Theoretical Study of the Effect of the Substituents on the Gas Phase Acidity of Alcohols and Silanols

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The opposite polarizability and inductive effects of the substituent groups on the gas phase acidity of alcohols and silanols are analyzed on the basis of a simple model that relates the proton affinity to the dipole polarizability. Inductive (electrostatic) effects are represented in terms of the variation in electronic chemical potential mediated by local softness at the basic center of the conjugated bases. Electronic (polarization) effects may be probed by the variations in local softness at the basic site. In alkyl alcohols, polarizability effects outweigh inductive effects, while in the corresponding silanol series, the opposite trend is observed. These results are in agreement with the experimental model of substituent effects proposed by Damrauer et al. (*J. Am. Chem. Soc.* **1991**, *113*, 4431): alkyl groups decrease silanol acidity, in contrast to alkyl group effects in alcohols.

1. Introduction

Substituent effects in the gas phase are useful in understanding how the replacement of atoms or groups in a molecule may affect their global and local reactivity patterns.[1] Chemical substitution may be viewed as global changes in the number of electrons (N) that elicit both global and local responses at the active site.[2−6] Substituent effects have been arbitrarily classified as electrostatic (inductive) and polarization, yet the complete understanding of this separation is still incomplete.[1−3,7] Brauman et al.[8] demonstrated in the early 1970s that β-methyl substitution effects on the acidity of alcohols in solution followed this order: $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$. This order is reversed in the gas phase.[8] The gas phase order was explained in terms of an increasing inductive effect by the alkyl groups.[8] A simple theoretical model of charge transfer associated with the proton transfer (PT) in the gas phase acid−base equilibria of a series of alkyl alcohols and alkyl thioalcohols has recently been presented.[9] Experimental gas phase acidity for these systems has been reproduced within that model.

On the other hand, it has been experimentally demonstrated that in the gas phase the alkyl groups decrease silanol acidity, in contrast to the observed alkyl group effects in alcohols.[10] Other substituents such as phenyl, methoxy, fluoro, and chloro led to an enhancement in the acidity of silanols. The authors concluded that for the alkyl substitution, the polarizability effect is attenuated relative to the inductive effect displayed by these substituents. With other substituents, such as phenyl, methoxy, fluoro, and chloro, these effects cooperatively contribute to increase the intrinsic acidity.[10] Geerlings et al.[11] reported a density functional study on the acidity of halogenated alcohols and silanols. The acidity of these species was interpreted in terms of a competition between polarizability and electronegativity effects.[11] The polarizability effects were rationalized in terms of regional (group) softness, as a measure of the charge capacity of the species to accommodate additional charge.[11]

In this work, we present a study of the substituent effect on the gas phase acidity of the alkyl alcohols and alkyl silanols. Within the present model, polarization effects are represented in terms of the dipole polarizability (hereafter polarizability) and the local softness condensed to the basic oxygen site of the conjugated bases, as a measure of the local polarizability induced by the different substituents. Inductive electrostatic effects on the other hand may be probed as fluctuations in electron density at the active site induced by chemical substitution.[9]

2. Model and Methods

Gas phase equilibria are governed by the proton affinity (PA), defined as the enthalpy for the deprotonation process (eq 1).

$$\mathrm{ROH} \rightarrow \mathrm{RO}^- + \mathrm{H}^+ \qquad (1)$$

From a theoretical point of view, the calculations of PAs are usually done within the supermolecule model as PA $\approx \Delta E = E(\mathrm{RO}^-) - E(\mathrm{ROH})$, where $E(\mathrm{RO}^-)$ and $E(\mathrm{ROH})$ are the total energy of the alkoxide ion and the neutral alcohol, respectively.

Inductive (electrostatic) effects may be represented as the variations of the electron density $\Delta\rho_k$ at active site k induced by changes in the number of electrons (ΔN), mediated by the regional Fukui function f_k at the active site ($\Delta\rho_k = f_k\Delta N$). However, this representation of inductive effects is strongly dependent on the population analysis performed to obtain the quantity ΔN. Population analyses are, in general, strongly dependent on the method and basis set used to obtain the electron density, and the regional (arbitrary) partition in overlap and atomic regions. An alternative representation of electrostatic inductive effects may be defined in terms of changes in electronic chemical potential $\Delta\mu$ rather than changes in ΔN. From the definition of local softness[12]

$$s(r) = \left[\frac{\partial\rho(r)}{\partial\mu}\right]_{v(r)} \qquad (2)$$

a regional analysis of the variations in electron density at the active site may be obtained, by performing, for instance, a regional integration over an arbitrary domain Ω_k, to obtain[9]

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$$\Delta\rho_k \approx s_k \Delta\mu \tag{3}$$

Equation 3 gives a simple yet useful criterion for analyzing the changes in electron population at any atomic center in a molecule, in terms of the variations of the electronic chemical potential induced by changes in the number of electrons. As proposed by Berkowitz and Parr,[13] eq 3 shows the meaning of regional softness as a capacity of a group in the molecule to acquire additional charge. Note that the higher the value of s_k, the softer (i.e., more polarizable) the group. Other useful relationships between charge capacity and softness as well as relationships between softness and polarizability have been discussed elsewhere.[14,15]

For the general reaction

$$\mathrm{RO^-} + \mathrm{R'OH} \rightarrow \mathrm{ROH} + \mathrm{R'O^-} \tag{4}$$

the inductive (electrostatic) substituent effects (ISEs) may be analyzed by adopting a model for the chemical potential of proton transfer such as $\Delta\mu_{\mathrm{pt}} = \mu_{\mathrm{products}} - \mu_{\mathrm{reactants}}$.[4,6] The variations of this quantity in the proton transfer reaction may be written as

$$\begin{aligned}\Delta\mu_{\mathrm{pt}} &= [\mu(\mathrm{R'O^-}) - \mu(\mathrm{RO^-})] + [\mu(\mathrm{ROH}) - \mu(\mathrm{R'OH})] \qquad (5)\\ &= \Delta\mu^- + \Delta\mu^N\end{aligned}$$

The pertinent quantity for analyzing the gas phase acidity around the electronic properties of the conjugated bases is $\Delta\mu^-$, defined as

$$\Delta\mu^- = \mu(\mathrm{R'O^-}) - \mu(\mathrm{RO^-}) \tag{6}$$

where CH_3O^- and SiH_3O^- (RO^-) are the reference systems for the series of substituted alcohols and silanols, respectively. The following definition for inductive substituent effects will be used:[9]

$$\begin{aligned}\mathrm{ISE} &= +I \text{ if } \Delta\mu^- > 0 \qquad (7)\\ \mathrm{ISE} &= -I \text{ if } \Delta\mu^- < 0\end{aligned}$$

where the changes in electronic chemical potential are evaluated with respect to the reference systems. Equation 7 used in connection with eq 3 will permit the evaluation of the inductive substituent effects. ISE = $+I$ means that site k has gained electron density due to the substituent effect, and conversely, ISE = $-I$ means that site k has lost electron density in the presence of a given substituent.[9]

The electronic (polarization) substituent effects (ESEs) may be described, on the other hand, in terms of the variations of local softness at active site k through[9]

$$\Delta s_k = s_k - s_k^\circ = S\Delta f_k + f_k^\circ \Delta S \tag{8}$$

where f_k is the condensed to atom k Fukui function[12] and S is the global softness of the molecule,[12] where $\Delta f_k = f_k - f_k^\circ$ and $S = S - S^\circ$; f_k° and S° are the regional Fukui function and the global softness of the unsubstituted molecule, respectively. The variations in local (regional) softness at the active site may be used to represent the electronic (polarization) substituent effects (ESEs) as[9]

$$\begin{aligned}\mathrm{ESE} &= +S \text{ if } \Delta s_k > 0 \qquad (9)\\ \mathrm{ESE} &= -S \text{ if } \Delta s_k < 0\end{aligned}$$

where ESE = $+S$ means that the substituent renders active site k softer than in the reference (unsubstituted) molecule and, conversely, ESE = $-S$ means that the substituent makes active site k less soft (i.e., harder) than in the reference molecule.

On the other hand, the dipole polarizability (α) of a system may also be used to represent polarization substituent effects. During the last years, numerous studies have been performed on the polarizability of the systems, including chemical reactions, in connection with the minimum polarizability principle.[16−18] Polarizability has also been proposed to have a close relationship with global softness.[19]

3. Computational Details

The quantities μ and S needed to evaluate the inductive (ISE) and polarization (ESE) substituent effects via eqs 3 and 8, respectively, were determined by three different methods. The first one involves single-point calculations performed at the B3LYP/6-31G(d,p) level of theory with a geometry optimized at the HF/6-311++G(d,p) level [B3LYP/6-31G(d,p)//HF/6-311++G(d,p)], using the GAUSSIAN94 package of programs.[20] The electronic chemical potential was approached using Koopman's theorem as $\mu \approx (\epsilon_H + \epsilon_L)/2$, in terms of the monoelectronic levels of the frontier molecular orbital HOMO (H) and LUMO (L).[12] Chemical softness was approached using the equation $S \approx 1/(\epsilon_L - \epsilon_H)$.[12] Following a suggestion made by a reviewer, a second type of calculation at the B3LYP/6-31++G-(d,p) level of theory with full geometry optimization was considered to include diffuse functions in both heavy and hydrogen atoms [B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p)]. The electronic chemical potential μ and global softness S were evaluated using Koopman's approximation. The third type of calculation was performed at the B3LYP/6-31++G(d,p) level of theory [B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p)$_{\mathrm{adiabatic}}$], but this time using the adiabatic formulas $\mu = (I + A)/2$ and $S = 1/(I - A)$ for the electronic chemical potential and chemical softness, respectively, with the ionization potential I and electron affinity A evaluated as the difference in total energy for the system with N electrons and $N - 1$ electrons and for the system with $N + 1$ electrons and N electrons, respectively.

The regional Fukui function condensed to atoms was evaluated by a method described elsewhere,[21] in terms of the coefficients of the frontier molecular orbitals and the overlap matrix. This approximation to the Fukui function has been used in a variety of studies yielding reliable results.[5,21,22] This method is independent of the type of population analysis needed to perform the finite difference approximation with reference to the system with $N + 1$ electrons (nucleophilic Fukui function) or to the system with $N - 1$ electrons (electrophilic Fukui function). However, the original derivation in the context of Kohn−Sham theory may be also recast as a frozen orbital approximation to the derivative of the electron density with respect to the number of electrons, by means of the Mulliken population analysis.[23] With the Fukui function values at hand, regional softness at site k is readily obtained through the relationship $s_k = f_k S$.

4. Results and Discussion

4.1. Global Analysis. Proton affinity values may be used as a descriptor for the gas phase acidity of molecules. High values of PA indicate that equilibrium 1 will be favored in the direction of the neutral species, ROH. This result is consistent with the well-known criterion establishing that the enhancement of gas phase acidity is correlated with an increase in the stability of the RO^- species. To validate the methodology used in the work

TABLE 1: Experimental and Predicted Absolute Proton Affinities and Proton Affinity Differences for the Series of Alkoxide and Silanoxide Ions[a]

	method 1		method 2		experimental	
RO^-	PA	δPA	PA	δPA	PA	δPA
CH_3O^-	407.2	0.0	387.7	0.0	379.2	0.0
$CH_3CH_2O^-$	403.0	−4.2	384.2	−3.5	376.1	−3.1
$(CH_3)_2CHO^-$	399.4	−7.8	380.7	−7.0	374.1	−5.1
$(CH_3)_3CO^-$	399.2	−8.0	380.3	−7.4	373.3	−5.9
SiH_3O^-	374.2	0.0	363.1	0.0	352.0	0.0
$CH_3SiH_2O^-$	375.9	1.7	364.8	1.7	353.0	1.0
$(CH_3)_2SiHO^-$	376.7	2.5	365.6	2.5	353.0	1.0
$(CH_3)_3SiO^-$	378.0	3.8	367.4	4.3	353.0	1.0

[a] Absolute proton affinities and proton affinity differences in kilocalories per mole. Method 1: B3LYP/6-31G(d,p)//HF/6-311++G(d,p) calculations. Method 2: B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p) calculations. Experimental proton affinity values for alkoxide ions from ref 27; experimental proton affinity values for silanoxide ions from ref 10.

presented here, the absolute proton affinity and proton affinity difference defined as $\Delta PA = PA(RO^-) - PA(\text{reference})$ for the series of alkoxide and silanoxide ions were compared with the available experimental data. The results are summarized in Table 1. Method 1 corresponds to B3LYP/6-31G(d,p)//HF/6-311++G(d,p) calculations, and method 2 corresponds to B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p) calculations. It may be seen that in general inclusion of diffuse orbitals in both heavy and hydrogen atoms significantly improves the representation of proton affinity. For the series of alkoxide ions, method 1 predicts the PA values with an average error of 7% with respect to the experiment. This average error is reduced to 2% by inclusion of diffuse orbitals. Note, however, that the proton affinity difference measuring the enhancement in gas phase acidity of alcohols induced by substitution with reference to CH_3O^- species ($\delta PA < 0$) or the decrease in the gas phase acidity of silanols induced by alkyl substitution with reference to SiH_3O^- ion ($\delta PA > 0$) is correctly described by both methods.

Both the stabilization of anions and the lowest PA of the conjugated bases criteria are consistent with Pearson's HSAB rule;[24] if we consider the H^+ species as absolutely hard, then the favorable interactions with the RO^- species in equilibrium 1 will demand that this species be as hard as possible, in the direction of ROH formation. This also means that low values of chemical hardness (i.e., high values of chemical softness) will favor equilibrium 1 in the direction of the formation of RO^-, i.e., in the direction of increasing acidity. If we assume that chemical softness and polarizability are proportional, then increasing the polarizability of the RO^- species will result in an enhancement of the gas phase acidity of the corresponding ROH species (i.e., a lowering of the PA values of the RO^- species). Figure 1 summarizes the relationship between PA and polarizability for a short series of alkyl alcohols and alkyl silanols evaluated at the B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p) level of theory. For the series of alcohols, it may be seen that increasing the level of substitution in the order $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, and $(CH_3)_3CO^-$ increases the gas phase acidity by lowering the corresponding PA values of the conjugated bases, with reference to CH_3O^- species. The relationship between polarizability and proton affinity is predicted to be linear, with a regression coefficient r of 0.9901. This linear relationship was also obtained at the B3LYP/6-31G(d,p)//HF/6-311++G(d,p) level (not shown in Figure 1) with a regression coefficient r of 0.9600, thereby showing the marginal effect of diffuse functions in the calculation of PAs for the series of alkoxide ions. Therefore, the increasing acidity pattern observed in the alkyl alcohol series in the gas phase may be directly traced to the enhancement in the polarizability (softness) of the parent RO^- species.

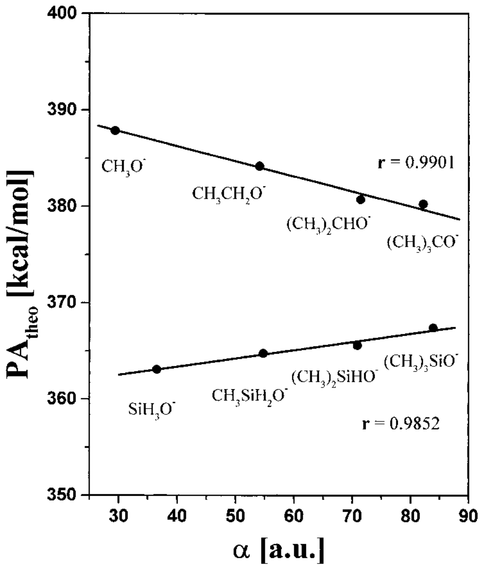

Figure 1. Linear relationship between theoretical proton affinities and dipole polarizabilities evaluated at the B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p) level of theory, for the alkyl alcohol and alkyl silanol series. r is the regression coefficient.

The series of alkyl silanols, on the other hand, exhibits the opposite pattern, in agreement with the experimental model proposed by Damrauer et al.[10] It may be seen that in the alkyl silanol series, increasing the level of substitution in the order $CH_3SiH_2O^-$, $(CH_3)_2SiHO^-$, and $(CH_3)_3SiO^-$ enhances the PA values of the conjugated bases, thereby lowering the gas phase acidity of the corresponding alkyl silanols within this series. The relationship between proton affinity and polarizability for the series of silanoxide ions was also predicted to be linear with a negative slope, with a regression coefficient r of 0.9915 for method 1 (not shown in Figure 1) and an r of 0.9852 for method 2.

In summary, it seems that the polarization substituent effect of the alkyl group measured on the basis of global polarizability α has an opposite effect on the series of alkyl alcohols and alkyl silanols. A more detailed analysis of the alkyl substitution effects at the active basic site of the conjugated bases of alkyl alcohols and alkyl silanols will be presented below.

4.2. Local Analysis of ISEs and ESEs. It has been experimentally demonstrated that polarizability effects outweigh inductive effects in the alcohol series. In contrast, methyl and ethyl substitution in silanols displays an opposite trend.[10] Since the substituent effects are better understood in terms of polarizability and inductive contributions, we propose to analyze both effects as responses at the active basic site of the alkyl alkoxide and the silanol derivative using the ISE and ESE descriptors summarized in eqs 7 and 9, respectively. Thus, while in alcohols the polarization effects outweigh the inductive effects (ESE > ISE), within the silanol series the opposite (ISE > ESE) is expected. As described in section 2, the ISE may be monitored as a response in the electron density at the active site (see eq 3), while the ESE may be probed by fluctuations in local softness at that site, induced by alkyl substitution (see eqs 8 and 9).

Table 2 shows the variations in electron density at the oxygen site using eq 3 and the partitioned variations in local softness

TABLE 2: Variations in Electron Density and Local Softness at Basic Sites

RO^-	$\Delta\rho_O$[a]	Δs_O[b]	$S\Delta f_O$	$f_O°\Delta S$
CH_3O^-	0.0	0.0	0.0	0.0
$CH_3CH_2O^-$	−0.0845	0.2022	−0.0717	0.2738
	−0.1079	0.1006	−0.1722	0.2728
	−0.0462	0.1040	−0.0833	0.1873
$(CH_3)_2CHO^-$	−0.1443	0.3010	−0.1197	0.4207
	−0.1583	0.1540	−0.3050	0.4590
	−0.0758	0.2097	−0.1106	0.3202
$(CH_3)_3CO^-$	−0.2102	0.6384	−0.0325	0.6709
	−0.2274	0.3078	−0.1710	0.4788
	−0.1050	0.4189	−0.0382	0.4571
SiH_3O^-	0.0	0.0	0.0	0.0
$CH_3SiH_2O^-$	0.0147	−0.1822	−0.0258	−0.1565
	0.0158	−0.2030	−0.0364	−0.1667
	0.0122	−0.1924	−0.0687	−0.1238
$(CH_3)_2SiHO^-$	0.0085	−0.2217	−0.0596	−0.1621
	0.0290	−0.2940	−0.0833	−0.2106
	0.0074	−0.2973	−0.0903	−0.2070
$(CH_3)_3SiO^-$	0.0031	−0.2184	−0.0648	−0.1536
	0.0441	−0.3226	−0.0899	−0.2328
	0.0037	−0.2988	−0.0608	−0.2380

[a] Variations in electron density at the oxygen site are in electron units. [b] Variations in local softness are in atomic units. The first entry corresponds to calculations using Koopman's approximation at the B3LYP/6-31G(d,p)//HF/6-311++G(d,p) level of theory; the second entry corresponds to calculations using Koopman's approximation at the B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p) level of theory, and the third entry corresponds to calculations using the adiabatic approximation at the B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p)$_{\mathrm{adiabatic}}$ level of theory.

for the series of alkyl alcohols and alkyl silanols, using eq 8. The first entry corresponds to calculations using Koopman's approximation at the B3LYP/6-31G(d,p)//HF/6-311++G(d,p) level of theory; the second entry corresponds to calculations using Koopman's approximation at the B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p) level of theory, and the third entry corresponds to calculations using the adiabatic approximation for I and A at the B3LYP/6-31++G(d,p)//B3LYP/6-31++G(d,p)$_{\mathrm{adiabatic}}$ level of theory. It may be seen that in the three methodologies $\Delta\rho_O < 0$, for the alkyl alcohol series, indicating that the alkyl group develops an ISE equal to $-I$, decreasing the electron density at the oxygen site with respect to the unsubstituted molecule. Therefore, within this series, the alkyl groups behave as electron-withdrawing substituents. This result is in agreement with those reported by Geerlings et al.[25] using group hardness and electronegativity for the alkyl-substituted alcohols. Conversely, in the alkyl silanol series, it may be seen that the variations in electron density at the oxygen site are positive, indicating that the inductive effect of the alkyl groups is equals $+I$. The alkyl groups in these systems increase the electron density at the basic site with respect to the reference system, indicating that they behave as electron-donating groups within this series. It is important to stress that alkyl groups are currently classified as electron-donating groups. However, it has been shown that a group cannot be considered as an electron donor or remover in absolute terms.[5,26] Their ability as good Lewis acids or Brönsted bases will depend on the substrate's intrinsic electronegativity.[26] On the other hand, the variations in local softness at the basic site show an opposite behavior in both families considered here. While the electronic substituent effect in the alcohol series produces an ESE equal to $+S$, indicating that the alkyl groups render the oxygen site softer (more polarizable) than in the reference system, in the silanol series the opposite trend is observed, in agreement with the experimental model of alkyl substitution.[10] On the other hand, within the alcohol series, it may be seen that the changes in local softness are greater than the inductive effects (ESE > ISE), while the opposite trend is observed in the silanol family (ISE > ESE). These results are again in complete agreement with those reported by Damrauer et al.[10]

It is also interesting to analyze the ESE on the basis of the partitioned expression quoted in eq 8. For instance, inspection of the fourth and fifth columns of Table 2 reveals that the local contribution $S\Delta f_O$ is deactivating in both series. Within the series of alkyl alcohols, however, the global contribution $f_O°\Delta S$ is significantly activating and drives the enhancement in local softness at the active site. Within the alkyl silanol series on the other hand, the global and local contributions to the changes in regional softness cooperatively contribute to the lowering in local softness at the active site. Therefore, the opposite polarization substituent effect between the alkyl alcohol and alkyl silanol series appears mostly related to opposite variations in the global activation contribution given by the second contribution in eq 8. This result reinforces the relationship found between the gas phase acidity and polarizability shown in Figure 1.

5. Concluding Remarks

The gas phase acidity of some alkyl alcohols and alkyl silanols has been analyzed in terms of a simple model that represents inductive and polarization effects in terms of global and local descriptors of reactivity. While the enhancement in the gas phase acidity in the alkyl alcohol series is correlated with an increase in the dipole polarizability of the alkoxide ions, the alkyl silanol series presents the opposite trend: an increase in dipole polarizability of the conjugated bases correlates with a decrease in the acidity of the corresponding silanol, in agreement with experimental results.[10] Inductive substituent effects (ISEs) and electronic (polarization) substituent effects (ESEs) may be assessed as responses at the active site, in terms of the variations in electron density and local softness (or local polarizability), respectively. In the alkyl alcohol series, the local polarizability effects outweigh inductive effects, while in the silanol series, the opposite trend is observed. These results are in agreement with the experimental model of substituent effects recently proposed in the literature. Moreover, the main conclusions reached in this study show no dependence on the basis set in the sense that inclusion of diffuse functions does not change the qualitative response of the ISE and ESE indexes.

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