Calculation of Acidity Constants of Protonated Weak Organic Bases by a New Method, III* Ethers

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Relative Basicity Parameter, Conductivity of Protonated Ethers, Calculation of pKₐ's for R₂OH⁺

It is shown in this paper that a consistent set of values of pKₐ⁺ for 24 ethers, in good agreement with the few which have been obtained by other methods, can be calculated from a correlation of the HCl solubility in the ethers with ΔG of the R groups, and also with the gas phase I.P.'s of the ethers. We find that in solution the order of basicity is ROH > R₂O > H₂O whereas in the gas phase it is R₂O > ROH > H₂O. Evidence for complete H⁺ transfer to R₂O is deduced for most cases, but a H-bonding "basicty" occurs for the less basic ethers. A brief review of previously obtained pKₐ⁺'s for some ethers, MeOH, and H₂O is also presented.

Introduction

The strengths of many organic acids [3] and many organic bases [4] have been previously correlated with the σᵣ, σᵣm, σᵣ, and σᵣt substituent constants.

Table I. Previously determined acidity constants for protonated ethers, R₂OH⁺.

<table>
<thead>
<tr>
<th>ROR'</th>
<th>pKₐ⁺ References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>1.80</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.08; 2.04</td>
</tr>
<tr>
<td>Me₂O</td>
<td>2.47; 2.52</td>
</tr>
<tr>
<td>Et₂O</td>
<td>3.83</td>
</tr>
<tr>
<td>MeOEt</td>
<td>4.13</td>
</tr>
<tr>
<td>MeO-n-Pr</td>
<td>2.60; 3.82</td>
</tr>
<tr>
<td>MeO-t-Pr</td>
<td>3.79</td>
</tr>
<tr>
<td>MeO-Bu</td>
<td>3.50</td>
</tr>
<tr>
<td>MeO-n-Bu</td>
<td>2.89</td>
</tr>
<tr>
<td>n-Pr₂O</td>
<td>4.40</td>
</tr>
<tr>
<td>i-Pr₂O</td>
<td>4.30</td>
</tr>
<tr>
<td>cy-C₅H₉O</td>
<td>2.08</td>
</tr>
<tr>
<td>cy-C₅H₉O₂</td>
<td>3.22; 1.58</td>
</tr>
<tr>
<td>MeOCH₃</td>
<td>2.79</td>
</tr>
<tr>
<td>MeO₂F</td>
<td>6.54</td>
</tr>
<tr>
<td>EtO₂F</td>
<td>6.44</td>
</tr>
<tr>
<td>n-PrO₂F</td>
<td>6.40</td>
</tr>
<tr>
<td>i-PrO₂F</td>
<td>5.80</td>
</tr>
<tr>
<td>s-BuO₂F</td>
<td>5.36</td>
</tr>
</tbody>
</table>

* References [1] and [2] should be considered as Parts I and II.

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In regard to the ethers [5a] the following pKₐ⁺ values were previously determined for diethyl ether: —3.50 [5b] by techniques involving distribution between solvents; —4.1 [6] by titration with perchloric acid in acetic acid; and —2.42 [7a] and —2.38 [7b] obtained from acid-base equilibria in aqueous sulfuric acid at 25 °C. Table I presents a summary of experimental values of pKₐ⁺'s for various ethers reported in the literature.

It has been shown that gas phase proton affinities of alcohols [8] and ethers [8, 9], regarded as intrinsic basicities, invariably follow the inductive order of the alkyl groups, the order being R₂O > ROH > HOH.

In solution or with a bulk solvent, however, the orders have often been found to be reversed or interchanged among the ethers, alcohols, and water: and also within a set of alcohols or ethers. This might be expected upon consideration of the many complicating factors in solution which may mask the intrinsic basicity to varying degrees, such as dielectric constant of the solvent, dipole-dipole interactions, polarizabilities between molecules, specific solvation and steric effects of anions, cations, and neutral molecules.

In the case of alcohols [10], it has been found that the gas phase acidities follow a trend opposite to that observed for solution, but the same trend as the solution basicities. Recent quantum mechanical calculations [11] have been used to estimate total energies of the neutral, protonated, and deprotonated molecules with the result that they have been able to reproduce the known orderings of gas phase proton affinities. It appears [11, 12] that methyl substitution makes possible the stabilization of...
both negative and positive ions relative to the neutral molecule; (CH$_3$OH > H$_2$O in both gas phase acidity and basicity), by providing an extended structure which can be more effectively polarized by both cationic and anionic centers.

The solubility of gaseous HCl in pure alcohols (moles HCl/moles of ROH) has been accurately measured [23] at 10 °C and it was concluded by the experimenters that, qualitatively, the solubility follows the inductive order with respect to basicity: Me$_2$COH > CH$_3$OH > ClCH$_2$CH$_2$OH. It would appear, therefore, that the HCl solubility data are actually representative of the basicity of the alcohols and are comparable to the intrinsic and theoretical ordering from their gas phase proton affinities.

Conductance studies [24] on these systems have shown that the interaction is predominately one of proton transfer since the solutions of HCl in the relative basicity parameter, $\beta$, has been defined

$$\beta = \frac{S_{ROH}}{S_{HOH}} - 1$$

where the S’s are the experimental solubilities of HCl in various pure alcohols and in water. It was shown that $\beta$ is a linear function of the ionization potentials of the alcohols (including water as the parent alcohol). Therefore

$$\beta = \log \frac{K_{BH^+}(H_2O)}{K_{BH^+}(ROH)}$$

or

$$pK_{BH^+}(ROH) = pK_{BH^+}(HOH) + \beta$$

Also [1],

$$pK_{BH^+}(ROH) = 5.73 - 0.727 E_1$$

where $E_1$ is the I.P. of the alcohol. This led [2] to the necessary linear dependence of $\beta$ on both $\sigma^*$ and $\sigma_1$, from which it was deduced [2] that this dependence must be a linear free energy relationship, resulting necessarily in a linear dependence of $pK_{BH^+}(ROH)$ on $\sigma_1$ [2]:

$$pK_{BH^+}(ROH) = pK_{BH^+}(HOH) + \varrho_1 \sigma_1$$

and

$$pK_{BH^+}(ROH) = -3.43 - 26.6 \sigma_1.$$  

It is seen from Eqs (2b) and (4a) that $\beta = \varrho_1 \sigma_1 = \pi_1$.

From these interrelated relationships, it is seen that the classical inductive order of alcohol basicities is, indeed, followed, and excellent quantitative agreement for CH$_3$OH ($-2.18$, identical with the experimental Raman value [19]), and for EtOH ($-1.93$) [7b] was obtained [2]. The calculated $pK_{BH^+}$ values for alcohols were found [1, 2] to fall within the range $-4.3$ for Et$_2$C-CH$_2$OH to $-1.5$ for t-BuOH when H$_2$O$^+$ was taken as the standard with $pK_{BH^+} = -3.43$. Water, of course, is the most important solvent in chemistry, and yet surprisingly little is known about its behavior as a base, particularly insofar as definitive quantitative data are concerned. For example, the $pK_{BH^+}$ of H$_2$O$^+$ has been estimated variously as $-1.8$ [13], $-2.35$ [14], $-3.43$ [15], $-5.9$ [16] and $-6.66$ [17].

**Calculation of the Basicity Constants for Ethers**

The basicity constants $pK_{BH^+}$ for ethers are defined for the reaction

$$R_2O + H_3O^+ = R_2^+OH + H_2O,$$

and are, of course, identical with the “hydrolysis” constants of the conjugate acids R$_2$OH$^+$ of the ethers.

If we have an absolute value for any one of the K’s of the ethers or water, we are in a position to establish a quantitative scale of K’s for the entire series of compounds. It is obvious from Table I that the values for the ethers are not known with any reasonable degree of certainty, and the values for water are widely disparate. We may therefore select one of the values for H$_2$O$^+$ upon which to construct the scale. The value decided upon, as in previous papers on the $pK_{BH^+}$ of the alcohols [1, 2], is $-3.43$ [15] for $pK_{BH^+}$ of H$_2$O$^+$, since this was obtained by what appears to be a valid experimental procedure and it is, incidentally, the median (and nearly the mean) value of the five values quoted above.

Using the solubility data [23] for HCl in pure ethers at 10 °C, given in column 3 of Table II, and applying Eq. (1), we have calculated the $\beta$ values for a considerable number of ethers, as shown in column 4 of Table II.

Figure 1 shows a plot of these $\beta$ values vs the inductive substituent constants [25, 26], $\Sigma_1$, taken from column 5 of Table II*. It is seen that a good correlation exists, the equation for the regression being:

$$\beta_{R_2O} = \beta_{H_2O} + \varrho_1 \Sigma_1.$$  

* The $\sigma_1$ values used are given in Table IV.
Table II. Solubility of HCl in various ethers; their gas phase I.P.’s and $\Sigma\sigma_1(R)$ values, and calculated “relative basicity parameters”.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ROR'</th>
<th>$S_a$ (mol HCl/mol R$_2$O)</th>
<th>$\beta_{\text{rel}}$</th>
<th>$\Sigma\sigma_1$</th>
<th>E$_1$ (eV)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HOH</td>
<td>0.380$^b$</td>
<td>0</td>
<td>0</td>
<td>12.59</td>
</tr>
<tr>
<td>2</td>
<td>Me$_2$O</td>
<td>--$^c$</td>
<td>0</td>
<td>--</td>
<td>10.00</td>
</tr>
<tr>
<td>3</td>
<td>Et$_2$O</td>
<td>0.892</td>
<td>1.35</td>
<td>--</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>MeOEt</td>
<td>--$^c$</td>
<td>0</td>
<td>--</td>
<td>9.81</td>
</tr>
<tr>
<td>5</td>
<td>MeO-n-Pr</td>
<td>0.896</td>
<td>1.36</td>
<td>--</td>
<td>9.27</td>
</tr>
<tr>
<td>6</td>
<td>MeO-i-Pr</td>
<td>--$^c$</td>
<td>0</td>
<td>--</td>
<td>9.27</td>
</tr>
<tr>
<td>7</td>
<td>MeO-n-Bu</td>
<td>0.788</td>
<td>1.07</td>
<td>0.092</td>
<td>9.20</td>
</tr>
<tr>
<td>8</td>
<td>MeO-i-Bu</td>
<td>--$^c$</td>
<td>0</td>
<td>--</td>
<td>9.13</td>
</tr>
<tr>
<td>9</td>
<td>n-Pr$_2$O</td>
<td>0.930</td>
<td>1.45</td>
<td>0.114</td>
<td>9.27</td>
</tr>
<tr>
<td>10</td>
<td>i-Pr$_2$O</td>
<td>0.978</td>
<td>1.58</td>
<td>0.130</td>
<td>9.20</td>
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<td>11</td>
<td>EtO-n-Bu</td>
<td>1.05</td>
<td>1.76</td>
<td>0.126</td>
<td>9.20</td>
</tr>
<tr>
<td>12</td>
<td>MeO-n-Hx</td>
<td>0.900</td>
<td>1.27</td>
<td>0.107</td>
<td>9.20</td>
</tr>
<tr>
<td>13</td>
<td>n-PrO-n-Bu</td>
<td>1.02</td>
<td>1.69</td>
<td>0.124</td>
<td>9.20</td>
</tr>
<tr>
<td>14</td>
<td>n-Bu$_2$O</td>
<td>0.890</td>
<td>1.34</td>
<td>--</td>
<td>8.94</td>
</tr>
<tr>
<td>15</td>
<td>t-Bu$_2$O</td>
<td>--$^c$</td>
<td>0</td>
<td>--</td>
<td>8.94</td>
</tr>
<tr>
<td>16</td>
<td>n-AnthO</td>
<td>0.914</td>
<td>1.40</td>
<td>0.128</td>
<td>9.42</td>
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<tr>
<td>17</td>
<td>cy-C$_5$H$_4$O</td>
<td>1.38</td>
<td>2.63</td>
<td>--</td>
<td>9.13</td>
</tr>
<tr>
<td>18</td>
<td>cy-C$_6$H$_5$O</td>
<td>1.046</td>
<td>1.75</td>
<td>--</td>
<td>9.25</td>
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<td>19</td>
<td>cy-C$_6$H$_5$O</td>
<td>1.26</td>
<td>2.32</td>
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<td>9.25</td>
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<tr>
<td>21</td>
<td>PhOMe</td>
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<td>0.58</td>
<td>+0.054</td>
<td>8.20</td>
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<tr>
<td>22</td>
<td>PhOEt</td>
<td>0.180</td>
<td>0.53</td>
<td>+0.045</td>
<td>8.20</td>
</tr>
<tr>
<td>23</td>
<td>PhCH$_2$OEt</td>
<td>0.728</td>
<td>0.92</td>
<td>--</td>
<td>8.08</td>
</tr>
<tr>
<td>24</td>
<td>PhCH$_2$O-n-Bu</td>
<td>0.681</td>
<td>0.79</td>
<td>--</td>
<td>8.08</td>
</tr>
<tr>
<td>25</td>
<td>(PhCH$_2$)$_2$O</td>
<td>0.540</td>
<td>0.42</td>
<td>--</td>
<td>8.08</td>
</tr>
<tr>
<td>26</td>
<td>Ph$_2$O</td>
<td>0.088</td>
<td>0.77</td>
<td>+0.20</td>
<td>8.08</td>
</tr>
<tr>
<td>27</td>
<td>(ClCH$_2$CH$_2$)$_2$O</td>
<td>0.209</td>
<td>0.45</td>
<td>--</td>
<td>8.08</td>
</tr>
<tr>
<td>28</td>
<td>(CF$_3$CH$_2$)$_2$O</td>
<td>0.276</td>
<td>0.27</td>
<td>--</td>
<td>8.08</td>
</tr>
</tbody>
</table>

$^a$ Ref. [23]; $^b$ ref. [42]; $^c$ solubility data not available; $^d$ from Eq. (1); $^e$ from Table IV; $^f$ ref. [28]; $^g$ $\sigma_1$ not available; $^h$ $E_1$ not available.

Fig. 1. The “relative basicity parameter” as a function of $\Sigma\sigma_1(R)$.

Since $\beta_{\text{H}_2\text{O}} = 0$ and the slope is found to be $-11.79$, we have therefore,

$$\beta_{\text{R}_2\text{O}} = -11.79 \Sigma\sigma_1.$$  \hspace{1cm} (5b)

Returning now to Eq. (2b) and again assuming $-3.43$ for $pK_{\text{BH}^+(\text{H}_2\text{O})}$, the $pK_{\text{BH}^+}$'s of the ethers may be calculated. These are shown in column 3 of Table III. It should be noted, as might be anticipated from previous work on alcohols in solution, that the $pK_{\text{BH}^+}$'s for ethers are somewhat more negative than those for the alcohols, indicating, in general, a lesser basicity.

Figure 2 is a plot of the newly calculated $pK_{\text{BH}}$'s versus $\Sigma\sigma_1$, which indicates a good correlation, the equation for which is:
Table III. Calculated pKBH\(^+\) values for the ethers from Eqs. (2b), (6b) and (8b).

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>ROR'</th>
<th>Eq. (2b)</th>
<th>Eq. (6b)</th>
<th>Eq. (8b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HOH</td>
<td>3.43</td>
<td>3.43</td>
<td>3.44</td>
</tr>
<tr>
<td>2</td>
<td>MeO</td>
<td>2.48</td>
<td>2.34</td>
<td>2.64</td>
</tr>
<tr>
<td>3</td>
<td>EtO</td>
<td>2.08</td>
<td>2.18</td>
<td>2.01</td>
</tr>
<tr>
<td>4</td>
<td>MeOEt</td>
<td>—</td>
<td>2.21</td>
<td>2.15</td>
</tr>
<tr>
<td>5</td>
<td>MeO-n-Pr</td>
<td>2.07</td>
<td>2.17</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>MeO-i-Pr</td>
<td>—</td>
<td>2.12</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>MeO-n-Bu</td>
<td>2.36</td>
<td>2.14</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>MeO-t-Bu</td>
<td>—</td>
<td>2.01</td>
<td>—</td>
</tr>
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<td>9</td>
<td>n-PrO</td>
<td>1.98</td>
<td>1.99</td>
<td>1.90</td>
</tr>
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<td>i-PrO</td>
<td>1.85</td>
<td>1.90</td>
<td>1.87</td>
</tr>
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<td>11</td>
<td>EtO-s-Bu</td>
<td>1.67</td>
<td>1.94</td>
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<td>MeO-n-Hx</td>
<td>2.16</td>
<td>2.17</td>
<td>—</td>
</tr>
<tr>
<td>13</td>
<td>n-PrO-n-Bu</td>
<td>1.74</td>
<td>1.97</td>
<td>—</td>
</tr>
<tr>
<td>14</td>
<td>n-BuO</td>
<td>2.09</td>
<td>1.94</td>
<td>1.86</td>
</tr>
<tr>
<td>15</td>
<td>t-BuO</td>
<td>—</td>
<td>1.88</td>
<td>1.75</td>
</tr>
<tr>
<td>16</td>
<td>n-AmO</td>
<td>2.03</td>
<td>1.92</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>cy-C(_2)H(_3)O</td>
<td>0.80</td>
<td>—</td>
<td>b</td>
</tr>
<tr>
<td>18</td>
<td>cy-C(_2)H(_4)O(_2)</td>
<td>1.68</td>
<td>—</td>
<td>b</td>
</tr>
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<td>b</td>
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<tr>
<td>21</td>
<td>PO Me</td>
<td>4.01</td>
<td>4.07</td>
<td>—</td>
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<tr>
<td>22</td>
<td>POEt</td>
<td>3.96</td>
<td>3.96</td>
<td>—</td>
</tr>
<tr>
<td>23</td>
<td>PhCH(_2)OEt</td>
<td>2.51</td>
<td>2.47</td>
<td>—</td>
</tr>
<tr>
<td>24</td>
<td>PhCH(_2)n-Bu</td>
<td>2.45</td>
<td>2.42</td>
<td>—</td>
</tr>
<tr>
<td>25</td>
<td>(PhCH(_2))(_2)O</td>
<td>3.01</td>
<td>2.82</td>
<td>—</td>
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<tr>
<td>26</td>
<td>PhO</td>
<td>4.20</td>
<td>5.79</td>
<td>—</td>
</tr>
<tr>
<td>27</td>
<td>(ClCH(_2))(_2)CH(_2)O</td>
<td>3.88</td>
<td>3.19</td>
<td>—</td>
</tr>
<tr>
<td>28</td>
<td>(ClCH(_2))(_2)CH(_2)CH(_2)O</td>
<td>6.73</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>(Cl(CH(_2))(_2))O</td>
<td>3.70</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) HCl solubility data not available; \(^b\) \(\sigma\) values not available; \(^c\) \(E_i\) not available; \(^d\) electron not lost from O atom on ionization; \(^e\) solubility questionable since THF is so readily cleaved by acids.

\[ p_{KBH^+}(R_2O) = p_{KBH^+}(H_2O) + \varphi_1\Sigma\sigma_1 \]  

(6a)

and

\[ p_{KBH^+}(R_2O) = -3.43 - 11.79 \Sigma\sigma_1 \]  

(6b)

The values calculated from Eq. (6b) are shown in column 4 of Table III.

On comparing the new \(p_{KBH^+}\) values from Eqs. (2b) and (6b) with those previously determined and shown in Table I, it is seen that the latter are, in general, more negative.

Relation of Basicity Constants to Ionization Potentials

It has previously been shown that the ionization potentials (\(E_i\)) of the ethers [27a], as well as the alcohols [27b], are also an excellent linear function of \(\Sigma\sigma_1\):

\[ E_i(R_2O) = E_i(H_2O) + a_1\Sigma\sigma_1 = 12.59 + 28.0\Sigma\sigma_1 \]  

(7)

and this relation has also been demonstrated for a wide variety of homologous series of organic [29] and organometallic compounds [30]. It has been consistently emphasized throughout the aforementioned series of papers on molecular ionization potentials that the lower the \(E_i\), the greater the electron density at the site of ionization, and consequently the greater basicity at the site. This is most obvious in the case of amines [31]. Therefore, the newly obtained \(p_{KBH^+}\) values for ethers might also be expected to be a linear function of \(E_i(R_2O)\) (given in the last column of Table II). That such is, indeed, the case is immediately evident from Fig. 3. The equation for this correlation is:

\[ p_{KBH^+}(R_2O) = b + a_1E_i(R_2O) \]  

(8a)

and

\[ p_{KBH^+}(R_2O) = 2.42 - 0.466E_i(R_2O) \]  

(8b)

The basicity constants for the ethers calculated from Eq. (8b) are given in the last column of Table III.

Relation Between \(p_{KBH^+}\) and Gas Phase Basicities

Accurate gas phase basicities have recently become available [8, 9], and it would seem reasonable that these too should be a linear function of our newly calculated solution basicities. The gas phase basicities are often given in terms of \(-\delta R_j^0\) values [32], which are the measured differences in the free energy change accompanying the reaction of some protonated reference base in the gas phase with the base under consideration, as represented by the equation:

\[ BH^+ + B' = B + B'H^+ \]

The data for several ethers with \(NH_3\) as the reference base are given in Table V and the corresponding plot of \(p_{KBH^+}\) vs \(-\delta R_j^0\) is shown in Fig. 4,
Conductance of HCl/R_2O Solutions

Concerning the question of proton transfer versus hydrogen-bond formation for the ethers, it should be pointed out that conductivity studies on the saturated HCl/R_2O solutions indicate a small, but finite conductivity [23]. For example, \( A_0 \) for HCl/Et_2O = 5.3 \times 10^{-4} mho cm^2-equiv. [33].

It is interesting to note that the inverse solubility studies, i.e., solid ethers in liquid HCl at —95 °C, have also been made [34], with the following results: although ice is practically insoluble in liquid HCl, the simple ethers are quite soluble and result in basic solutions, indicating the production of excess HCl—by removal of protons from the solvent [34]. The phase diagram of Et_2O in HCl shows a 1:1 compound formed (m.p. = —92 °C) which was interpreted as the oxonium salt [35]. Raman spectral studies of Me_2O • HBr and Me_2O • DCI were interpreted [36] as definitely proving the presence of Me_2OH^+ although Me_2^+ • HCl was considered a borderline case, which could be predominantly an H-bridged complex. Conductance experiments on these systems show that highly conducting solutions result [37] with all the simple ethers in liquid HCl, and titration of the solution with BCl_3 give generally sharp end-points indicating in all cases a 1:1 complex [38], R_2OH^+ • Cl^−. The equivalent conductances were determined [38] and found to be: Et_2OH^+ • Cl^−, \( A = 10 \) mho cm^2-equiv. at \( C = 1.0 \) M; Me_2OH^+ • Cl^−, \( A = 0.43 \) at \( C = 0.26 \) M; Me(Ph)OH^+ • Cl^−, \( A = 0.021 \) at \( C = 0.32 \) M; CF_3OH^+ • Cl^−, \( A = 1.7 \times 10^{-3} \) at \( C = 0.38 \) M. By way of comparison with Me_2O, methanol in liquid HCl has a considerably lower conductance [38] (\( A = 0.13 \) at \( C = 0.51 \) M), and in this case the presence of MeOH^+ is well established. Thus from these studies of ethers in liquid HCl, we find the same general basicity order as found in the gas phase proton affinities: R_2O > ROH > H_2O; but in the case of HCl in ethers the general order is ROH > R_2O > H_2O, and, as mentioned above, this different ordering is due almost certainly to the large difference in dielectric constant between the alcohols and ethers.

All in all, then, there can be little doubt that the HCl/R_2O solutions do, indeed, deal with a proton transfer reaction, though the weak acids F−•OH and O_2NΦNH_2 in ether solvents undoubtedly are too weak for H^+ transfer, and are therefore H-bonded to the ether oxygen, as has been assumed by Taft [39] and by Kainlet [40].

The processes under consideration may be represented as follows [41]:

\[
S + HA \xrightleftharpoons[K_1]{K_2} [S...H-A] \xrightarrow{\text{(ionization)}} \text{SH}^+...A^- \xrightarrow{\text{(H-bridged)}} \text{SH}^+_{\text{solv.}} + A^-_{\text{solv.}}
\]
where \( S \) is a basic solvent molecule and \( HA \) an acidic solute. The first two equilibria occur to an extent determined by the basicity of the base and the acidity of the acid, whereas the third equilibrium takes place to an extent determined, of course, largely by the dielectric constant of the solvent, and by its ability of solvate the dissociated cations and anions. For solvents with dielectric [42] constants > 40, the product \( K_1K_2K_3 \) can be obtained with little error from conductivity data [41], simply from the ratio \( \lambda / \rho \). If the acid and base are both very weak, the reaction will proceed only as far as \( K_1 \); if either the acid or base is sufficiently strong, the reaction will proceed at least to \( K_2 \); and if the dielectric constant is relatively high, the reaction will proceed to \( K_3 \). In a medium of very low dielectric constant (\( \varepsilon = 5.02 \), but \( \text{MeOH} \), \( \varepsilon = 32.6 \), both at 25 °C), a non-conducting or slightly conducting solution of ion pairs may result (as with the ethers), even if considerable ionization has taken place [41].

**Conclusions**

Contrary to the generally accepted view [43], therefore, we are of the opinion that because of the high acidity of HCl that the HCl/ROR solutions consist, to a considerable extent, of oxonium salts \( \text{R}_2\text{O}^+ \text{HCl}^- \) [44]. Regardless of which physical measurement is taken as an evaluation of hydrogen-bonding acceptor ability or basicity, it is interesting to note that the same order of basicity of the ethers persists in the gas phase [8]; in HCl/ROR solutions; in aqueous HCl solutions of ethers [43]; in \( p\)-FC\(_6\)H\(_4\)OH/CCL\(_4\) solutions [39]; in \( p\)-NO\(_2\)C\(_6\)H\(_4\)OH/R\(_2\)O solutions [40, 45]); and in \( p\)-NO\(_2\)-C\(_6\)H\(_4\)-NH\(_2\) and C\(_6\)H\(_4\)NEt\(_2\)/R\(_2\)O solutions [40].

Undoubtedly, the reason for the generally lower solubility of HCl in the ethers as compared to the corresponding alcohols is due to their much lower dielectric constants as a group. Despite the higher intrinsic basicity of the ethers the resulting \( p\)K\(_{bhr}^\dagger \)'s as calculated in this paper, reflect this difference, and therefore show a reversed order of basicity compared to gas phase protonation studies where \( \text{R}_2\text{O} > \text{ROH} > \text{H}_2\text{O} \). In the present paper, therefore, we have found the general order of basicity in solution to be \( \text{ROH} > \text{R}_2\text{O} > \text{H}_2\text{O} \), in agreement with all previous estimates, both qualitative and quantitative. Within the ether series itself, however, we find a strict ordering in agreement with the alkyl inductive effect [26].

In the next paper of this series we shall discuss the relations between the \( p\)K\(_{bhr}\) of ethers and alcohols and various H-bond acceptor parameters, such as the \( p\)K\(_{hrh}\) of Taft [39], the \(-\Delta\rho\) of Kamlet [40], and Taft's H-bonded ion-pair parameter [46].
[26] a) L. S. Levitt, Z. Naturf. 34b, 81 (1979);
[27] a) B. W. Levitt and L. S. Levitt, Experientia 26, 1183 (1970);
   b) ibid. 1964, 201, 606.