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Acidity of Alkyl Substituted Alcohols : Are Alkyl Groups Electron-donating or Electron-withdrawing ?

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Abstract : Two important functional group properties, the group electronegativity and hardness, are calculated for a number of alkyl groups. The results indicate that alkyl groups become less electronegative and hard with increasing group size. The calculated properties are used in a study of the inversion of the alkyl alcohol acidity scale when going from aqueous solution to the gas phase. Finally, the Sanderson electronegativity equalization principle using functional group properties is shown to be a valuable tool in describing the charge distribution of these molecular systems.

INTRODUCTION

In describing the effects of structure on chemical reactivity, organic chemists like to use functional group properties (substituent constants) to predict charge transfer between different regions of a molecule. Many of the derived substituent constants result from acid-base equilibria in solution, thus being a measure of the intrinsic properties of the functional group modulated by the solvent. When the acid-base equilibrium is studied in the gas-phase however, the observed acidity and basicity sequences can be traced back to the intrinsic properties of the molecule.

In the gas-phase, a number of well known and "traditional" solution acidity or basicity sequences are inverted [1-5]. Most of these involve alkyl substituted molecules ; well known examples are the acidities of alkyl substituted alcohols or carboxylic acids and the basicities of alkyl amines. In aqueous solution, the acidity or basicity of these systems decreases with increasing alkyl group size : this finding is in accordance with the traditional view of alkyl groups as being electron-releasing. In the gas-phase, the opposite trend occurs, thus giving the impression that alkyl groups act as electron-withdrawing species.

In the past, a number of studies (theoretical and experimental) were dedicated to this apparant anomaly between the behaviour of alkyl groups in solution and in the gas-phase [6-20]. The attention has been focussed mainly on the basicity of the alkyl amines and considerably less studies were devoted to the case of acidity, e.g. the carboxylic acid or alcohol acidity scales. Some differences can however be expected to exist between these two types of systems, e. g. the nature of the charged form in the acid-base equilibrium, bearing a positive charge in case of the amines and a negative charge in the case of the alcohols or the carboxylic acids.

In this paper, two functional group properties, the group electronegativity and hardness are calculated for a number of alkyl groups. The calculated properties are used, together with the Sanderson electronegativity equalization principle [21, 22] and the Pearson Hard and Soft Acids and Bases (HSAB) principle [23], to rationalize the acidity sequences for the alkyl substituted alcohols ROH with R=Me, Et, *n*-Pr, *i*-Pr, *n*-Bu and *t*-Bu, whose solution and gas-phase acidity sequences are opposite, by considering their role in both sides in the acid-base equilibrium.

THEORETICAL BACKGROUND

In Density-functional theory (DFT) [24], the electronegativity χ, commonly known by chemists, is defined as the negative of the partial derivative of the energy E of an atomic or molecular system with respect to the number of electrons N, for a constant external (i.e. due to the nuclei) potential $\upsilon(\underline{r})$ [25] :

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{\upsilon(\underline{r})} \tag{1}$$

Moreover, a proof was given, within this framework, for the long known Sanderson electronegativity equalization principle, which states that when two or more atoms or functional groups, initially different in electronegativity, combine to form a compound, their electronegativities become adjusted to the same intermediate value [21, 22]. This principle has been the basis for a number of methods involving the calculation of molecular charge distributions [26-30].

In the 1960s, Pearson introduced the terms hardness and softness, together with the well-known Hard and Soft Acids and Bases (HSAB) principle. This states that hard acids prefer to bond to hard bases and soft acids to soft bases [23]. Originally based on an empirical classification, Density-functional theory offered the theoretical framework to explicitly calculate the hardness (η) of a chemical species as the second derivative of the energy with respect to the number of electrons [31]:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\underline{r})} \tag{2}$$

This hardness measures the resistance of the chemical species towards charge transfer.

Finally, the softness S is introduced as the inverse of the hardness [32] :

$$S = \frac{1}{2\eta} \tag{3}$$

The simple and straightforward definition of electronegativity and hardness allows one to calculate them in a non-empirical way.

In the past, we obtained group electronegativities and hardnesses, using a finite difference approximation of definitions (1) and (2), considering the N_0, N_0+1 and N_0-1 systems, N_0 being the number of electrons in the reference system, at the same geometry (constant $v(\underline{r})$) for thirty functional groups, frequently occurring in organic molecules [33]. These properties already showed to be very important tools in the interpretation of acidity and basicity sequences [34, 35, 36].

The methodology, outlined in [33], was adopted here to calculate the group electronegativities and hardnesses for a series of alkyl groups R, with R=Me, Et, *n*-Pr, *i*-Pr, *n*-Bu and *t*-Bu . Here, the calculations were performed both at Hartree-Fock (HF) and MP2 through MP4 levels using the 6-31G* basis set whereas in our previous paper, they were performed only for some of these groups at the Hartree-Fock and CISD levels, with the 6-31++G** basis set [37]. It can be shown that the trends for the group electronegativities and hardnesses for the MP and CI level are similar and that, in the case of the alkyl groups, extension of the basis set to a 6-31+G* or a 6-31++G** basis set leaves the sequences for χ and η unchanged. Moreover, extending the basis set with diffuse functions results in an increase in computational time and is not advisable since most of the alkyl groups possess metastable anions [38].

Both the alcohols R-OH and their conjugated bases RO^- were optimized at the Hartree-Fock level with the 6-31+G* basis [39]. Their reactivity in relation to their gas-phase and solution phase acidities was studied using the Molecular Electrostatic Potential (MEP) [40], defined as the interaction energy of the charge distribution (with electron density $\rho(\underline{r})$ and nuclei with charges Z_A and position vectors $\underline{R}_A$) with a unit positive charge (H^+) at a position $\underline{R}$:

$$V(\underline{R}) = \sum_A \frac{Z_A}{|\underline{R}-\underline{R}_A|} - \int \frac{\rho(\underline{r})}{|\underline{r}-\underline{R}|} d\underline{r} \tag{4}$$

Atomic charge distributions were obtained by means of a Mulliken population analysis [41] using the same basis set.

All calculations were done using the Gaussian 92 program [42], running on the Cray Y-MP2E/116 of the Brussels Free Universities.

In the electronegativity equalization calculations, the "experimental" electronegativities of OH and O, obtained via experimental ionization energies and electron affinities [24, 43], were used.

RESULTS AND DISCUSSION

Table 1 summarizes the calculated group electronegativities χ of the different alkyl groups.

A remark should be made concerning hydrogen. The experimental electronegativity of this element equals 7.17 eV [24], which is higher than all the alkyl groups, and wich is, compared to the other atoms, a relatively high atomic electronegativity.

As can be seen, the group electronegativity decreases when the size of the alkyl group increases, a trend which persists at all levels of theory. Substituting the hydrogen atoms in the methyl group by alkyl groups (the series Me, Et, *i*-Pr and *t*-Bu), results in a decreasing electronegativity. This is in accordance with the classical view of alkyl groups as being electron-donating species.

Table 1. Electronegativities (eV) of the Alkyl Groups at the Different Levels with the 6-31G* Basis Set.

Group	HF	MP2	MP3	MP4
Me	3.85	4.37	4.33	4.35
Et	3.32	3.80	3.76	3.76
n-Pr	3.24	3.73	3.69	3.68
i-Pr	3.01	3.49	3.44	3.44
n-Bu	3.16	3.62	3.60	3.57
t-Bu	2.83	3.36	3.29	3.30

The trends are also in accordance with the experimental electronegativities of the corresponding radicals [43]. Concentrating on the two series of isomeric groups *n*-Pr, *i*-Pr on one hand and *n*-Bu, *t*-Bu on the other, it can be seen that the electronegativity of the group decreases when going from a primary central carbon atom for the group to a secondary and tertiary central carbon atom respectively. This result is in agreement with the conclusions made by Wiberg et al. [44], who found that the relative ordering of electron-withdrawing abilility of alkyl groups was $CH_3 > RCH_2 > RR'CH > RR'R''C$

In the *i*-Pr and *t*-Bu groups, two, respectively three, electron donating methyl groups are attached to the central carbon atom, thus decreasing the electronegativity of this atom with respect to the primary carbon atom found in the *n*-Pr and *n*-Bu groups.

The group hardnesses, listed in Table 2, show the same trends as the group electronegativities : η decreases with an inreasing alkyl group size.

Table 2. Hardnesses (eV) of the Alkyl Groups at the Different Levels with the 6-31G* Basis Set.

Group	HF	MP2	MP3	MP4
Me	6.20	6.00	6.00	5.98
Et	5.77	5.47	5.49	5.45
n-Pr	5.57	5.20	5.25	5.17
i-Pr	5.43	5.07	5.10	5.04
n-Bu	5.49	5.07	5.15	5.05
t-Bu	5.12	4.71	4.76	4.69

The experimental hardness of hydrogen equals 6.42 eV [24], which is again higher than all the alkyl groups. In spite of the relative high electronegativity of hydrogen, it possesses a high hardness (low softness and charge capacity), which will prevent it from accumulating large amounts of negative charge. The hardness of the alkyl groups is seen to decrease upon increasing alkyl group size, again at all levels of theory. This effect can be identified with an increasing charge capacity, softness and polarizability [45] of the alkyl groups with the number of carbon atoms. In fact, as can be seen from figure 1, a very good linear correlation (but inverse) is found between the group hardnesses η and the polarizability constant σ_α, introduced by Taft et al. [46], based on the ab initio calculation of polarizability potentials, which expresses the molecular or functional group polarization produced by a unitary point charge [47].

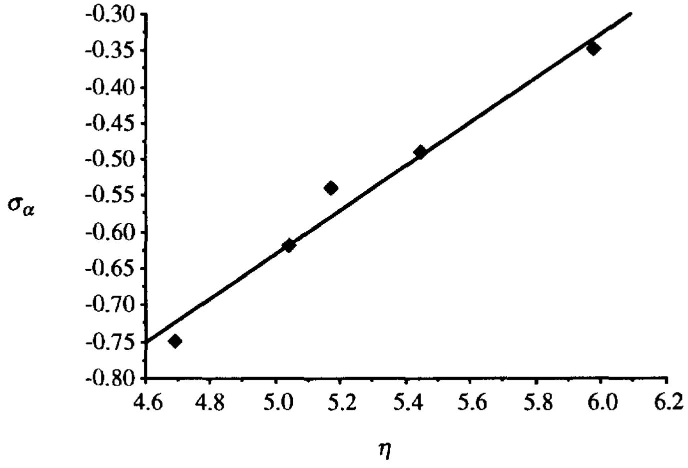

Figure 1. Correlation of the group hardnesses η (MP4 values(eV)) and the σ_α values (kcal mole^{-1}), relative to hydrogen.(*n*-Bu group not included in the correlation, since Taft et al. calculated no σ_α value for this group).

The above made conclusions are now used in the study of the acidities of alkyl substituted alcohols. The gas-phase and solution phase acidities (ΔG_{acid} and $\Delta G_{acid}(aq)$) of these alcohols can be found in Table 3.

Two important features emerge from these data : the acidity trend in the gas-phase (the opposite of the trend in solution) and the large change in magnitude between the two quantities when going from the gas-phase to aqueous solution. The latter phenomenon was ascribed to the large stabilization of the conjugated base form in the solvent.

Table 3. Experimental Acidities of the Alkyl Alcohols R-OH in the Gas-phase (ΔG_{acid}) [48] and in Aqueous Solution ($\Delta G_{acid}(aq)$) [49]. All Values are in kcal mole^{-1}.

R-OH	ΔG_{acid}	$\Delta G_{acid}(aq)$
MeOH	375.0	20.7
EtOH	370.7	21.8
n-PrOH	369.5	22.1
i-PrOH	368.8	23.4
n-BuOH	368.8	22.1
t-BuOH	368.1	26.3

Table 4 summarizes the calculated properties of the neutral systems R-OH of the alcohols : the charge on the acidic proton and the MEP at a distance of 4 a.u. from this hydrogen atom, on a line connecting the hydroxyl oxygen and hydrogen. In the past, we found that the MEP values in that region were very reliable indicators of a compounds acidity [34].

Table 4. Calculated Properties of the Alcohols R-OH ; the Charge on the Acidic Proton q_H and the MEP. All Values are in a.u.

R-OH	q_H	MEP
MeOH	0.4862	0.025165
EtOH	0.5010	0.024385
n-PrOH	0.5014	0.024120
i-PrOH	0.4866	0.023918
n-BuOH	0.5054	0.023933
t-BuOH	0.4974	0.023727

Since the MEP is normally used in the description of reactivity with respect to an electrophile, the interpretation of the MEP has to be changed. We considered MEP regions, unsuitable for an electrophilic attack, as being more suitable for a nucleophilic attack, a strategy which was already proven to be succesfull in the past [50, 51].

As can be seen from Table 4, there is no clearcut relationship between the charge on the acidic proton and the acidities of the alcohols. The MEP values however seem to decrease as the alkyl group size increases ; the interaction with nucleophiles (electron donating molecules) seems to get less favourable. At first sight, this seems to be in contradiction with an increasing gas-phase acidity. However, the MEP values indicate a larger charge transfer from the alkyl groups to the hydroxyl group as the size of the alkyl groups increases, since they become less positive. This is again in accordance with the group properties of R.

Table 5 summarizes the calculated properties of the conjugated bases RO^- : the charge on the oxygen atom q_O, the minimum of the MEP in the region of this oxygen and the MEP at a distance of 4 a.u. from the oxygen, on a line connecting this atom and the minimum of the MEP.

Table 5. Calculated Properties of the Conjugated Bases RO^-.

RO^-	q_O	minimum MEP	MEP
MeO^-	-0.9359	-0.37533	-0.24537
EtO^-	-0.9132	-0.36721	-0.24034
n-PrO^-	-0.9098	-0.36528	-0.23879
i-PrO^-	-0.8869	-0.35983	-0.23662
n-BuO^-	-0.9034	-0.36438	-0.23820
t-BuO^-	-0.8408	-0.35556	-0.23299

As can be seen, the values all become less negative as the alkyl group size increases, being an indication of a less pronounced or localized negative charge in the oxygen region. This result is also in accordance with the decreasing hardness (or increasing softness, polarizability or charge capacity) of the alkyl groups with increasing number of carbon atoms. As a result, the negative charge becomes more delocalized, resulting in a less negative charge on the oxygen atom or less deeper MEP minimum in this region.

All of these findings can be also be explained by a simple application of an electronegativity equalization scheme with functional groups. In the case of functional groups, it can be shown that the electronegativity of a functional group A in a molecule depends on the change in number of electrons ΔN_A of this group upon molecule formation by the following approximative relation (where the perturbation on the group due to the external potential, leading to connectivity-dependent charge transfers, is neglected) [9, 24] :

$$\chi_A = \chi_A^0 - 2\eta_A^0 \Delta N_A \tag{5}$$

Here, χ_A^0 and η_A^0 are the electronegativity and hardness of the isolated functional group A and

$$\Delta N_A = N_A - N_A^0 \tag{6}$$

the charge transfer to or away from A, where N_A and N_A^0 are the number of electrons in the functional group in the molecule and in the isolated group respectively.

Writing this relation for the group R and the OH group in R-OH and for R and O in RO⁻ and using charge conservation relations (i.e. $\Delta N_R + \Delta N_{OH} = 0$ or $\Delta N_R + \Delta N_O = 1$), the charge tranfer ΔN_{R_I} to R in R-OH and $\Delta N_{R_{II}}$ to R in RO⁻ can be calculated as :

$$\Delta N_{R_I} = \frac{\chi_R^0 - \chi_{OH}^0}{2(\eta_R^0 + \eta_{OH}^0)} \tag{7}$$

and

$$\Delta N_{R_{II}} = \frac{\chi_R^0 - \chi_O^0}{2(\eta_R^0 + \eta_O^0)} + \frac{\eta_O^0}{\eta_R^0 + \eta_O^0} = \Delta N_{R_{II,1}} + \Delta N_{R_{II,2}} \tag{8}$$

The sign of the charge transfer ΔN_{R_I} in the alcohols R-OH is determined by the electronegativity difference of the hydroxyl group and the alkyl groups. Since the electronegativity of the alkyl group is less than that of OH for all R, the resulting charge transfers are all negative, which indicates that the alkyl groups all loose electrons. Since, in addition, the group electronegativity and hardness of the alkyl groups decrease with an increasing alkyl group size, the ΔN_{R_I} become more negative with increasing alkyl group size, so that in the case of the alcohols R-OH, the alkyl groups behave as electron donators, as shown in figure 2.

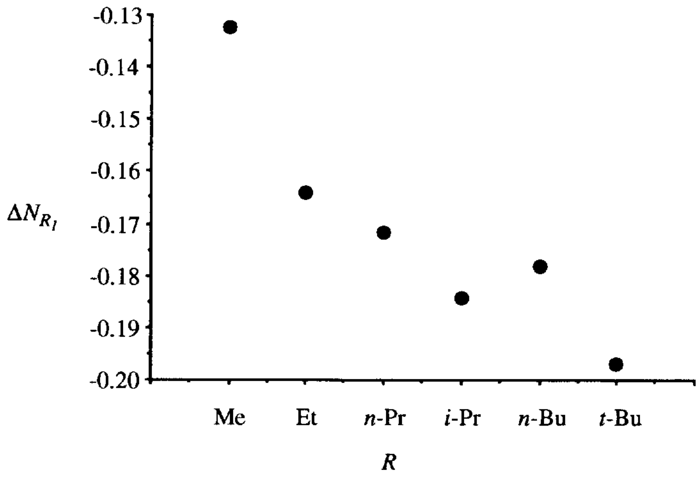

Figure 2. Charge transfer ΔN_{R_I} from the alkyl groups in the alcohols R-OH (a negative sign indicates that electrons are transferred from the alkyl to the OH group).

The expression for the charge transfer in the conjugated base RO⁻ contains two terms : one term, indicated as $\Delta N_{R_{II,1}}$, which is of the same form as ΔN_{R_I}, and an additional term $\Delta N_{R_{II,2}}$, which appears due to the fact that the charge tranfser is measured in a charged system, and which contains only group hardnesses. As can be seen from figure 3, the first term becomes slightly more negative as the alkyl group size increases, again indicating that the electron-donating capacity of the alkyl groups increases with increasing alkyl group size. In contrast, the second term is a positive and larger contribution to $\Delta N_{R_{II}}$ which becomes slightly more positive with increasing group size, indicating that alkyl groups become electron-withdrawing.

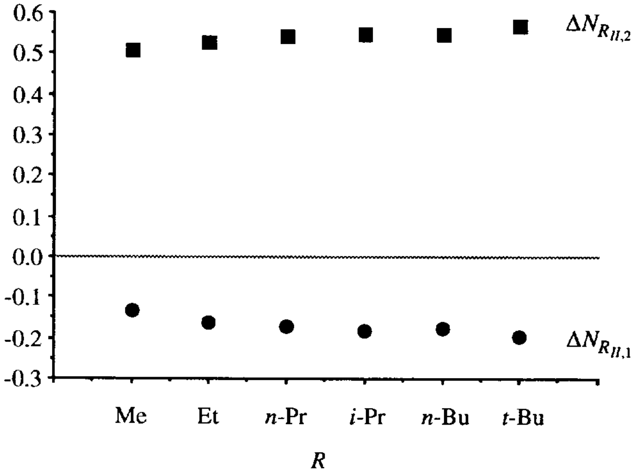

Figure 3. Charge transfers $\Delta N_{R_{II,1}}$ and $\Delta N_{R_{II,2}}$ from the alkyl groups in the conjugated bases RO⁻.

It can thus be concluded that, besides an electronegativity dominated term with negative values for the alkyl groups, a larger and hardness dominated term appears due to which they globally act as electron acceptors. Finally, the charge transfer $\Delta(\Delta N_R)$ undergone by the alkyl groups upon deprotonation of the alcohol can be calculated as :

$$\Delta(\Delta N_R) = \Delta N_{R_{II}} - \Delta N_{R_I} \tag{9}$$

When the approximation is made that $\chi_O^0 \approx \chi_{OH}^0$ and $\eta_{OH}^0 \approx \eta_O^0$ (i.e. the reasonable approximation that the electronegativity and hardness of the functional group is mainly determined by the electronegativity and hardness of the central atom of the group if saturated with hydrogens), this expression can be rewritten as :

$$\Delta(\Delta N_R) \approx \frac{\eta_O^0}{\eta_R^0 + \eta_O^0} \tag{10}$$

This term only contains group hardnesses. This $\Delta(\Delta N_R)$, which can be considered as the ability of alkyl groups to stabilize negative charge in the process of deprotonation, correlates well with the gas-phase acidities ΔG_{acid}, as shown in figure 4, indicating that the larger $\Delta(\Delta N_R)$ value is accompanied by an increasing gas phase acidity.

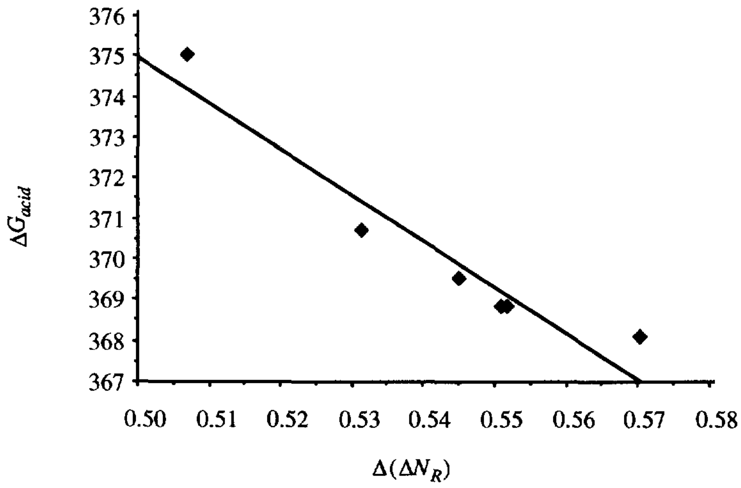

Figure 4. Correlation of the $\Delta(\Delta N_R)$ values with the experimental gas-phase acidities ΔG_{acid}.

Looking at the previous results, it can concluded that in order to correctly describe the acid-base properties of organic compounds, one preferentially must look at the molecular electronic properties of the charged form of the acid-base equilibrium. The duality in the nature of the alkyl group, i.e. the electron-donating or electron-withdrawing capacity, can be explained by considering group electronegativities and hardnesses in combination with a simple electronegativity equalization scheme.

The results obtained are easily extended to other cases where alkyl groups were found to show electron withdrawing properties, e.g. carbanions [52] and carboxylic acids [34], where they are placed on negatively charged carbon atoms or reaction centers.

CONCLUSION

The functional group properties of a number of alkyl groups were calculated, based on Density-functional theory concepts, using simple ab initio molecular orbital calculations. The electronegativity of alkyl groups was found to decrease upon increasing group size, in accordance with the traditional view of alkyl groups as being electron releasing. The group hardness was found to decrease along with the group electronegativity in accordance with an increasing group polarizability (softness).

The gas-phase acidity sequences of a number of alkyl substituted alcohols could be rationalized using the calculated substituent constants. The electron-donating and electron-withdrawing character of the alkyl groups could be explained by considering the two above mentioned functional group properties, together with the Sanderson principle of electronegativity equalization.

It can be concluded that Density-functional theory offers the possibility to calculate these important functional group properties from first principles and in a non-empirical way. In conjunction with the Sanderson electronegativity equalization scheme, they offer direct availability of charge distributions of large molecular systems, which could be of importance in reactivity studies.

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