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CALCULATION OF THE BASIC IONIZATION CONSTANTS OF ALCOHOLS FROM THE POLAR AND INDUCTIVE SUBSTITUENT CONSTANTS

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The acid strengths of organic acids[1] and the base strengths of organic bases[2] have been correlated, in considerable detail, with the σ_p, σ_m, σ^*, and σ_I substituent constants.

The pK_{BH^+} values for alkylammonium ions, $R\overset{+}{N}H_3$, and alkylphosphonium ions, $R\overset{+}{P}H_3$, which are accurately known, have been correlated with the substituent constants for the various R-groups.[3,4]

The *acid* ionization constants of the aliphatic alcohols have been determined by a conductivity procedure[5] in aqueous solution for the reaction:

$$RCH_2OH + H_2O \rightleftharpoons RCH_2O^- + H_3O^+.$$

It was found[5] that $pK_a = 15{\cdot}9 - 1{\cdot}42\,\sigma^*$ for the case where RCH_2OH is a substituted MeOH.

The *basicity* constants,[6] pK_{BH^+}, for the alcohols, defined for the reaction

$$ROH + H_3O^+ \rightleftharpoons ROH_2^+ + H_2O$$

have recently[7] been related to the ionization potentials of the alcohols, where it was determined that

$$pK_{BH^+} = +5{\cdot}73 - 0{\cdot}727\,E_I. \tag{1}$$

The pK_{BH^+} values for various alcohols have not previously been correlated with the substituent constants because the pK's were known only to an approximate order of magnitude. Thus, the pK_{BH^+} values were thought[8] to fall within the range -2 to -4. A later study[9] of CH_3OH in aqueous H_2SO_4 using Raman spectroscopy yielded a value of $-2{\cdot}2$ for the pK_{BH^+} of $CH_3\overset{+}{O}H_2$, but the method was judged[9] unreliable for EtOH, i-PrOH, and t-BuOH by the experimenters. Subsequently, two investigations of the basicity of alcohols determined by solvent extraction[10] and by their solubilities[11] in varying concentrations of aqueous H_2SO_4, were carried out. The following pK_{BH^+} values were arrived at: MeOH[11] ($-2{\cdot}5$); n-BuOH[10,11] ($-2{\cdot}3$); s-BuOH[10,11] ($-2{\cdot}2$); and t-BuOH[10,11] ($-2{\cdot}6$). It was concluded[10] that the effect of a change in structure of the R-group on the basicity of the alcohol is probably too small to be resolved by these experimental methods. A still more recent Raman spectral study[12] has yielded pK values much more negative (by about 2·5 units) than those obtained previously. However, Nixon and Bursey,[13] by means of ion cyclotron resonance determinations of the relative NO_2^+ ion affinities of gas phase alcohols, have arrived at the following basicity order: $H_2O < MeOH < EtOH < i\text{-}PrOH$; $EtOH < n\text{-}PrOH < n\text{-}BuOH$. This sequence follows the trend expected on the basis of the inductive effect, though the authors prefer to relate the observed order to "substituent polarizability".[14] Little is known about the behavior of water as a base,[8] particularly insofar as definitive quantitative data are concerned: the pK_{BH^+} of $H_3\overset{+}{O}$ has been estimated in various ways as $-1{\cdot}80$,[15] $-2{\cdot}3$,[16] $-3{\cdot}43$,[17] $-5{\cdot}9$,[18] and $-6{\cdot}66$.[19]

Gerrard and Macklen[20] have measured the solubility of anhydrous HCl in various pure alcohol solvents and have found, in general, that the alcohols with electron-releasing R-groups absorb larger quantities of gaseous HCl than those which have electron-attracting R-groups. This behaviour was interpreted, qualitatively, in terms of the relative electron densities at the oxygen atom. For example, the magnitude of the solubility of HCl at 10°, (in moles HCl/mole ROH), is found to be in the following order: $(CH_3)_3COH \gg CH_3OH \gg Cl_3CCH_2OH$.

One may legitimately raise the question whether the solubility of the hydrogen halide in the alcohol (at a fixed temperature) actually constitutes a measure of the basicity of the alcohol; or rather does it represent a combination, in varying proportions, of the base strength, hydrogen-bonding interactions between solute and solvent molecules, dipole–dipole interactions between solute and solvent, polarizability effects, and extraneous ionic field effects.[21] Conductance measurements[22] on these systems have shown that the interaction is predominantly one of proton transfer since solutions of HCl in alcohols produce considerable conductivity, the Λ_0 in the case of HCl in MeOH approaching that of HCl in H_2O.[23]

We have reported[7] in a recent paper that these HCl solubilities, S, can be quantitatively related to the ionization energies of the alcohol by means of a "relative basicity parameter", β, referred to H_2O as the standard, where

$$\beta = (S_{ROH}/S_{HOH}) - 1 \tag{2}$$

It was shown, in fact, that β is a linear function of the ionization potentials of the alcohols.[7]

It would appear, therefore, that the HCl solubility data *are* actually representative of the basicity of alcohols, and should also, therefore, correlate with the polar and inductive substituent constants, σ^* and σ_I. Such, indeed, we find to be the case. Table 1 presents the solubility data, and the σ^*,[24] and σ_I[25] values for the corresponding R-group of the alcohol (or water). In order to interpolate water into the series of alcohols, we have calculated the solubility of gaseous HCl in H_2O at 10° from data in the literature.[26] Also included in Table 1 are the "relative basicity parameters", β. The data are presented graphically in Fig 1 where the β values are plotted as a function of σ^*, and it is easily seen that an excellent correlation exists. Note that water has been included as a special case of the simplest alcohol and it fits right into the correlation.

It is common knowledge that the Hammett and the Taft equations are linear free-energy relationships[28] and, as such, involve log K or log k functions. It is apparent,

TABLE 1

ROH	S HCl Solubility (mol HCl/mol ROH)	β "Relative basicity parameters"	σ^*	σ_I
HOH	0·380[a]	0	+0·49	0
MeOH	0·857	1·26	0	−0·046
EtOH	0·950	1·50	−0·10	−0·055
n-PrOH	0·956	1·52	−0·12	−0·058
n-BuOH	0·964	1·53	−0·13	−0·060[c]
i-PrOH	1·030	1·71	−0·19	−0·064
t-BuOH	1·115	1·93	−0·30	−0·074
cy-$C_6H_{11}OH$	1·030	1·71	−0·15	−0·027[e]
$ClCH_2CH_2OH$	0·550	0·45	+0·38	[d]
Cl_3CCH_2OH	0·087	−0·77	+0·90[b]	[d]
F_3CCH_2OH	0·060	−0·84	+0·92	[d]

[a] Calculated from solubility data in Ref. 26.
[b] Estimate.
[c] Newer value suggested in Ref. 27.
[d] Reliable value not available.
[e] The σ_I value for cyclohexyl is obviously in error and is not used in the plots.

therefore, that our "relative basicity parameter"[29] must be essentially a ratio log (K_1/K_2). We have decided (as described previously)[7] to select arbitrarily one of the values for $H_3\overset{+}{O}$ upon which to construct a pK_{BH^+} scale for alcohols and water. The value selected was that of Hammett and Deyrup,[17] −3·43, for pK_{BH^+} of $H_3\overset{+}{O}$, 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 quoted above. The

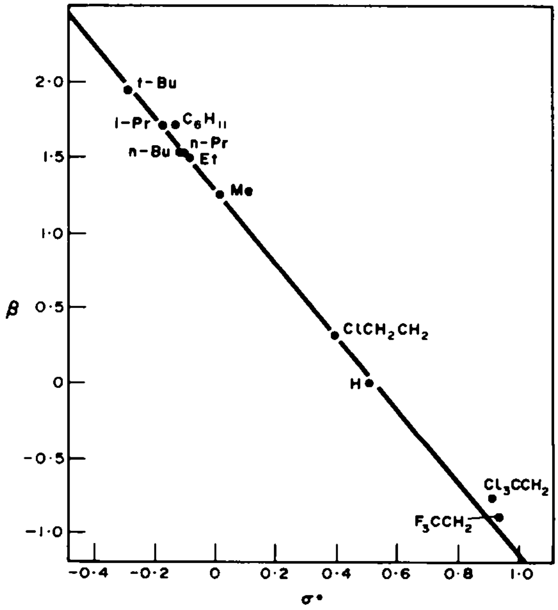

FIG. 1. A plot of the relative basicity parameter, β, against the polar substituent constants, σ^*

relation of Fig 1 makes it apparent that the β values[29] are linear in σ^*, and, therefore, we must have a linear free-energy relationship.[7, 28] Thus,

$$\beta = \log\left[\frac{K_{BH^+}(H_2O)}{K_{BH^+}(ROH)}\right] \tag{3}$$

from which

$$pK_{BH^+}(ROH) = pK_{BH^+}(H_2O) + \beta = -3{\cdot}43 + \beta \tag{4}$$

In Table 2, the pK_{BH^+} values calculated from Eq. (4) are presented.

In Fig 2 we have plotted the new pK_{BH^+} values for the alcohols versus the corresponding σ^* values from Table 1. The excellent correlation would appear to justify the assumptions and the procedures adopted here. It should be noted that our pK_{BH^+} value for $CH_3\overset{+}{O}H_2$ (−2·17) is in close agreement with the older Raman experimental[9] value, −2·2, in fair agreement with the H_2SO_4 solubility value[10, 11] of −2·5. but in poor agreement with the newer Raman value[12] of −4·86. The equation for the straight line of Fig 2 relating the pK_{BH^+} of $R\overset{+}{O}H_2$ to the polar substituent constants is given by:

TABLE 2

Alcohol	Calculated pK_{BH^+} values for alcohols pK_{BH^+} From β (Eq. 4)	From σ^* (Eq. 6)	From σ_I (Eq. 8)	From E_I (Eq. 1)
HOH	−3·43[a]	−3·33	−3·43	−3·44
MeOH	−2·17	−2·18	−2·21	−2·17
EtOH	−1·93	−1·94	−1·97	−1·92
n-PrOH	−1·91	−1·90	−1·89	−1·70
n-BuOH	−1·90	−1·87	−1·83	−1·68
i-PrOH	−1·72	−1·73	−1·73	−1·67
t-BuOH	−1·49	−1·47	−1·46	−1·49
cy-$C_6H_{11}OH$	−1·72	−1·82	[b]	[b]
$ClCH_2CH_2OH$	−2·98	−3·08	[b]	[b]
Cl_3CCH_2OH	−4·20	−4·30	[b]	[b]
F_3CCH_2OH	−4·27	−4·35	[b]	[b]

[a] Standard.

[b] Not available.

$$pK_{BH^+} = -2{\cdot}18 + \rho^*\sigma^* \tag{5}$$

The slope of the line, ρ^*, is found to be −2·36 and therefore:

$$pK_{BH^+} = -2{\cdot}18 - 2{\cdot}36\,\sigma^*. \tag{6}$$

The reaction constant, ρ^*, may be compared with those obtained for $R\overset{+}{N}H_3$ as an acid[3] ($\rho^* = -3{\cdot}14$) and also for $R\overset{+}{P}H_3$ ($\rho^* = -2{\cdot}64$).[4] Also included in Table 2 are the pK_{BH^+} values calculated from Eq. (6) and from the I.P. (Eq. 1).[7] The agreement is seen to be quite good.

Should a different value for the pK_{BH^+} of H_3O^+ be adopted, this relation should still be valid, and the only change would be a shift in the line of Fig 2 up or down, correspondingly.

The high degree of correlation between the pK_{BH^+}'s of the alcohols and σ^* should likewise be true for pK_{BH^+} and σ_I values for alkyl groups. Using the R-groups whose σ_I's are known to at least two figures,[25] we have constructed the other plot in Fig 2 which, again, gives an excellent correlation between the calculated pK_{BH^+} and the inductive substituent constants. The equation for this correlation line is

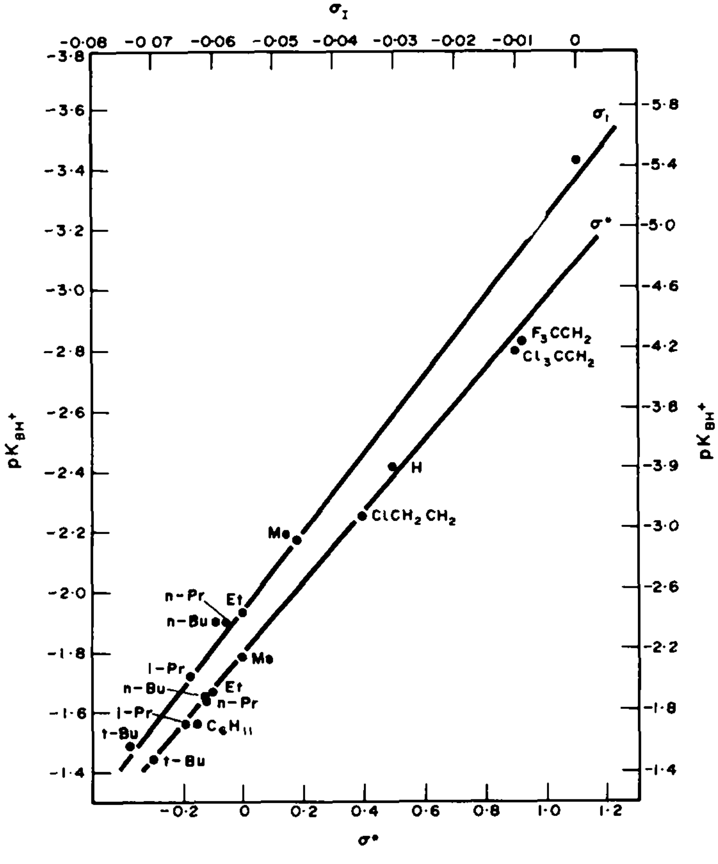

FIG 2. Plots of the calculated pK_{BH^+} versus σ^* and the inductive substituent constant, σ_I. The pK_{BH^+} scale to the left pertains to the σ^* plot and that to the right to the σ_I plot

$$pK_{BH^+}\,(ROH) = pK_{BH^+}\,(H_2O) + \rho_I\sigma_I \tag{7}$$

The slope, ρ_I, is found to be $-26{\cdot}6$ and therefore:

$$pK_{BH^+}\,(ROH) = -3{\cdot}43 - 26{\cdot}6\,\sigma_I \tag{8}$$

Thus, the value for the inductive reaction constant is somewhat higher than those observed[30] for $R\overset{+}{N}H_3$ ($\rho_I = -20{\cdot}6$), for $R\overset{+}{N}H_2Et$ ($\rho_I = -20{\cdot}2$) and for N-substituted guanidinium ions, $RNH\text{-}C(NH_2)_2^+$ ($\rho_I = -24{\cdot}1$). The large value obtained for the inductive reaction constant indicates that the basicity of the set of alcohols correlated here through the new pK_{BH^+} values is extremely susceptible to small changes in the inductive properties of the attached alkyl substituent on the oxygen of the alcohol molecule.

As we noted in footnote (*e*) of Table 1, the σ_I value for cyclohexyl must be greatly in error. This is obvious merely on comparing the tabulated values for σ^* for C_6H_{11}- (between n-Bu and i-Pr) with the σ_I value for this group (between H and Me). This observation along with the experimental β value leads to a new and better estimate of $\sigma_I = -0{\cdot}062$ for cy-C_6H_{11}. In similar fashion we estimate the following values of σ_I for the haloalkyl groups: $ClCH_2CH_2$— ($-0{\cdot}015$), Cl_3CCH_2— ($+0{\cdot}031$), and F_3CCH_2— ($+0{\cdot}033$).

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[30] We have recently shown[27] that the ionization potentials of the alcohols are also a linear function of the σ^* and the σ_I values, in accordance with the relation $E_{I(ROH)} = +10{\cdot}8 + 3{\cdot}44\sigma^* = 12{\cdot}6 + 37{\cdot}5\,\sigma_I$. If E_I be eliminated between this Eq. and Eq. (1) one again obtains Eq.'s (6) and (8). It should also be noted, by comparison of Eq.'s (4) and (7), that $\beta = \rho_I\sigma_I$.

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