

A suitable choice of conditions usually allows separation of the peak for the base under study from those of the solvent and any decomposition products and also from any other bases that are present. Thus, as will be shown in a future paper, it has been possible by this technique to measure simultaneously the basicities of *cis*- and *trans*-2,5-dimethyltetrahydrofuran even though they were not separated before the study. In principle, given the proper column, it would be possible to determine simultaneously the  $pK_a$ 's of all the compounds described here and in future papers in one run with a series of acids.

When the organic layer is analyzed by spectrophotometry there is little advantage of this method over the usual Hammett indicator method and, as we have mentioned for

nitrobenzene and benzoic acid, specific effects of water on the spectrum of the compound in the organic layer can make spectra uninterpretable. For compounds that do not suffer from this effect the use of solvent extraction and spectrophotometry in selected cases may be advantageous in that the spectrum of the compound in the organic layer does not show sensitivity to the complicated medium effects that are such a nuisance in the application of the Hammett indicator method to spectra in aqueous acid.<sup>3-5,9,29</sup>

**Acknowledgment.**—It is a pleasure to express our appreciation for discussions with Professors Quintus Fernando and Norman Deno during the development of this method.

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## Base Strengths of Some Aliphatic Ethers in Aqueous Sulfuric Acid<sup>1,2</sup>

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The  $pK_a$ 's for the oxonium ions of twelve saturated aliphatic ethers in aqueous sulfuric acid have been determined by the solvent extraction-g.l.c. method.<sup>4,8</sup> Validity is given to the method by comparing the results with independent estimates of the basicity range to be expected of saturated ethers. Comparison is also made with basicity data for some of these ethers in other non-aqueous systems and with results for analogous amines and phosphines. It is found that  $pK_a$ 's for six methyl ethers correlate with Taft's  $\sigma^*$ -parameters, but that the other classes of ethers are sterically controlled. The results mainly support the predictions of previous theories<sup>20,21</sup> that oxygen bases are more sensitive to steric effects than their amine analogs, but indicate that in aqueous solution the important factor is steric hindrance to solvation and not B-strain. The matter of the basicities of ethers, alcohols and water is considered in the light of recent evidence.

In previous papers<sup>4,5</sup> we have described the importance and difficulty of measuring the  $pK_a$ 's of aliphatic oxonium ions in aqueous strong acids. Although the basicities of alkyl phenyl ethers<sup>5</sup> might appear to provide a partial answer to the question of how alkyl groups influence the basicity of ether oxygen, the large contributions from steric inhibition of resonance observed in that series obscure the influences of other steric factors as well as the polar and solvation effects whose combined action may be expected to decide the base strengths of aliphatic ethers.

We shall present here our results for non-cyclic saturated ethers obtained by the method of solvent extraction-g.l.c.<sup>4,8</sup> In addition to comparing these results with those obtained by other workers for the same ethers with other acid systems and with basicities of comparable amines and phosphines, we shall consider the matter of the basicities of ethers *vis á vis* alcohols and water and the solvation of ethers. Further comments on these matters will be presented in a following paper on the basicities of saturated cyclic ethers.

### Results

In Table I are the  $pK_a$ 's of the oxonium ions of twelve selected aliphatic ethers and anisole<sup>4,5,8</sup>

(1) Stereoelectronic Effects in Organic Bases, VII; previous paper in this series, ref. 4.

(2) This investigation was supported by a Public Health Service research Grant (A-3643 B.B.C.) from the National Institute of Arthritis and Metabolic Diseases. The Perkin-Elmer 21 infrared spectrophotometer used in conjunction with this work was purchased with the aid of the National Science Foundation. We wish to express our gratitude for this support.

(3) The greater part of the work presented here is taken from the thesis of Ching Yong Wu presented to the Chemistry Department of the University of Pittsburgh in March, 1961, as partial fulfillment of the requirements for the Ph.D. degree.

(4) E. M. Arnett, C. Y. Wu, J. N. Anderson and R. D. Bushick *J. Am. Chem. Soc.*, **84**, 1674 (1962).

(5) E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 5660 (1960).

measured for the most part at room temperature by distribution between cyclohexane and aqueous sulfuric acid solutions. Although it is difficult to assign an error precisely to these results, it appears likely that most of the  $pK_a$ 's are known to  $\pm 0.10$ - $0.20$   $pK_a$  unit.<sup>4</sup>

Although we have already<sup>4</sup> presented considerable evidence for the validity of this method for measuring the strengths of weak bases, it will be seen below that the data in Table I lend further support to the technique as it applies to ethers. However, in view of the hazards inherent in the method<sup>4</sup> and the fact that conflicting estimates in the literature for the strengths of other saturated weak bases often cover many powers of ten, we wish first to present several independent arguments that the data in Table I are of the right general order of magnitude.

TABLE I  
DISSOCIATION CONSTANTS OF CONJUGATE ACIDS OF ALIPHATIC ETHERS<sup>a</sup>

Number	Ethers	$pK_a$	$\frac{\%}{H_2SO_4}$ at $pK_a$	$K_D^{1b}$	Slope
1	Dimethyl	-3.83	54.4	0.435	0.81
2	Methyl ethyl	-3.82	54.2	1.65	.92
3	Methyl <i>n</i> -propyl	-3.79	54.0	9.0	.903
4	Methyl isopropyl	-3.47	51.0	4.85	.84
5	Diethyl	-3.59	52.3	6.52	.94
6	Methyl <i>n</i> -butyl	-3.50	51.3	35.0	.70
7	Methyl <i>t</i> -butyl	-2.89	45.2	12.3	.69
8	Ethyl <i>n</i> -butyl	-4.12	56.9	104	.97
9	Ethyl <i>t</i> -butyl	-2.84	44.8	41.0	1.03
10	Di- <i>n</i> -propyl	-4.40	59.5	93.0	1.14
11	Diisopropyl	-4.30	58.6	15.5	1.03
12	Di- <i>n</i> -butyl	-5.40	68.1	150	1.18
	Anisole	-6.54	78.2	105	1.028

<sup>a</sup> Each  $pK_a$  value is based on nine to twelve points covering a range of 2.5 to 4  $H_0$  units. <sup>b</sup> Using cyclohexane as solvent.

Searles, Tamres and Barrow<sup>6</sup> have observed a shift of 96  $\text{cm.}^{-1}$  for the O-D stretching frequency of deuteriomethanol, when it is dissolved in diethyl ether, relative to its value in carbon tetrachloride. On the basis of a large plot<sup>7,8</sup> of known values of the  $pK_a$ 's of many strong and weak bases and the deuteriomethanol infrared shifts produced by them, one may estimate a value for the  $pK_a$  of diethyl ether of approximately  $-4.2$ . In our experience diethyl ether might be expected to have enough steric hindrance to give a low estimate of its basicity by this method. In any event it is not far from the value given in Table I. By the same method the  $pK_a$  of anisole oxonium ion may be estimated as  $-6.9$  in reasonable agreement with the true value.<sup>5</sup>

Bartlett and McCollum<sup>21</sup> estimated the  $pK_a$  of the isopropyl alcohol oxonium ion to be  $-3.2$ . Subsequent work in Bartlett's Laboratory<sup>9,10</sup> has cast doubt on this value.

Roček and Krupička<sup>11</sup> have in turn arrived at a  $pK_a$  of  $-4.1$  for the same oxonium ion, while Deno, Edwards and Perizzolo<sup>12</sup> have found a  $pK_a$  of  $-3.8 \pm 0.4$  for *t*-butyl alcohol oxonium ion and about the same value for that of 1-methylcyclohexanol.<sup>13</sup> Unless there is an unexpectedly large difference between the basicities of alcohols and ethers this would seem to indicate that our results are of the right order of magnitude.

The results of Bartlett and McCollum<sup>21</sup> show furthermore that at an acidity of  $H_0 = -3.75$  diethyl ether is still an effective hydride transfer agent for the reduction of carbonium ions. This suggests that its  $pK_a$  is at least not very much more positive than  $-3.75$ .

**The Parachor Test.**—Since the  $pK_a$  of nitrobenzene cannot be obtained by solvent extraction<sup>4</sup> because of anomalous solubility behavior,<sup>14</sup> we must consider the possibility that some of our measurements for aliphatic ethers are disturbed by the same factor. A test for the incursion of this effect is suggested by the recent paper of Deno and Berkheimer<sup>15</sup> who show that for many classes of organic compounds (including aliphatic ethers) the distribution constant between water and an immiscible solvent is an additive structural property related directly to the parachor. Since  $K_D'$  is the distribution constant for the unprotonated ether

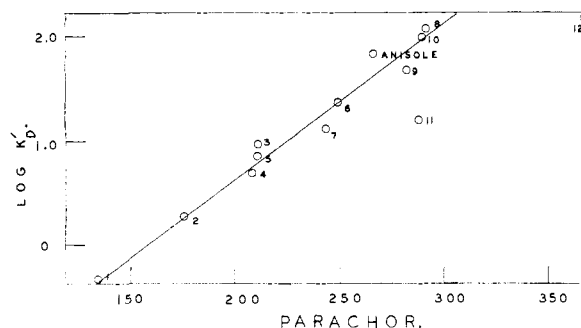


Fig. 1.

between cyclohexane and aqueous acid of  $H_0$  close to the  $pK_a$  of the ether where the activity coefficients of the unprotonated ethers will be roughly unity,<sup>16,17</sup> we may expect that  $\log K_D'$  will be a linear function of the parachors<sup>18</sup> of the ethers. In Fig. 1 it is shown that a fairly good linear relation is found and that the value for anisole<sup>19</sup> for which anomalous solubility need not be considered<sup>4</sup> lies close to the line. We may conclude from this that, except for diisopropyl ether and di-*n*-butyl ether, which lie rather far from the line, probably none of the ethers investigated is much influenced by Hammett-Chapman effects. Di-*n*-butyl ether is so insoluble that considerable doubt must be attached to its  $K_D'$  value and its  $pK_a$  presented in Table I may be in error by as much as  $0.5 pK_a$  unit. We cannot account for the anomalous position of diisopropyl ether.

No useful relationship between the structures of the ethers and the slopes of the plots of  $H_0$  versus  $\log D/(K_D' - D)$  is apparent to us.

### Discussion

Having presented evidence that our values for the  $pK_a$ 's of ether oxonium ions fall in a reasonable region of acidity and that they are probably not seriously perturbed by anomalous solubility factors, we now consider the variation of basicity with structure of the ether. Table I shows that although the examples studied cover a fairly broad range of basicity, there appears to be no single simple factor controlling the base strength. We would indeed expect from what is known about amines (see below) that a delicate balance of inductive, steric and solvation forces might be involved in the ethers. In considering the rather sparse and often conflicting data that were available several years ago for the basicities of oxygen compounds, Hine and Hine<sup>20</sup> and later Bartlett and McCollum<sup>21</sup> concluded that B-strain is of great (if not primary) importance and that elaboration of the alkyl groups attached to oxygen should generally serve as a base-weakening factor quite overwhelming the base-strengthening

(6) S. Searles, M. Tamres and G. M. Barrow, *J. Am. Chem. Soc.* **75**, 71 (1953).

(7) We have alluded to this correlation previously<sup>9</sup> and expect to present the combined results when more reliable data for several classes of weak bases become available. Although much use of the correlation of  $\Delta\nu$  with  $pK_a$  has been made within given classes of compounds by many workers, we believe that it is not recognized how broad and generally reliable this correlation is, provided sterically hindered compounds and certain other classes are omitted.

(8) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 4999 (1960).

(9) E. M. Arnett, unpublished results. We are grateful to Professor Bartlett for permission to refer to these results.

(10) W. F. Smith, Jr., Thesis, Harvard University, 1960.

(11) J. Roček and J. Krupička, *Coll. Czech. Chem. Comm.*, **23**, 2068 (1958).

(12) N. C. Deno, T. Edwards and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 2111 (1957).

(13) N. C. Deno, private communication.

(14) L. P. Hammett and R. P. Chapman, *J. Am. Chem. Soc.*, **56**, 1282 (1934).

(15) N. C. Deno and H. B. Berkheimer, *J. Chem. Engineering Data*, **4**, 1 (1959).

(16) N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957).

(17) Relative to a standard state of aqueous acid (say 20%) in which salting out has become constant.<sup>16</sup>

(18) O. R. Quayle, *Chem. Revs.*, **53**, 439 (1953).

(19) This is based on a value for  $K_D'$  for anisole using cyclohexane as a solvent instead of the iso-octane employed in the control experiment in ref. 4. Anisole must be studied in acid of such high strength that activity coefficients have probably begun to depart from unity.<sup>17</sup>

(20) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(21) P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956).

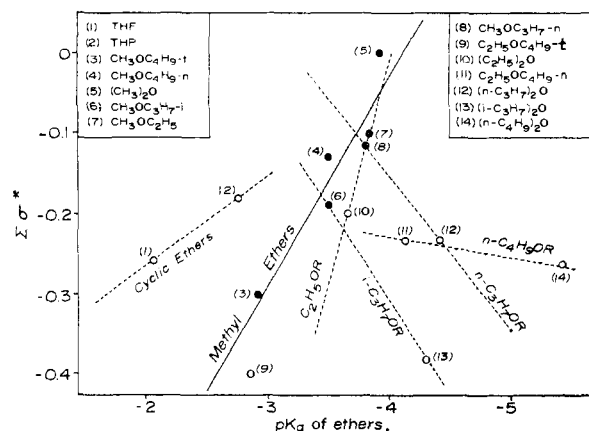


Fig. 2.—Taft  $\Sigma\sigma^*$  plot for saturated ethers.

inductive effect. With this in mind we were quite unprepared for the steady increase in basicity encountered in the series of methyl ethers  $MeOR$  as the size of  $R$  is increased. In Fig. 2 the  $pK_a$ 's of the ethers are plotted against Taft's substituent parameters  $\Sigma\sigma^*$  and it is seen that the six methyl ethers generate a crude straight line indicating that for this series steric effects are small enough or constant enough for the inductive effect to assert itself. If the other ethers are considered in the same way it is clear that increasing the size of the alkyl groups lowers the basicity and the decrease is more abrupt the larger the groups are. Admittedly, the data are too few and the changes in basicity too small to warrant a detailed analysis, but the over-all pattern suggests that the line between inductive and steric control falls between the ethyl ethers and the propyl ethers, and that steric factors are not necessarily always overwhelming. The few results presented here for  $n$ -propyl, isopropyl and  $n$ -butyl ethers indicate that for series of alkyl ethers where a group larger than ethyl is held constant, the most important effect of increasing the size of the other group is to lower basicity, in conformity with the ideas of Hine and Hine and Bartlett and McCollum. The main exceptions are the  $t$ -butyl ethers which are both highly basic.<sup>22</sup>

**Comparison with Other Measures of Basicity of Ethers.**—Most of the ethers in Table I have been studied as bases against such non-aqueous acids as deuteriomethanol,<sup>23,24</sup> hydrogen chloride,<sup>25,26</sup> iodine,<sup>27,28</sup> perchloric acid in acetic acid,<sup>29</sup> phenol,<sup>30</sup> dinitrogen tetroxide<sup>31</sup> and boron trifluoride.<sup>32,33</sup>

(22) Dr. A. K. Hoffmann of the American Cyanamid Co. has informed us that di- $t$ -butylamine is one of the most basic of the secondary amines. Di- $t$ -butyl ether has been found to be highly basic toward phenol<sup>30</sup> but much less so toward dinitrogen tetroxide.<sup>31</sup>

(23) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940); **9**, 204 (1941).

(24) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

(25) W. Gerrard and E. D. Macklen, *Chem. Revs.*, **59**, 1105 (1959).

(26) W. Strohmeier and A. Echte, *Z. Elektrochem.*, **61**, 549 (1957).

(27) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **75**, 3561 (1953).

(28) J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952).

(29) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5198 (1951).

(30) R. West, L. S. Whatley and K. J. Lake, *ibid.*, **83**, 761 (1961).

(31) J. G. Whanger and H. H. Sisler, *ibid.*, **75**, 5188 (1953).

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

(33) D. E. McLaughlin and M. Tamres, *ibid.*, **82**, 5618 (1960).

The results indicate that aliphatic ethers are less basic than cyclic ones and are much more basic than are alkyl aryl ethers. However, the order of basicity which is found for the simple alkyl ethers varies considerably from one acidic system to another.

As originally defined,<sup>34</sup> "B-strain should depend greatly upon the size of the groups attached to the . . . central atom, but should be relatively independent of the size of the adding group." The profound effect of the adding group upon the basicity order of the ethers clearly rules out B-strain as the main factor. A more likely steric influence which is compatible with our results and most of the observations so far reported by other workers is that ethers are quite sensitive to "F-strain" and that steric hindrance to water of solvation on the oxonium ion behaves operationally as though the hydrated proton were a medium sized Lewis acid.

**Comparison of Ethers with Amines and Phosphines.**—One of the most troublesome problems for the simple electronic theory of organic chemistry has been the failure of the  $pK_a$ 's of alkyl ammonium ions to follow the order predicted by inductive effects.<sup>35,36</sup> A number of workers<sup>32,34-44</sup> have attempted to study the coordination of the amines with acidic systems free of hydroxylic solvents in hope that this might result in an inductive sequence. The resulting orders of basicity for the amines in these various systems show the same type of erratic variation with the acid system that we have remarked for the ethers and argue against B-strain as the important general factor in favor of solvation effects.

Perhaps the most valuable clarification of the problem is the recent discovery of Hall<sup>45</sup> that the members of each class of amine—primary, secondary and tertiary—may be correlated with Taft's  $\sigma^*$ -substituent parameters to generate three separate straight lines. Hall concluded that his results argued against B-strain and that steric hindrance to solvation was the important steric effect in the interaction of amines with hydrated protons. He found the best correlation with the tertiary amines, the ones for which B-strain should be greatest and which should be expected to be the best analogs for the ethers we are considering here from the standpoint of solvation.<sup>45,46</sup> Recently Henderson and Streuli<sup>47</sup> have found that

(34) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *ibid.*, **66**, 435 (1944).

(35) For reviews of this problem see: 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; see also ref. 36.

(36) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(37) L. Sacconi, G. Lombardo and R. Ciofalo, *J. Am. Chem. Soc.*, **82**, 4182 (1960).

(38) L. Sacconi and G. Lombardo, *ibid.*, **82**, 6266 (1960).

(39) L. Sacconi, G. Lombardo and P. Paoletti, *ibid.*, **82**, 4185 (1960).

(40) R. T. Claunch, T. W. Martin and M. M. Jones, *ibid.*, **83**, 1073 (1961).

(41) R. G. Pearson and F. V. Williams, *ibid.*, **76**, 258 (1954).

(42) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958).

(43) V. K. LaMer and H. C. Downes, *ibid.*, **53**, 888 (1931).

(44) J. W. Bales and A. F. Taylor, *J. Chem. Soc.*, 417 (1961).

(45) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957); see also ref. 48.

(46) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

the basicities of the aliphatic phosphines can also be interpreted in the same general way.

A least squares treatment of the  $pK_a$  versus  $\Sigma\sigma^*$  data for the methyl ethers gives the equation  $pK_a = -3.90 - 3.33 \Sigma\sigma^*$ . In Table II this is compared to the corresponding equations for the tertiary amines and tertiary phosphines and the electronegativities of the central atoms. As might be supposed the more electronegative central atoms are most sensitive to the abilities of alkyl groups to release electrons as evidenced by the slopes of the Taft plots. The conformity of the methyl ethers to the general pattern may be considered as further evidence for the validity of our results.

TABLE II

Compounds	Equation, $pK_a =$	Electro-negativity <sup>48</sup>
Phosphines	$7.85 - 2.67 \Sigma\sigma^*$	2.1
Amines	$9.61 - 3.30 \Sigma\sigma^*$	3.0
Methyl ethers	$-3.90 - 3.33 \Sigma\sigma^*$	3.5

**Implications for the Basicities of Water and the Alcohols.**—It has been commonly supposed that water is more basic than the alcohols which in turn are more basic than the ethers and this anti-inductive order has been attributed to B-strain.<sup>20,21</sup> Although there may be found many data in the literature to support this sequence<sup>49</sup> by inference, we are aware of only one study which has actually compared members of each class under the same conditions. Gerrard and Macklen<sup>25</sup> mention measurements of theirs of the solubility of gaseous hydrogen chloride in water, 1-butanol and di-*n*-butyl ether at several temperatures and find that on going from 50° to 1° the order changes from alcohol > water > ether to ether > alcohol > water with the order at intermediate temperatures being alcohol > ether > water.

As for the available data on the actual  $pK_a$ 's of water, alcohol and ether oxonium ions, the various estimates that may be found in the literature<sup>49,50</sup> for each type of compound conflict within themselves over several powers of ten, a considerably greater range than one might actually expect to find between the  $pK_a$ 's of the classes of compounds themselves.

To our knowledge the only reliable measurement that has been made of an alcohol and comparable ether in an aqueous acid system is that for phenol and anisole which shows the latter to be definitely more basic than the former.<sup>5</sup> In view of the importance of resonance effects and steric influences on them in this series,<sup>5</sup> it would be risky to suggest that this is unequivocal evidence for ethers being generally more basic than comparable alcohols by virtue of inductive effects. However, when the basicity values quoted above for isopropyl alcohol<sup>11,21,12</sup> and *t*-butyl alcohol<sup>13</sup> are compared with our values for the  $pK_a$ 's of the methyl ethers of these alcohols it appears likely that these

aliphatic ethers are also somewhat more basic than the alcohols.

A final question may be raised about whether real meaning can be attached to the notion of a single, simple basicity constant for water or the alcohols. We may expect hydroxylic compounds in water solution to form various aggregates with themselves and with the solvent. As the proton level of the solvent increases the respective populations of different types of aggregates may very well change too as the amount of "free" water (not tied up in the solvation of ions) decreases. If there are important differences between the basicities of the different types of aggregates one would expect the apparent basicity of the substrate to change as the acidity varies. It is possible that the wide discrepancies in apparent basicities of water and the alcohols are not due to experimental errors but instead are due to there being a number of effective bases present whose relative concentration changes simultaneously as the medium used to measure the basicity changes so that different "constants" are determined by different methods.<sup>51</sup> This problem should not exist in the case of the amines because they may be studied in a region of acidity where there is a large excess of "free" water and perhaps also because they do not fit into the structure of the solvent to the same extent as do the hydroxylic bases.

In this connection we have attempted to determine the basicity of phenol by solvent extraction with spectrophotometric analysis of the organic phase. This compound should serve as a partial guide to the applicability of the solvent-extraction basicity method to alcohols. At 0° using isooctane a  $pK_a$  of  $-6.64$  was obtained which may be compared with  $-7.04$  by the Hammett indicator method. Phenol is sufficiently different in activity coefficient behavior from the indicators used to establish the  $H_0$  scale in the neighborhood of its  $pK_a$  so that even for the indicator study a plot of the logarithm of the indicator ratio versus  $H_0$  has a slope of about 0.81. The logarithmic plot of the extraction data, on the other hand, has a slope of only  $-0.714$ .

This behavior of phenol contrasts sharply with that of anisole,<sup>4</sup> suggesting that alcohols in general may not be amenable to study by solvent extraction. This matter is being investigated further.

We have made several attempts to estimate the basicities of alcohols and water by applying the same differences between tertiary, secondary, primary amines and ammonia to the appropriate oxygen analogs. The general failure of this type of approach to give internally consistent results prevents us from discussing them here. Very likely solvation factors are so different for free and coordinated nitrogen and oxygen bases that this is an abortive approach.

### Experimental

**Materials.**—All of the compounds except methyl ethyl ether and methyl isopropyl ether were available either from the Fisher Scientific Co. or K. and K. Laboratories. All of the ethers except dimethyl were purified by drying over Drierite, by passage through an alumina column to remove peroxides, and by fractional distillation. The purity was

(47) W. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960).

(48) L. Pauling, "The Nature of the Chemical Bond," 3rd. ed., Cornell University Press, Ithaca, N. Y., 1960, p. 90.

(49) See ref. 11, 20, 25 and 50 for reviews of these results.

(50) Thesis of C. Y. Wu, University of Pittsburgh, 1961.

(51) We are grateful to Professor Bartlett for this suggestion.

TABLE III  
CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS

Ether	Concn. of stock soln., vol. %	Column <sup>a</sup> packing	Column temp., °C.	Flow rate, ml./min.
Dimethyl	1	P	44	74
Methyl ethyl	2	T	62	60
Methyl <i>i</i> -propyl	3	T	54	95
Methyl <i>n</i> -propyl	2	T	60	60
Diethyl	2 <sup>c</sup>	T	59	70
Diethyl <sup>b</sup>	2	T	62	70
Di- <i>n</i> -propyl	5	B	62	100
Di- <i>i</i> -propyl	2	A	74	90
Methyl <i>t</i> -butyl	2	A	82	100
Methyl <i>n</i> -butyl	2	A	76	110
Ethyl <i>t</i> -butyl	4	A	74	100
Ethyl <i>n</i> -butyl	5	B	67	92
Di- <i>n</i> -butyl	2	T	90	80
Anisole	3	A	120	76

<sup>a</sup> Burrell Corporation packings used as follows: A, Apiezon L on firebrick; B,  $\beta,\beta'$ -oxydipropionitrile on Celite; P, polyethylene glycol on Celite; T, Tween on Celite. <sup>b</sup> Solvent was carbon tetrachloride in this case. Cyclohexane used as extraction solvent in all other cases except anisole for which isoöctane was used (see previous paper). <sup>c</sup> Sample volume in this case was 10  $\mu$ l. In all other cases 50  $\mu$ l. was used.

confirmed by comparison of boiling point and refractive index with literature values and by infrared spectrum. A final check was made for impurities by gas chromatography.

Methyl ethyl ether was prepared by the action of 40 g. (0.73 mole) of sodium methoxide on 114 g. (0.73 mole) of ethyl iodide in 200 ml. of methyl alcohol as solvent.<sup>52</sup> The highly volatile product was distilled through a reflux condenser and collected by means of a Dry Ice condenser. Fractional distillation gave a portion boiling between 10–11°. The yield was 73%.

(52) D. McIntosh, *J. Am. Chem. Soc.*, **30**, 1098 (1908).

Methyl isopropyl ether was made by the procedure of Wirth, Jackson and Griffiths.<sup>53</sup>

The acids and solvents for distribution studies were prepared as described in the previous paper in this series.

**Procedure.**—The method has been described in the previous paper in this series.<sup>4</sup> Details of the gas chromatography for the compounds are presented in Table III.

Dimethyl ether is a gas at room temperature, the 1% solution was approximated in this case by bubbling the ether into chilled solvent until the volume increased by 1%.

Data for a typical series of extraction experiments with methyl ethyl ether are presented in Table IV.

TABLE IV  
SOLVENT EXTRACTION OF METHYL ETHYL ETHER FROM CYCLOHEXANE AT 20°

% H <sub>2</sub> SO <sub>4</sub>	H <sub>0</sub>	D	$\log \frac{D}{K_D' - D}$	pK <sub>a</sub>
39.70	-2.39	1.622	1.849	-4.24
43.54	-2.74	1.469	0.922	-3.66
46.82	-3.06	1.367	.692	-3.75
48.84	-3.26	1.150	.366	-3.63
49.92	-3.37	1.005	.196	-3.57
53.73	-3.79	0.964	.149	-3.94
56.71	-4.11	.622	-.215	-3.89
57.44	-4.19	.465	-.404	-3.79
60.30	-4.51	.415	-.472	-4.04
62.13	-4.58	.298	-.656	-3.92

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(53) H. E. Wirth, M. J. Jackson and H. W. Griffiths, *J. Phys. Chem.*, **62**, 871 (1958).

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## Base Strengths of Some Saturated Cyclic Ethers in Aqueous Sulfuric Acid<sup>1,2</sup>

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The  $pK_a$ 's of the oxonium ions of eight cyclic ethers have been determined by the solvent extraction-g.l.c. technique and found to follow the same order of basicity as was previously determined for the same ethers against six other acidic systems. The saturated cyclic ethers are more basic than their open chain analogs and steric hindrance to solvation is of much less importance than in acyclic compounds. A reverse I-strain order is found in the series: hexamethylene oxide  $\geq$  tetrahydrofuran > tetrahydropyran, and also appears to obtain for the analogous imines. This cannot be explained by the usual polar or steric factors. An interpretation is advanced in terms of electron-correlation forces in the free base which lead to relief of non-bonded interactions upon protonation. When compared to the position of morpholine on the scale of basicities of saturated amines, dioxane is surprisingly basic. An explanation for this anomaly is presented.

In previous papers in this series we have evaluated the effect of changing structure on the basicities of aromatic<sup>4</sup> and acyclic saturated<sup>5,6</sup> ethers.

(1) Stereoelectronic Effects in Organic Bases, VIII; previous paper in this series, ref. 6.

(2) This investigation was supported by a Public Health Service research grant (A-3643 B.B.C.) from the National Institute of Arthritis Metabolic Diseases. The Perkin-Elmer 21 spectrophotometer used in conjunction with this work was purchased with the aid of the National Science Foundation. We wish to express our gratitude for this help.

(3) Most of the work presented here is taken from the thesis of Ching Yong Wu submitted to the Department of Chemistry of the University of Pittsburgh in March, 1961, as partial fulfillment of the requirements for the Ph.D. degree.

(4) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).

In this article we shall present our results for the  $pK_a$ 's of the oxonium ions of cyclic saturated ethers in aqueous sulfuric acid and interpret them in terms of polar, steric and solvation factors by comparison with basicities of the same ethers against non-aqueous acidic systems and with amine analogs. In doing this we shall make the usual assumption of the physical organic chemist, that modest changes in free energy of ionization may be understood in simple structural terms.

Cyclic ethers offer a distinct advantage over

(5) E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 4999 (1960).

(6) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1680 (1962).