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Acidity of Zeolites and Silanols: Study of the Influence of Size and Softness of the Global System on the Electronegativity−Softness Competition in Halogenated Model Systems

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The influence of halogenating Si in zeolite type model systems ($SiH_{3-n}F_n$−OH−AlH_3 and $SiH_{3-n}Cl_n$−OH−AlH_3 with n =0, 1, 2, and 3) and silanols ($SiH_{3-n}F_n$−OH and $SiH_{3-n}Cl_n$−OH with n =0, 1, 2, and 3) was investigated by calculating different properties of the hydroxyl group (IR frequencies, integrated IR intensities) and comparing these with gas-phase acidities, ΔG_{acid}. The trends in these quantities are explained in terms of the competition between electronegativity and softness as a function of the systems considered. The results of this competition are reflected in the electronic charges on the hydrogen and oxygen in the hydroxyl group and compared to previously reported trends for halogenated silanols.

Introduction

The competition between electronegativity (χ) and softness (S),[1] the latter property being closely related to the polarizability,[2] seems to offer, in the absence of resonance, an explanation for most reactivity trends. Whereas electronegativity reflects the electron attracting ability of an atom or group in a particular environment, the softness quantifies the ability of this atom or group to accommodate incoming charge. These effects show a different trend when going from top to bottom in a given column of Mendele'ev's table: the electronegativity decreases,[3] whereas the softness increases,[4] thereby provoking the previously mentioned competition.

This competition was previously used to study the influence of halogen substitution on the gas-phase acidity of alcohols and silanols[5] and discussed by the present authors in a broader context.[6] On the basis of those results, a study of the same property (gas-phase acidity) is now undertaken for a number of zeolite type model systems ($SiH_{3-n}F_n$−OH−AlH_3 and $SiH_{3-n}Cl_n$−OH−AlH_3 with n =0, 1, 2, and 3), differing from the silanols in the presence of an additional group (AlH_3). These model systems were used in the study of the Bronsted acidity of zeolites as a function of the framework electronegativity[7,8] (changing Si:Al ratio) mimicked by introducing fluorine atoms in α the position of the bridging hydroxyls.[9,10]

In order to establish these acidity trends for these model systems as well as for the silanols ($SiH_{3-n}F_n$−OH and $SiH_{3-n}F_n$−OH with n = 0, 1, 2, and 3) the gas-phase acidities, ΔG_{acid} (vide infra), were calculated and compared with IR frequencies and integrated IR intensities.

The trends in these quantities are clarified using the effects of the above mentioned properties (electronegativity and softness) as reflected in the electronic charges on the hydrogen and oxygen in the hydroxyl group.

Theory and Computational Details

The calculated gas-phase acidity, ΔG_{acid}, of an acid AH is defined as the change in Gibbs free energy for the reaction

$$AH \rightarrow H^+ + A^- \tag{1}$$

The zero-point energies and a thermal correction for a temperature of 298.15 K, obtained via frequency calculations, are added to the electronic energies calculated at the Hartree−Fock level (vide infra). These calculations also yielded the IR-frequencies and the integrated IR intensities, obtained in the double harmonic approximation,[11,12] both of which can be used in the study of the acidity of the zeolite model systems.[9,13] Another quantity frequently used[5,9,10] to study the acidity of the bridging hydroxyl, the charge on the hydrogen atom, q_H, was also obtained. In addition the charge on oxygen in the conjugated bases, q_{O^-}, was calculated at the optimized geometry of the conjugated base. Both charges were used to clarify the influence of the hardness and electronegativity of the substituents on the charge distribution in the system considered.

Furthermore the global softness S,[14] defined as the inverse of the global hardness η,[15] was considered.

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{\nu(\mathbf{r})} \tag{2}$$

where μ is the electronic chemical potential,[16] N the number of electrons in the system, and $\nu(\mathbf{r})$ the external potential. In a finite difference approximation S can be calculated as

$$S = \frac{1}{I - A} \tag{3}$$

where I is the ionization potential and A is the electron affinity.

All calculations were performed at the Hartree−Fock level using the 6-31G basis set[17] (augmented with a diffuse function (localized on the oxygen atom) in the case of calculations on the conjugated bases of the acid structures considered, in order to get a better description of the anionic system[18]). Use was made of the Gaussian94[19] and the Gaussian92[20] program in combination with the Unichem3.0[21] graphical user interface running on a Silicon Graphics ONYX Extreme workstation. Atomic charges were obtained using the Mulliken population analysis[22] in order to allow comparison with previous results.[5]

Results and Discussion

All quantities calculated in this study are given in Tables 1 and 2. First we consider the results of the frequency calcula-

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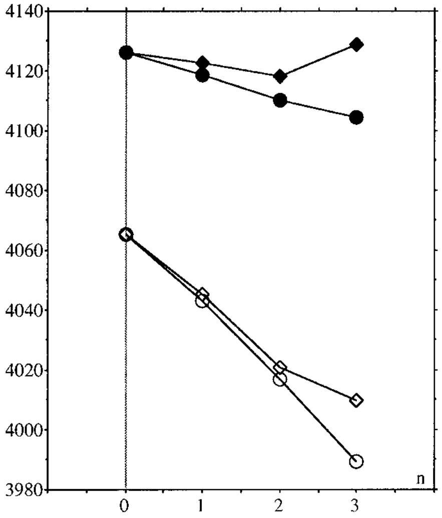

Figure 1. IR-frequencies (cm^{-1}) for silanols ($SiH_{3-n}F_n$−OH (♦) and ($SiH_{3-n}Cl_n$−OH) (●)) and zeolites ($SiH_{3-n}F_n$−OH−AlH_3) (◇) and ($SiH_{3-n}Cl_n$−OH−AlH_3 (○)) and as a function of *n*.

TABLE 1: Calculated Values of the OH Stretching IR Frequencies (ν) (cm^{-1}) and Intensities (A) (km/mol), ΔG_{acid} (kJ/mol), q_H (au), q_{O^-} (au) for the Conjugated Base, and S (au) for $SiH_{3-n}F_n$−OH−AlH_3 and $SiH_{3-n}Cl_n$−OH−AlH_3 for n = 0, 1, 2, and 3

system	ΔG_{acid}	ν	A	q_H	q_{OH^-}	S
SiH_3−OH−AlH_3	1303	4065	171	0.492830	−0.748450	2.48
SiH_2F−OH−AlH_3	1255	4045	223	0.508334	−0.817647	2.32
$SiHF_2$−OH−AlH_3	1198	4021	247	0.523993	−0.828193	2.31
SiH_3−OH−AlH_3	1128	4009	278	0.533281	−0.780469	2.40
SiH_2Cl-OH−AlH_3	1244	4043	207	0.509817	−0.682495	2.39
$SiHCl_2$−OH−AlH_3	1194	4016	231	0.521815	−0.590752	2.57
$SiCl_3$−OH−AlH_3	1138	3989	263	0.526649	−0.472993	2.83

TABLE 2: Calculated Values of the IR frequencies (ν) (cm^{-1}), IR intensities (A) (km/mol), and ΔG_{acid} (kJ/mol) for $SiH_{3-n}F_n$−OH and $SiH_{3-n}Cl_n$−OH for n = 0, 1, 2, and 3

system	A	ν	ΔG_{acid}
SiH_3−OH	87	4126	1581
SiH_2F−OH	117	4122	1514
$SiHF_2$−OH	154	4118	1450
SiF_3−OH	196	4128	1371
SiH_2Cl−OH	127	4118	1473
$SiHCl_2$−OH	165	4110	1395
$SiCl_3$−OH	202	4104	1333

tions. The most obvious quantity to use is the IR frequency of the bridging hydroxyl as it is directly related to the force constant of the OH bond. A decrease in frequency coinciding with a decrease of the force constant is generally considered as an indication of increasing acidity of the system. As the acidity increases with the number of electronegative halogens introduced in the model structure (vide supra), the frequencies should decrease. Looking at Tables 1 and 2 and Figure 1, this is obviously the case for both the fluorine and the chlorine substitution.

This confirms (Figure 2) the results of earlier work[9] where it was found that IR intensities increase with increasing acidity and thus with increasing substitution.

On the other hand the influence of substituting hydrogen by the fluorine atoms should be compared to the influence of substituting hydrogen by the less electronegative but softer chlorine atoms. In the case of the IR frequency the effect (decrease) is larger when considering chlorine substitution. This is in perfect agreement with what one would expect on the basis of the competition between the electronegativity and the hardness of the considered halogens. In the study of the silanols the softness was found to be important, even determining, for the magnitude of the effect of the electronegativity. An explanation was given in terms of the charge capacity of the halogen atoms, as they were the only possible candidate to accommodate the dislocated charge, i.e. the electrons drawn from the hydroxyl group (there were no other sites in the small molecules to harbor these electrons). Fluorine atoms are so hard that the effect of the electronegativity is weakened to such an extent that chlorine finally has a larger effect. On the other hand the influence (increase) on the IR intensity, known to be more sensitive than the IR frequency,[11] is larger for the fluorine substitution. This is a first indication of the role of the AlH_3 group in the current study of the presence of an additional possibility for accommodation of charge.

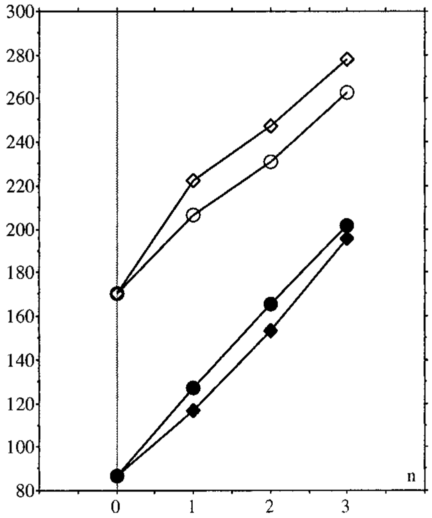

Figure 2. IR intensities (km/mol) for silanols ($SiH_{3-n}F_n$−OH (♦) and $SiH_{3-n}Cl_n$−OH (●)) and zeolites ($SiH_{3-n}F_n$−OH−AlH_3 (◇) and $SiH_{3-n}Cl_n$−OH−AlH_3 (○)) as a function of *n*.

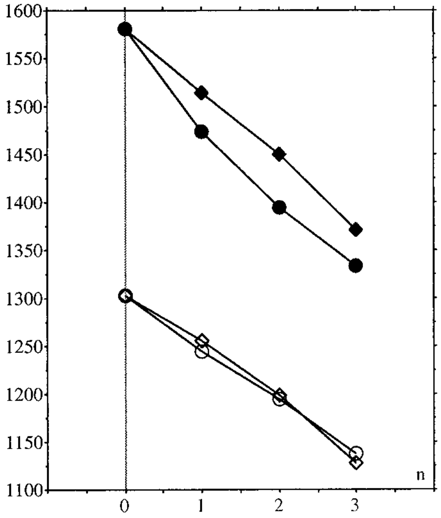

Figure 3. ΔG_{acid} (kJ/mol) for silanols ($SiH_{3-n}F_n$−OH (♦) and $SiH_{3-n}Cl_n$−OH (●)) and zeolites ($SiH_{3-n}F_n$−OH−AlH_3 (◇) and $SiH_{3-n}Cl_n$−OH−AlH_3 (○)) as a function of *n*.

A second indication of the different substitution effects in the presence of an additional group can be found when considering the calculated gas-phase acidity, ΔG_{acid}. A decrease in ΔG_{acid} , corresponding with an increase in the acidity, is expected with an increasing number of electronegative substituents. This is obviously the case (see Tables 1 and 2 and Figure 3). When the acidity trends obtained for the mono- and disubstituted systems are compared, substitution by chlorine leads to a higher acidity, this time in perfect agreement with

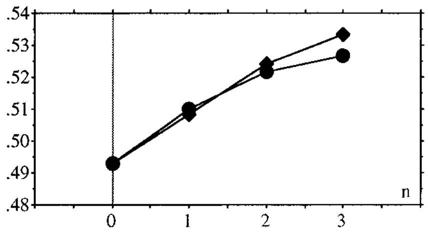

Figure 4. q_H (au) for zeolites ($SiH_{3-n}F_n-OH-AlH_3$ (♦) and $SiH_{3-n}Cl_n-OH-AlH_3$ (●)) as a function of *n*.

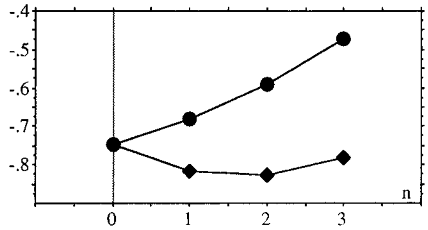

Figure 5. q_{O^-} (au) for zeolites ($SiH_{3-n}F_n-O^--AlH_3$ (♦) and $SiH_{3-n}Cl_n-O^--AlH_3$ (●)) as a function of *n*.

the case of the silanols, where ΔG_{acid} values were also calculated. In the trisubstituted case, however, there is an inversion of the sequence (three fluorines have a larger effect than three chlorines). Again we have a possible influence of the additional AlH_3 group as compared to the silanols.

In the following section an attempt is made to specify this effect by means of a study of the charge on the hydrogen atom, q_H, and the charge on the oxygen atom in the conjugated base, $q_{O}-$, considering the global softness, *S*, of the systems. When comparing the *S* values for the substituted silanols[5] to those for the substituted zeolites (Table 1), it is seen that the zeolite type systems are softer than the corresponding silanols. This can be expected as a relatively soft group was introduced in the system. This assumption can be made on the basis of the hardness value of the central atom (2.77 [23]) and the fact that the group softness of AH_3 groups is essentially determined by the softness of the central atom.[24] In addition the rest of the molecule, being all but the $SiH_{3-n}X_n$ group (i.e. the AlH_3 group in the case of zeolites) can accommodate some charge. Thus, the relative importance of the softness of the halogens can be expected to be smaller than in the case of the silanols, where it was found to be dominant. These softness effects should show up when one looks at the two charges mentioned above.

The charge on hydrogen (Table 1) is a hardness related quantity[25,26] which should describe acidic characteristics of the hydroxyl group fairly well. As an increase in q_H indicates an increase in acidity, it is seen (Figure 4) that this quantity predicts the correct trend in the acidity when there is an increasing number of fluorines or chlorines.

Furthermore it is seen that the two curves are shifted closer to each other as compared to the case of the silanols,[5] In the case of the monosubstituted model system the sequence still is Cl > F, but already in the disubstituted case there is an inversion. This means that the influence of the electronegativity of fluorine can play its role to a bigger extent due to the softness of the zeolite system and the presence of the additional AlH_3 group once a certain threshold is reached.

Further proof can be found by using the charges on oxygen (Table 1) in the conjugated base. In Figure 5 we can see that the absolute value for q_{O^-} decreases as expected in the case of chlorine substitution. In the case of fluorine substitution, however, there is an increase when the first substitution is considered, a trend that is carried through in the second substitution, but is not as outspoken. These effects can be explained by using the idea of a competition between the electronegativity and the softness (hardness) of the fluorine atoms (cf refs 16 and 26). In both cases the lack of softness is the dominant factor, but in the disubstituted case the role of the rest of the system (vide supra) becomes important. Whereas in the silanols changes in the charge distribution could only take place on oxygen and/or the SiH_3 group, this is not the case for the zeolite type model systems. Here a partial shift of charges to the soft AlH_3 group is probably more favorable than adding to the already highly negative charge on oxygen. This effect is even amplified in the trisubstituted case, where a decrease in charge is found.

Conclusions

The effects of different kinds of halogenations on the charge distribution in a (re)active site of a molecule are studied for the first time as a function of the global softness of the system considered. The effects of fluorination and chlorination are established in the study of the gas-phase acidity trends in a series of zeolite type model systems and silanols. The global softness was found to affect the competition between polarizability and electronegativity observed in an earlier study of silanols and methanols. This was clarified by considering the atomic charges on hydrogen and oxygen, indicating that the effect of hardness (lack of polarizability) of the F atom is reduced upon increasing global softness.

These results open some interesting perspective concerning the study of the acidity of zeolites. The changes in acidity upon variations in the Si:Al ratio which were solely attributed to the changing framework electronegativity might also be influenced by the framework softness.

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