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HSAB Analysis of Charge Transfer in the Gas-Phase Acid−Base Equilibria of Alkyl-Substituted Alcohols

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A simple model to analyze charge redistribution associated with proton transfer (PT) reaction is derived from a classical ion transport model. The model is applied to the gas-phase acid−base equilibria of alkyl alcohols. Proton transfer is simulated as the motion of a charged particle in an applied external potential defined by the chemical environment of the proton, and represented by the difference in proton affinity (PA) of the conjugated bases RO^- and CH_3O^-; the latter is taken as reference. The electronic chemical potential of transfer accounts for both the amount and direction of charge transfer (CT). The relative acidity for a short series of alkyl alcohols is determined by the difference in proton affinity ($\Delta PA = PA(RO^-) - PA(CH_3O^-)$) of the conjugated bases. The predicted charge transfer is in agreement with the CT pattern obtained from the group hardness and electronegativity analysis.

1. Introduction

The relative gas-phase acidities of alkyl alcohols have been determined by ion cyclotron resonance spectroscopy by Brauman and Blair.[1] The acidity order in this phase is $(CH_3)_3CCH_2OH > (CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH$.[1] In classical physical organic chemistry, this acidity order has been attributed to the electronic inductive effect that the alkyl groups exert on the oxygen atom of the alkoxide ion that stabilizes the RO^- species.[2] The acid−base equilibrium is usually represented by the heterolytic cleavage reaction 1.

$$ROH \Leftrightarrow RO^- + H^+ \tag{1}$$

Equilibrium 1 in the gas phase is governed by the PA, defined as the enthalpy for the deprotonation process (1). A low value of PA of the conjugated bases RO^- entails a great acidity of ROH. This result may be easily understood in terms of the hard and soft acids and bases (HSAB) principle, proposed by Pearson.[3] This principle establishes that, in an acid−base interaction, soft likes soft and hard likes hard (i.e., soft−soft and hard−hard interactions display a lower enthalpy than the crossed interactions). The HSAB rule may be directly applied to the reverse reaction 1, if we consider that the proton is the hardest electrophile in nature; a higher value of global softness (the inverse of global hardness[4]) of RO^-, will produce less stable ROH species, thereby increasing the acidity of ROH. The global softness (hardness) of the RO^- species may be modified by electronic substituent effects of the alkyl group thereby changing the relative stability of species involved in equilibrium 1. For instance, an increasing electron-withdrawing substituent effect will render the basic oxygen site in RO^- less hard than that of the reference CH_3O^-.[5] This decrease in the hardness of the RO^- ion will result in an increasing acidity of the corresponding ROH species. This result based on a HSAB criterion is in agreement with the explanation offered by Geerlings et al.[6,7] These authors used a group property analysis (group electronegativity and hardness) based on Sandersons electronegativity equalization principle (EEP)[8,9] to show that in the gas phase, alkyl groups act as electron-withdrawing species in the alkyl alcohols series.[6,7] The EEP also provides a useful operational formula to deal with the charge transfer ΔN_t, associated with proton transfer in gas-phase acid−base equilibria. It was first derived by Pearson in terms of the electronic chemical potential difference $\Delta\mu$ for an arbitrary acid−base pair A, B and the sum of their global hardness ($\eta_A + \eta_B$) as[10]

$$\Delta N_t = \frac{-(\mu_A - \mu_B)}{(\eta_A - \eta_B)} \tag{2}$$

Equation 2 is the molecular equivalent of Ohm's law, where the total hardness acts as a resistance to the CT.[3] In this work, we present a quite simple scheme to deal with the charge transfer that is associated with PT in the gas-phase equilibrium of alkyl alcohols. It is based on the PA difference of the conjugated bases RO^- and CH_3O^- and the changes in electronic chemical potential variations associated with the migration of a proton from ROH to CH_3O^-.

2. Model and Computational Details

It is well known that, associated with the proton motion in a PT process, there is an electron flux in the opposite direction.[11−13] On the basis of this result, the apparent proton motion in a PT reaction may be viewed as the motion of a charged particle in an applied external field. This field is characterized by an external potential defined by the chemical environment of the proton. This driven potential may be conveniently represented by the PA difference between the conjugated bases RO^- and CH_3O^-. The model is illustrated in Figure 1.[13] Consider now the general acid−base equilibria

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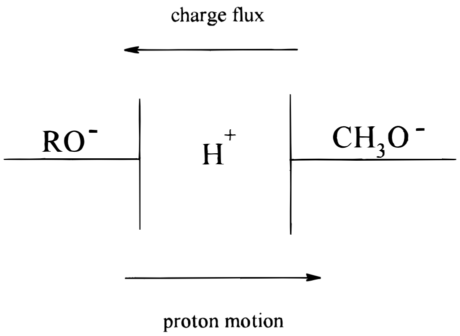

Figure 1. Classic ion transport model for the charge transfer associated with proton transfer between and alkoxide ion pair. CH_3O^- is the reference.

$$CH_3O^- + H^+ \rightarrow CH_3OH; \quad \Delta H = -PA(CH_3O^-) \quad (3a)$$

and

$$ROH \rightarrow RO^- + H^+; \quad \Delta H = PA(RO^-) \quad (3b)$$

that lead to the following net PT reaction:

$$CH_3O^- + ROH \rightarrow CH_3OH + RO^-; \quad \Delta H_{PT} = \Delta PA \quad (4)$$

The enthalpy change for the PT process is given by the PA difference $\Delta H_{PT} = \Delta PA = PA(RO^-) - PA(CH_3O^-)$. It is assumed that this quantity is the driven potential for the proton motion between the RO^- and CH_3O^- moieties.[13]

Proton affinities for the series considered here were obtained from the total energy difference between the alkoxide ion and the corresponding neutral alcohol, for both processes 3a and 3b. The calculations were performed at the HF/6-31G(d) level of theory using the GAUSSIAN94 package.[14] The chemical potential of transfer $\Delta\mu_t$ may be obtained from the net PT reaction 4 as $\Delta\mu_t = \mu_{products} - \mu_{reactants}$ and it is given by

$$\Delta\mu_t = [\mu(CH_3OH) + \mu(RO^-)] - [\mu(CH_3O^-) + \mu(ROH)]$$
$$= [\mu(RO^-) - \mu(CH_3O^-)] + [\mu(CH_3OH) - \mu(ROH)] \quad (5)$$

or

$$\Delta\mu_t = \Delta\mu^- + \Delta\mu^N \quad (6)$$

where

$$\Delta\mu^- = [\mu(RO^-) - \mu(CH_3O^-)] \quad (7)$$

and

$$\Delta\mu^N = [\mu(CH_3OH) - \mu(ROH)] \quad (8)$$

respectively. The electronic chemical potential of proton transfer contains two contributions. The first one $\Delta\mu^-$ contains the contribution to charge transfer from the charged species and it is related to the CT from the alkyl R group to O moiety of the corresponding alkoxide ion RO^-, with reference to CH_3O^-. $\Delta\mu^N$ contains the contribution to charge transfer from the alkyl R group to the OH moiety of the corresponding alcohol ROH, with reference to the standard CH_3OH. This partition is similar to the one proposed by Geerlings et al.,[6,7] in the analysis of charge distribution upon proton transfer, based on the EEP. The neutral contribution ($\Delta\mu^N$) is expected to be smaller than that of the charged species. This means that the electron-withdrawing effect in the alkoxide ions is more significant in the alkoxide series than the corresponding neutral alcohols. These quantities were obtained at the same level of the theory, using the approximate relationship described in ref 4,

$$\mu = \left[\frac{\partial E}{\partial N}\right]_v \approx -\left(\frac{I + A}{2}\right) \approx \frac{\epsilon_H + \epsilon_L}{2} \quad (9)$$

in terms of the ionization potential I and electron affinity A, or using Koopmans' theorem, in terms of the one electron energies of the frontier molecular HOMO and LUMO. This latter approximation was used here.

TABLE 1: Decomposition of Electronic Chemical Potential of Proton Transfer $\Delta\mu_t$ [eV] in Terms of the Neutral and Ionic Contributions, and the Electronic Chemical Potential of Alkyl Alcohols and Their Alkoxide Ions in eV[a]

alkoxyde alcohol	$\mu(RO^-)$	$\Delta\mu^-$	$\mu(ROH)$	$\Delta\mu^N$
CH_3O^-	5.4322	0.0		
CH_3OH			−2.9452	0.0
$CH_3CH_2O^-$	4.8964	−0.5357		
CH_3CH_2OH			−2.8973	−0.0479
$(CH_3)_2CHO^-$	4.5114	−0.9208		
$(CH_3)_2CHOH$			−2.8910	−0.0541
$(CH_3)_3CO^-$	4.1120	−1.3202		
$(CH_3)_3COH$			−2.9645	0.0193
$(CH_3)_3CCH_2O^-$	3.7966	−1.6356		
$(CH_3)_3CCH_2OH$			−2.9449	−0.0003

[a] Calculated values on optimized structures at HF/6-31G (d) level of theory.

The theoretical analysis of charge transfer processes has been currently done on the basis of population analysis. The gas-phase acidity of alcohols has been usually associated with electronic population analysis on the basic oxygen atom in RO^- and ROH species, to relate the stabilization of anions with substituent effects. This procedure has recently been implemented within the EEP by Geerlings et al.[6,7] That method is based on group properties analysis, namely group electronegativity and group hardness. The present approach based on the HSAB rule has a potential advantage with respect to the EEP-based model of substituent effect, namely the transferability of group properties is not necessary within the present approach, since chemical substitution is probed as local responses at the active center of the substrate. This aspect makes the present approach quite general, in the sense that it could be applied to other gas-phase acid−base processes. Another advantage of the present approach is that it is rather independent of the population analysis.

3. Results and Discussion

In Table 1 are compiled the values for $\Delta\mu^-$ and $\Delta\mu^N$ for the series of alkyl alcohols. It may be observed that for all the molecules considered here, the contributions from the charged species $\Delta\mu^-$ are largely over the corresponding neutral contribution $\Delta\mu^-$ and negative for the whole series. This means that in the leading term $\Delta\mu^-$, using definition 7 yields $\mu(RO^-) < \mu(CH_3O^-)$, and our model predicts that the electronic charge will flow from CH_3O^- to RO^-. The effect of CT from the neutral species ($\Delta\mu^N$) is marginal and makes no significant contributions to the global CT involved in equilibrium 4. Increasing the substituent size increases the difference in electronic chemical potential (in absolute value), indicating that the charge flow will be enhanced by increasing the alkyl group size. This result is in agreement with the proposal made by

TABLE 2: Theoretical and Experimental PA Differences [kcal/mol], Global Softness, Total Hardness, and Electronic Chemical Potential of Proton Transfer [eV] and Charge Transfer [Electron Units] for the Gas-Phase Acid−Base Equilibrium of Alkyl Alcohols

alkoxyde ion	$\Delta PA^{theo\ a}$ ΔPA^{exp}	$S(RO^-)$	$-\Delta\mu_t$	η_t	ΔN_t
CH_3O^-	0.0 0.0	0.1360	0.0	14.7094	0.0
$CH_3CH_2O^-$	−3.1 −3.1	0.1417	0.5836	14.4111	0.0405
$(CH_3)_2CHO^-$	-5.1 -5.0	0.1452	0.9749	14.2407	0.0685
$(CH_3)_3CO^-$	−6.6 −6.0	0.1491	1.3009	14.0610	0.0925
$(CH_3)_3CCH_2O^-$	−9.4 −7.9	0.1553	1.6359	13.7951	0.1186 −5.0

[a] Calculated values on optimized structures at HF/6-31G (d) level of theory.

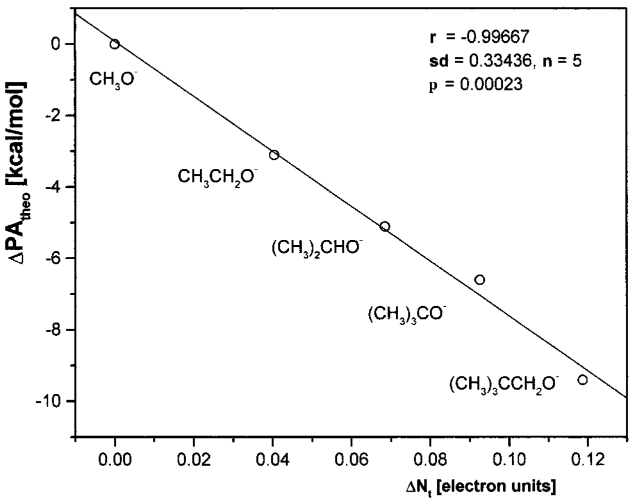

Figure 2. Correlation between charge transfer between the (RO^-, CH_3O^-) pair and the theoretical gas-phase acidity of alkyl alcohols measured by $\Delta H_{PT} = \Delta PA = PA(RO^-) - PA(CH_3O^-)$. r is the regression coefficient; sd is the standard deviation; n is the number of points, and p is the probability that the observed correlation is randomly obtained.

Geerlings et al.,[6,7] pointing out an enhancement of the charge capacity of the alkyl group in going from CH_3O^- to $(CH_3)_3CCH_2O^-$.

The theoretical $\Delta PA = PA(RO^-) - PA(CH_3O^-)$ values are depicted in Table 2. They are compared with the experimental data reported by Bartmess et al.[15] It may be seen that, at the level of theory used, the theoretical proton affinity differences are correctly assessed within the series. The increasing negative values of this quantity confirm the experimental trend given by Brauman and Blair[1] for the acidity scale in the series $(CH_3)_3CCH_2OH > (CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH$. As correctly suggested by a referee, diffuse functions are required to properly describe ionic species. However, in the present case, the calculation of ΔPA using a HF/6-31++G(d) did not improve the values obtained at the HF/6-31G(d) level of theory. The theoretical ΔPA values obtained with diffuse functions were −2.6 kcal/mol for $CH_3CH_2O^-$, −4.1 kcal/mol for $(CH_3)_2CHO^-$, −5.2 kcal/mol for $(CH_3)_3CO^-$ and −6.2 kcal/mol for $(CH_3)_3CCH_2O^-$. Comparison of these values with the ones quoted in Table 2 shows that the introduction of diffuse functions systematically overestimates the ΔPA quantity, in this case. The introduction of diffuse functions did not show qualitative changes in the variation pattern of the ΔN_t quantity; the predicted ΔN_t values for the series $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, and $(CH_3)_3CCH_2O^-$ were 0.0467, 0.0784, 0.1119, and 0.1179 electron units, respectively, at the HF/6-31++G(d) level of theory. Comparison with the values quoted in Table 2 shows that the introduction of diffuse functions maintains the increasing pattern of charge transfer within the series.

In Table 2 are also compiled the global softness for the alkoxide ions. They can be used to explain the gas-phase acidity pattern within the HSAB rule with reference to the reverse reaction described in eq 1. It may be seen that the increasing acidity pattern within the series, as probed by the PA variations of the corresponding alkoxide ions in going from CH_3O^- to $(CH_3)_3CCH_2O^-$, is correlated with an increasing global softness (i.e., a decreasing hardness pattern). This means, according to the HSAB principle, that the hard (H^+)−soft (RO^-) interaction leading to the formation of the corresponding alcohol ROH will proceed with an unfavorable enthalpy change. This result is in agreement with the classical explanation about the gas-phase acidity pattern within this series in terms of the thermodynamic stabilization of the corresponding alkoxide ion induced by the alkyl substituent effect. The total change in electronic chemical potential $\Delta\mu_t$ obtained from eq 6, together with the total hardness $\eta_t = [\eta(RO^-) + \eta(CH_3O^-)]$, is also displayed in Table 2. The absolute hardness for each species was obtained from the finite difference formula given in ref 4 in terms of the one-electron orbital energies of the frontier molecular orbitals HOMO and LUMO as

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_v \approx \left(\frac{I - A}{2}\right) \approx \frac{\epsilon_L + \epsilon_H}{2} \tag{10}$$

With the values of $\Delta\mu_t$ and η_t at hand, we may have an estimate of the CT associated with the proton transfer equilibrium 4, by replacing these quantities in Pearson's eq 2 to obtain

$$\Delta N_t = \frac{-\Delta\mu_t}{\eta_t} \tag{11}$$

The predicted ΔN_t obtained from eq 11 are listed in the last column of Table 2. It may be seen that, in going from CH_3O^- to $(CH_3)_3CCH_2O^-$, the charge transfer relative to CH_3O^- from the basic oxygen atom in RO^- to the alkyl group increases with the group size, revealing the electron-withdrawing properties of the alkyl groups when they are directly bound to a negative charged oxygen atom in the RO^- species. This result is also in agreement with those reported previously by Geerlings et al.[6,7] and obtained from a different model. The quantity ΔN_t may also be viewed here as a measure of the ability of alkyl groups to stabilize negatively charged species in the deprotonation process described in eq 4. In the present approach, the acidity of the ROH species is explained again on the basis of a HSAB rule as follows: the increasing electron-withdrawing ability of the alkyl group along the series results in a decrease in the hardness at the basic oxygen atom in RO^-. This means, using Pearson's HSAB rule, that the reverse equilibrium described in eq 4 will have a less favorable enthalpy,[3] which means that the conjugated RO^- bases will be stabilized with respect to the reference CH_3O^- ion, accounting for the increasing acidity along the series of alkyl alcohols considered in the present study. In Figure 2, a correlation between the theoretical acidity and ΔN_t is presented, confirming the previous result that the increasing ΔN_t value is associated with an increasing gas-phase acidity as measured by the driving potential $\Delta H_{PT} = \Delta PA = PA(RO^-) - PA(CH_3O^-)$.

It is also interesting to note that there is a relationship between the proton affinity differences and the electronic chemical potential of transfer. This relationship follows from Pearson's eqs 2 and 11 derived from the EEP, as we shall show below; we first rewrite eq 11 as

$$\Delta N_t = -\Delta\mu_t\left[\frac{1}{\eta_t}\right] = -\Delta\left[\frac{\Delta E}{\Delta N_t}\right]_v\left[\frac{\Delta N_t}{\Delta\mu_t}\right]_v \tag{12}$$

Since the total energy difference in a proton transfer process yields directly the proton affinity, $\Delta E = \text{PA}$, and using the relationship

$$S_t = \frac{1}{\eta_t} \approx \left[\frac{\Delta N_t}{\Delta\mu_t}\right]_v \tag{13}$$

we may then write

$$\Delta\mu_t = -\left[\frac{\Delta\text{PA}}{\Delta N_t}\right]_v \tag{14}$$

Equation 14 is a useful expression relating the variations in proton affinity, electronic chemical potential, and charge transfer. Note that the minus sign in the right-hand of eq 14 accounts for the opposite direction of the apparent proton motion and the charge flux in a PT process. The uselfulness of eq 14 may be illustrated for a hard–hard interaction as follows: in a hard–hard regime, the charge transfer ΔN_t associated with the proton-transfer process is expected to be small, as well as its first-order variations along a series of related molecules. In such a case, a linear relationship between the proton affinity variations ΔPA and the changes in the electronic chemical potential of transfer $\Delta\mu_t$ is expected. Such a linear relationship is displayed in Figure 3. The regression coefficient $r = 0.9951$ confirms the quality of the prediction based on eq 14. This result suggests that the PA and acidity order in the gas phase for a family of related Brönsted acids may be qualitatively predicted from the knowledge of the changes in electronic chemical potential of transfer of the conjugated bases involved in the acid–base equilibria, relative to a reference system.

4. Concluding Remarks

A simple model of charge transfer associated with proton transfer in the gas-phase acid–base equilibria of a series of alkyl alcohols has been presented. The relative gas-phase acidity has been correctly accounted for by introducing the proton affinity difference between the conjugated RO^- species with reference to CH_3O^- as the driving potential for the PT process. Charge transfer associated with the PT process is correctly assessed by using the variations of the electronic chemical potential as a descriptor of charge transfer, within a simple scheme based on a classic ion transport model. The electron-withdrawing ability of the alkyl group is found to increase with the alkyl group size, in agreement with previous results obtained from group hardness and electronegativity analysis. The gas-phase acidity of the alkyl alcohol series considered here may be rationalized in terms of a local HSAB rule. The consistency between our results based on the HSAB principle and the ones obtained from the EEP shows that both empirical rules consistently complement each other.

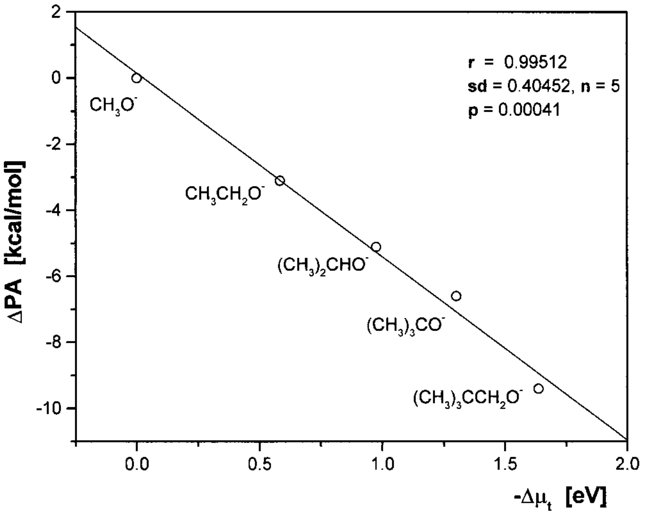

Figure 3. Correlation between the electronic chemical of transfer variations of RO^- species with reference to CH_3O^-, and the theoretical gas-phase acidity of alkyl alcohols measured by $\Delta H_{PT} = \Delta PA = PA(RO^-) - PA(CH_3O^-)$. *r* is the regression coefficient; sd is the standard deviation; *n* is the number of points, and *p* is the probability that the observed correlation is randomly obtained.

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