co. In one case gravimetric determination of sulfate was used in addition to the other methods. We found several discrepancies as large as 0.50 H_0 unit between measured H_0 values based on two different Hammett indicators. In such cases we would usually find that agreement of our results and the Paul and Long values were much better with one indicator than with another. We believe that these differences may be due to a number of factors. Most discrepancies were observed in the region around 75% sulfuric acid where H_0 values are generally recognized as being dubious due to poor matching and overlap of indicators.[15] Secondly, it must be remembered that the H_0 values currently in use are all based on data obtained by Hammett and his co-workers over twenty-five years ago without the advantages of modern precision spectrophotometric equipment. We have been surprised to find how rarely modern workers in this field have checked their solutions by actual H_0 indicator measurements. Usually total reliance is placed on tabulated wt. %-H_0 data. Recently Bascombe and Bell[16] have recalibrated part of the H_0 scale using refined equipment similar to ours and find, as we have, that Hammett's original values are mostly very good in the lower acidity range, but that in the region of high acidity, where most of our work was done, the H_0 scale loses precision. In view of disagreement regarding pK_a values of the indicators used for constructing the scale and the fact that Bascombe and Bell have not extended their improved values to the region of high acidity, we are basing our values on the Paul and Long scale so that they may be compared to other currently accepted values for weak bases. If at some future time an improved H_0 scale is forthcoming, our values may be shifted to concur with it. In any event their relative magnitudes should be firm.

The purity of the indicators was checked by melting point and found to agree with literature values.

Our spectrophotometric measurements were made either with a Beckman DU or a Cary-14 spectrophotometer (mostly with the latter). Matched silica cells were used and complete curves run at every acidity for every compound so that corrections for solvent effects might be made at the best wave lengths.

In both instruments the cell holders were kept in tight fitting brass jackets through which thermostated water circulated.

Procedure for Optical Density Measurements.—Stock solutions of the purified phenolic ethers were prepared shortly prior to use in Spectrograde anhydrous methanol. The concentrations of these were arranged so that when a 0.10-ml. sample of stock was added to 25.00 ml. of water, the final optical density would be 0.50 to 0.80. Stock solutions were kept in a tightly stoppered storage chamber of a Macalaster Bicknell microburet (catalog number 4591). This type of microburet is very useful for reproducibly preparing solutions of the same concentration without the consumption of large quantities of acid; it has a total calibrated volume of 0.20 ml. and may be estimated to the nearest 0.0001 ml. using a capillary magnifier. If kept scrupulously clean and proper drainage time is allowed, it yields remarkably reproducible results and is easier to manipulate than the usual macroburet.

Before preparing a solution of phenolic ether in acid, a suitable quantity of acid solution of the required H_0 was chilled in ice for an hour. A 25-ml. volumetric flask was then filled about three-quarters full with chilled acid and 0.1000 ml. of stock solution delivered into the volumetric flask in such a way as to prevent drops from running down the neck. The tip of the buret and the neck of the flask were then rinsed with chilled acid solution from a dropper. The volumetric flask was stoppered and shaken vigorously for 1 minute to ensure solution of the ether.[17] The flask was now filled to the mark with chilled acid; the contents mixed by further shaking for a minute and then quickly transferred to the spectrophotometer cell. Balancing this cell in the other compartment of the spectrophotometer was a matching cell containing a previously prepared solution of 0.1000 ml. of pure methanol in acid solution of the same strength. Fogging on the cell faces was prevented by circulation of a stream of air that had been cooled and dried by passage through a Dry Ice trap.

Errors.—Temperature in the cells was maintained at close to zero by circulation of ice-water from a stirred ice slurry in a large Dewar jug through insulated hoses.

The combined errors from preparation of the indicator solutions and measuring their optical densities were estimated on the Beckman DU by preparing ten replica solutions of *p*-chloro-*o*-nitroaniline of the same acidity. The average optical density was 0.252 and the estimated standard deviation from this value was 0.005. Several other replica solutions measured on the Cary 14 gave estimated standard deviations of 0.002 for optical densities in the range 0.30 to 0.50. These errors correspond to an uncertainty of about 0.01 H_0 unit in the position of any point due to experimental

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[10] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 289.

[11] We are concerned here with the protonation of the phenolic compound, not with the protonation of phenoxide ions which has been extensively studied and is an entirely different matter.

[12] D. P. N. Satchell, *J. Chem. Soc.*, 3917 (1956).

[13] A. I. Gelbstein, G. G. Shcheglova and M. I. Temkin, *Zhur. Neorg. Khim.*, 1, 282, 506 (1956).

[14] See for example, A. I. Vogel, *J. Chem. Soc.*, 616 (1948).

[15] Reference 5, p. 17.

[16] K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

[17] There is probably no more common cause of errors in acidity function work than failure to dissolve the indicator completely in each solution. The quantities used are so small that precipitation is often impossible to detect with the eye.

error in preparation of the solution. Paul and Long[18] consider the minimum error for H_0 values based on the Hammett scale to be 0.05 unit. This error combines experimental errors with more subtle difficulties such as mis-matching of indicators and failure of the activity coefficient postulate. The results of Bascombe and Bell[16] show, as do ours, that the first source can be reduced considerably by using a thermostated precision spectrophotometer. However, in the region of acidity in which most of our measurements were made, the second type of error still leaves doubt about the absolute values of the H_0's of the solutions and therefore of the pK_a's of the compounds determined with them. We believe that by far the greatest error in our pK_a values lies in the acidity scale on which they are based.

Each pK_a value is based on six to ten points on a plot of H_0 *versus* the logarithm of the indicator ratio in the important region within one H_0 unit of the pK_a where the indicator ratio is changing most rapidly and where precision is highest. In all cases this plot was clearly linear and with unit slope (see Calculations).

A final check on the over-all reproducibility is afforded by two complete replica measurements of the pK_a of *n*-butyl phenyl ether. Although this is one of the more insoluble ethers, both sets of data gave exactly the same value of −6.99. More recently Mr. Ronald Bushick, of this Laboratory, has made four complete replica measurements of the pK_a of acetophenone and these agree within an estimated standard deviation of 0.015 pK_a unit; the same error estimated by Bascombe and Bell for their measurements.[16]

Calculations.—For molecules that conform to the Hammett treatment, the base strength is expressed in terms of the acidity of the conjugate acid as[6]

$$pK_a = H_0 + \log (C_{BH^+}/C_B) \qquad (a)$$

where the C's represent concentrations of free indicator base, B and its conjugate acid, BH$^+$. In terms of the observed optical densities of the free base, D_B and that of its conjugate acid D_{BH^+} and the optical density of a given solution containing both species, D, we have

$$pK_a = H_0 + \log (D_B - D/D - D_{BH^+}) \qquad (b)$$

assuming that all optical densities are measured at the same wave length and that all solutions are of the same stoichiometric concentration.

Use of expression b requires knowledge of the optical densities of both the free base and its completely protonated form. Phenolic compounds are sulfonated so rapidly, even at 0°, that we could never observe the latter directly. At higher acidities suitable values of D were obtained by plotting the usual pseudo-first order expression[19] for change in optical density with time and back-extrapolation to the time of mixing.

As a weak base is exposed to a series of increasingly strong acid solutions, it is usually observed that changes occur in its spectrum which must be ascribed to solvent effects as well as to ultimate protonation; the over-all changes being due to superimposition of both influences. This complication has elicited several treatments[20,21] for separating out the change due to protonation alone. We were unable to use any of the existing methods because *we could not observe either* D_B or D_{BH^+} *directly* and, furthermore, our curves showed only one maximum which shifted laterally instead of having two peaks one of which rises as the other falls such as is required by the Davis–Geissman[21] treatment. The method which we have developed gives satisfactory results in our case and, in our experience, gives more precise and unambiguous results than the treatments referred to above. It may be applicable to any type of spectrum change of a Hammett weak base that combines a medium effect and protonation provided that the a wave length maximum corresponding to an N → V transition is chosen.[22]

We assume: (1) that protonation of the weak base follows equations a and b above; (2) that the optical densities of the various species follow Beer's law; and (3) that in the region of maximum change of optical density, close to the pK_a, the effect of medium change on optical density is negligible compared to the effect of protonation. If these assumptions are correct, one may expect a plot of observed optical density D *vs.* H_0 to give a crude form of sigmoid titration curve and that an approximation of the pK_a could be obtained from the inflection point of this plot.

Taking antilogs converts equation b into

$$K_a = h_0(D - D_{BH^+})/(D_B - D) \qquad (c)$$

and this may be rearranged to

$$D(K_a + h_0) = K_aD_B + D_{BH^+}\,h_0 \qquad (d)$$

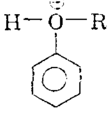
if we take the value of K_a approximated from the crude titration curve plot of D *vs.* H_0 and use this as a constant in equation d, a plot of the left-hand member against h_0 should give a straight line of slope D_{BH^+} from whose intercept D_B may be obtained. The approximations correspond to hypothetical values of D_{BH^+} and D_B which would be observed if the indicator were of the Hammett base type and solvent effects were absent. These approximations of the optical densities of free base and its conjugate acid may be inserted into equation b and an improved estimate of pK_a obtained from a plot of log indicator ratio *versus* H_0. This cycle may be repeated until it fixes on unvarying values of the limiting optical densities and pK_a.

To our surprise we have found in practice that the crude approximation from the sigmoid plot is usually within 0.1 pK_a unit of the final value and that convergence is usually reached after one cycle. Mr. Ronald Bushick has tested the sensitivity of the method to errors in the initial choice of pK_a by substituting various false values into our data for acetophenone whose pK_a is well established.[7,20] He finds that the method corrects choices of pK_a that are in error down to 0.05 pK_a unit. We are puzzled why our final reproducibility should be better than this figure. Use of the H_R[6,23] function instead of H_0 gave no convergence showing that the data could not be forced to conform to an acidity function involving activity coefficient terms that differ much from those of a Hammett base.

Figures 1, 2 and 3 show the application of the method to the case of *sec*-butyl phenyl ether data. Although the assumptions used in our treatment deprive it of rigor, the self-consistency and rapid convergence of the results are compelling evidence that a true H_0 type of equilibrium is being observed and that phenolic ethers follow the activity coefficient postulate.

Results and Discussion

The Position of Protonation.—One of our primary goals in this program has been to use pK_a's of conjugate acids of phenolic compounds and anilines as a means for comparing stereoelectronic effects on oxygen and nitrogen. In order for our results to be employed to this end, we must establish that the primary site of protonation in the phenolic compound is the oxygen. Current theory[24,25] suggests other possible points which must be considered. In addition to the oxonium compound I the conjugate acid could be a π-complex II or a σ-complex III with the donated hydrogen attached to the p- or either o-position.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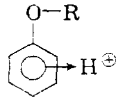
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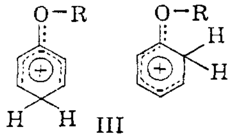
III

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(18) Reference 5, page 11.

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 37.

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

(21) C. T. Davis and T. A. Geissman, *ibid.*, **76**, 3507 (1954).

(22) We have applied it with success to the 290 mμ band of aromatic ketones, but find it inapplicable to the 250 mμ band.

(23) N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, THIS JOURNAL, **81**, 2344 (1959).

(24) K. L. Nelson and H. C. Brown, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, edited by B. T. Brooks, C. E. Boord, S. S. Kurtz and L. Schmerling, Reinhold Publishing Corp., New York, N. Y., 1955, Chapter 56.

(25) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3619 (1955).

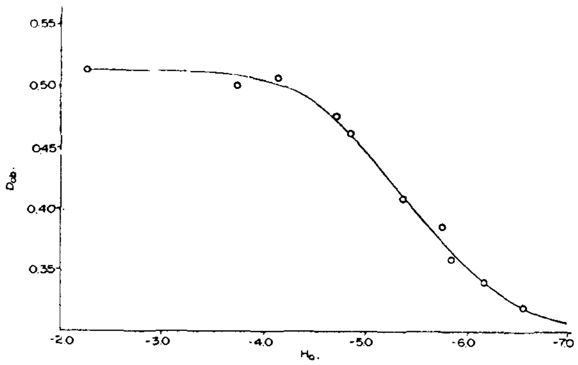

Fig. 1.—Crude "titration curve" for *sec.*-butyl phenyl ether. Plot of observed optical density *vs.* H_0 gives estimated pK_a of conjugate acid as -5.46 from inflection point.

Although doubtless all of these types of complexes occur to some extent in our solutions, we believe that by far the predominate protonated species is the oxonium acid I for the reasons given below.

Some of the best evidence for the transitions assigned to the N→V band[10] in phenolic compounds and anilines is the fact that when aniline is converted to its conjugate acid this strong band disappears and the spectrum assumes a form nearly identical to that of toluene due to removal of the resonance interaction of the nitrogen lone pair with the π-electron system of the ring. Exactly the same behavior has been observed in all of the phenolic compounds we have studied provided that optical densities are extrapolated back to zero time.[26] Nelson and Brown[24] have reviewed the enormous literature of aromatic substitution and the intermediate complexes and have concluded that there will be little or no change in ultraviolet spectrum upon formation of a π-complex since there is little disruption of the electronic system of the donor molecule. As one approaches the formation of an actual σ-complex, the spectrum undergoes large changes. Charge-transfer complexes[27] and true aromatic σ-complexes[24] seem to be invariably associated with development of visible color because the presence of the Lewis acid allows the transition from the ground state to the polarized form to occur at a lower energy. Kilpatrick and Hyman[28] have observed spectral changes during the protonation of aromatic hydrocarbons of relatively high basicity such as mesitylene or hexamethylbenzene where protonation can lead only to π- or σ-complex formation or some mixture of these with intermediate forms. Protonation of mesitylene produces two new peaks at 255 and 355 mμ. We have never observed formation of colors or of new bands down to 250 mμ. In short, the behavior of our spectra is completely consistent with that expected for the formation of an oxonium ion and does not correspond at all to the changes usually observed for other types of complex formation.

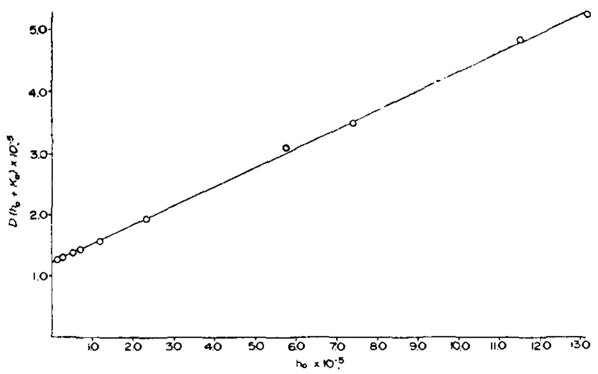

Fig. 2.—Estimation of D_B and D_{BH^+} using equation d and crude pK_a from Fig. 1.

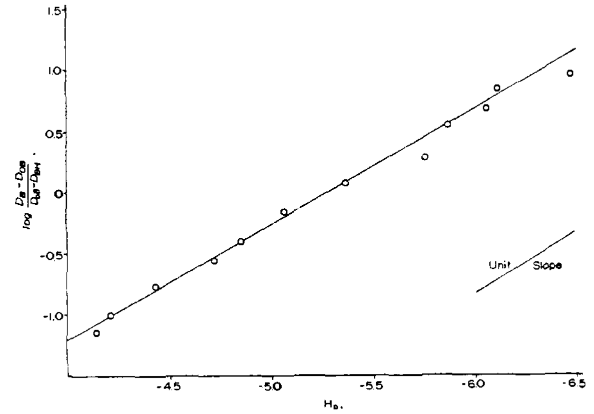

Fig. 3.—Final plot of H_0 *vs.* log indicator ratio for *sec.*-butyl phenyl ether giving $pK_a = -5.36$.

Comparisons of Phenolic Ethers with their Nitrogen Analogs.—It is well known[29,30] that the comparison of equilibria or rate data taken at a single temperature as a means for structural interpretation is hazardous especially when dealing with small changes produced by modifications of alkyl groups. However, for reasons that are presently unexplained, such correlations are often quite successful and much of our current interpretation of organic structural theory is based on the use of equilibria and rate data in condensed systems as though they really were pure potential energy terms. Furthermore, these data often give much better structure–reactivity correlations than do the apparently more meaningful enthalpy and entropy factors. With these reservations in mind, one may approach the results presented in Table I which compare the over-all response of protolytic equilibria of the conjugate acids of phenolic compounds with their nitrogen analogs. We see that effects run nearly parallel in the two series when straight alkyl chains are attached to the hetero atom. Increasing the chain produces a rapid tapering off through hydrogen, methyl and ethyl such as would be ascribed to the inductive effect. Following this a decrease in basicity is observed in both series—a

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(26) O. Goldschmid, THIS JOURNAL, 75, 3780 (1953), has observed a strong maximum in the 284 mμ region for the spectrum of phenolic compounds in concentrated sulfuric acid. We observe the rapid development of this band in strong sulfuric acid solutions and can follow its rate of formation in less strongly acid media showing that it is not a simple protonated form whose appearance would be instantaneous.

(27) L. E. Orgel, *Quart. Revs.*, 8, 422 (1954).

(28) M. Kilpatrick and H. H. Hyman, THIS JOURNAL, 80, 77 (1958).

(29) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter III.

(30) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter V.

small decrease beginning with the *n*-propyl group in the case of the anilines and a much sharper drop beginning with the *n*-butyl group in the phenolic ethers. Such discontinuities in what is usually supposed to be a smooth approach to an asymptote may be observed in rate and equilibria data from several series of reactions[31] and at one time were the subject of lively controversy. The basicity decrease in the phenolic ether series is a good deal larger than is seen in the carboxylic acids and anilinium ions. Insofar as the steric requirements around ether oxygen are more severe than around nitrogen, the fact that we see such a large effect here supports the idea that the discontinuity is steric in origin. However, whatever its cause, its reality seems to be unquestionable and one may cite also discontinuities in the heats and entropies of ionization in addition to the free energies.[31f,32] It is interesting that further lengthening of the chain in phenyl *n*-amyl ether appears to reduce the basicity even further, a trend that is not observed in the carboxylic acids.[31a] Unfortunately, there are no data for N-*n*-amylaniline for comparison and phenyl *n*-amyl ether is so insoluble that its pK_a is the most dubious of these presented here and may well be in error.

TABLE I

DISSOCIATION CONSTANTS OF CONJUGATE ACIDS OF PHENOLIC COMPOUNDS AND NITROGEN ANALOGS

	C_6H_5–O–R		C_6H_5–NH–R
R	pK_a[a]	ϵ[b]	pK_a[c]
Hydrogen	−6.74 (−7.04)[d]		5.06 (4.58)[d]
Methyl	−6.54	1579	5.15 (4.85)
Ethyl	−6.44	1938	5.41 (5.11)
n-Propyl	−6.40		5.32 (5.02)
Isopropyl	−5.80	1920	
n-Butyl	−6.99		5.25 (4.95)
Isobutyl	−6.69		
sec-Butyl	−5.36		
t-Butyl	Rapidly cleaved	454	7.25 (6.95)
n-Amyl	−7.40		
5,5-Dimethylhomochroman	−1.94		

[a] Measured at 0° and based on Long and Paul H_0 scale.[5] [b] From ref. 35. [c] From data tabulated in ref.-3. [d] Bracketted figures are observed pK_a's. Others are corrected for symmetry (S. W. Benson, THIS JOURNAL, **80**, 5151 (1958)). Diphenyl ether, 2,6-dimethylanisole and phenyl cyclohexyl ether were too insoluble to study.

Branching of the alkyl chain results in a sharp increase in basicity. Here again we are seriously hampered by the paucity of data for the N-alkylaniline series. However, the very high basicity of N-*t*-butyl-aniline has been discussed[33] as mainly the result of steric inhibition of resonance and its low extinction coefficient[33] relative to unhindered aniline supports this. The large decrease in extinction coefficient for phenyl *t*-butyl ether quoted in Table I indicates that steric inhibition of resonance must be extreme in this case also. We were unable to measure the pK_a of this interesting compound due to its extreme sensitivity to acid. Although phenyl ethers are usually considered to be relatively difficult to cleave and sulfuric acid is a poor cleaving agent,[34] we find that phenyl *t*-butyl ether is cleaved rapidly at zero degrees by 18% sulfuric acid. This must be due to the combination of high basicity and a low activation energy required for the conversion of the highly strained molecule to a transition state in which the phenolic system is regaining its resonance energy simultaneously as the bulky *t*-butyl group departs to give a rather stable carbonium ion.

Baddeley, Smith and Vickars[35] (Table I) also list, 2,6-dimethylanisole and homochroman as being phenolic ethers with unusually low extinction coefficients. We found the former to be too insoluble for study but were successful in measuring the pK_a of 5,5-dimethylhomochroman[36,37] and found that it was indeed extremely basic compared to the acyclic phenyl ethers.

To our knowledge the difference of 4.60 pK_a units on going from anisole to 5,5-dimethylhomochroman is the largest effect of steric inhibition of resonance yet observed for an equilibrium. It is much larger than the 2.73-unit difference found in the aniline system indicating that phenyl ethers may have a greater over-all resonance energy than the anilines. We have already[1] suggested an explanation for this surprising result. One may estimate from the data of Gordy and Stanford[38] and Searles and Tamres[39] that tetrahydrofuran may have a pK_a in the neighborhood of −1 to −2. This would make our value for −1.96 for 5,5-dimethylhomochroman by no means unreasonable and indeed this is probably the most reliable approximation available at present for the order of basicity to be expected for aliphatic cyclic ethers. A number of studies[39–44] indicate strongly that cyclic ethers are more basic than their open chain analogs.

Branching in the alkyl chain in the less extreme cases of iso-butyl, iso-propyl and *sec*-butyl phenyl ethers must also involve base-strengthening components from inductive electron release and steric inhibition of resonance. There is much evidence in the literature[40–44, 45] that oxygen compounds are far more sensitive to steric effects of substituents than are their amine analogs and that this usually works strongly as a base-weakening effect in the

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(31) For example: (a) J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938); (b) H. O. Jenkins and J. F. J. Dippy, THIS JOURNAL, **62**, 483 (1940); (c) J. F. J. Dippy and H. O. Jenkins, *Trans. Faraday Soc.*, **37**, 370 (1941); (d) D. H. Everett and W. F. K. Wynne-Jones, *ibid.*, **37**, 373 (1941); (e) E. M. Arnett, J. G. Miller and A. R. Day, THIS JOURNAL, **72**, 5635 (1950); (f) H. C. Brown, M. D. Taylor and S. Sujishi, *ibid.*, **73**, 2464 (1951).

(32) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd. ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 667.

(33) B. M. Wepster, "Progress in Stereochemistry," Vol. II, ed. by W. Klyne and P. B. D. de la Mare, Academic Press, Inc., New York, N. Y., 1958, Chapter 4.

(34) R. L. Burwell, *Chem. Revs.*, **54**, 615 (1954).

(35) G. Baddeley, N. H. P. Smith and M. A. Vickars, *J. Chem. Soc.*, 2458 (1956).

(36) Kindly supplied by Professor Harold Hart of Michigan State University.

(37) H. Hart and C. Wagner, *Proc. Chem. Soc.*, 284 (1959).

(38) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

(39) S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951).

(40) P. A. McCusker and S. M. Kennard, *ibid.*, **81**, 2976 (1959).

(41) L. N. Ferguson, *ibid.*, **77**, 5288 (1955).

(42) H. C. Brown and R. M. Adams, *ibid.*, **64**, 2557 (1942).

(43) W. Gerrard and E. D. Macklen, *Chemistry & Industry*, 1070 (1959).

(44) *Ibid.*, 1549.

(45) P. D. Bartlett and J. D. McCollum, THIS JOURNAL, **78**, 1446 (1956).

aliphatic series through B-strain[45] and steric inhibition to solvation of the oxonium ion. Thus, there seems to be little doubt that alcohols are considerably more basic than their cognate ethers[45,46] in contrast to the simple secondary amines which are usually more basic than primary amines of the same carbon content.[4] The large increase in basicity that accompanies branching close to the ether oxygen in the phenolic ethers we have studied, shows that these base-weakening factors are overwhelmed by strengthening factors and in view of the usually modest contributions from the inductive effects of alkyl groups and the large effects that we have seen from steric inhibition of resonance, we believe that the latter is the main factor when branching is close to oxygen. Further evidence that inductive effects are inadequate to explain these increases is obtained by plotting Taft's[47] σ^*-values for the alkyl groups *vs.* the pK_a's of the alkyl phenyl ethers. Only a wide scatter of pointsis seen.

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(46) R. L. Burwell, Jr., and M. E. Fuller, THIS JOURNAL, **79**, 2332 (1957).

(47) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 591.

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The Dipole Moments of Some Heptafulvene Derivatives

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The dielectric constants and densities of dilute solutions of heptafulvene-8,8-dinitrile, 8-ethoxycarbonylheptafulvene-8-nitrile, tropylmalononitrile, ethyl tropylcyanoacetate, diethyl tropylmalonate, ditropylmalononitrile and ethyl ditropylcyanoacetate in benzene or dioxane have been measured and used to calculate the dipole moments of the molecules. From these data, the moments of heptafulvene and 7-methylcycloheptatriene were calculated to be 3.07 and 0.13 D. In the former compound, the negative end of the moment is on the side of a methylene group, while in the molecule of the latter compound negative charges accumulate in the ring at the expense ot those around the carbon atom of a methyl group.

Introduction

Measurements have already been made on the dipole moments of tropone, tropolone and a number of their derivatives,[1] and the results have been used for the elucidation of the structures of these molecules. One of the simplest and the most fundamental molecules having a cycloheptatriene ring is that of heptafulvene, which, however, is not stable and readily polymerizes.[2] The molecule of this compound is feasible for theoretical treatment. In fact, Berthier and Pullman[3a] discussed this problem by both the valence bond method and the molecular orbital method, the moment calculated by the latter method being 2.35 D.; later, Bergmann, *et al.*,[3b] carried out a molecular orbital treatment on this molecule and gave a moment of 4.6 D. in rather poor agreement with the value mentioned above. However, these authors seem to lay emphasis on the direction of the moment in the molecule rather than on the exact numerical magnitude. They predicted that the molecule of heptafulvene has a moment with its negative pole at a methylene group, whereas the moment of a fulvene molecule is directed along the opposite direction. Against these authors' prediction, a contradictory opinion was raised by Julg,[4] who applied a seld-consistent molecular field method to a heptafulvene molecule. The results of his calculation differ considerably from those obtained by the aforementioned LCAO method, the dipole moment being calculated as 0.14 D. in the opposite direction to that given in the older references.

The present investigation was undertaken in order to determine both the magnitude and the direction of the moment of heptafulvene on the basis of the observed moments of some heptafulvene derivatives. The dipole moments of some compounds having a tropyl group or groups were also studied for comparison.

Experimental Method and Results

The samples of heptafulvene-8,8-dinitrile (I, m.p. 200°), 8-ethoxycarbonylheptafulvene-8-nitrile (II, m.p. 63.5°), tropylmalononitrile (III, m.p. 63°), ethyl tropylcyanoacetate (IV, b.p. 138–141.5° (5 mm.)), diethyl tropylmalonate (V, b.p. 128–132° (4 mm.)), ditropylmalononitrile (VI, m.p. 107°) and ethyl ditropylcyanoacetate (VII, m.p. 125°) were synthesized and purified by two of the present authors (T. M. and T. N.) in Tohoku University.[5] The measurements of dipole moments were carried out at 25° on dilute solutions in benzene, except heptafulvene-8,8-dinitrile, which was sparingly soluble in this solvent and therefore was studied in dioxane solutions. The dielectric constants were measured by means of a heterodyne beat apparatus provided with a platinum cell.[6] For each solute, determinations were made on solutions of four different concentrations appropriately chosen below 3 weight per cent. The graphical plot of the dielectric constant as well as the density of solutions against the concentration in weight per cent. gave linear dependence within experimental errors. The slopes of these straight lines were evaluated by the least-squares method and the

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