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THE METHYL INDUCTIVE EFFECT ON ACID-BASE STRENGTHS

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The methyl group is usually classified as electron-releasing (relative to hydrogen) in an ordering of inductive substituents. This is partly based on the observed effect of methyl substitution on liquid phase acid and base strengths. Methylamines are stronger bases than ammonia and this has been interpreted in terms of transfer of electrons from methyl to nitrogen. Similarly, the fact that acetic acid is a weaker (aqueous) acid than formic suggests electron transfer from methyl into the carbonyl group. There are, however, a number of experimental observations that cast doubt on this interpretation. Methylation reduces the electric dipole moment of ammonia, suggesting electron withdrawal by methyl. Also, it has recently been shown that, in the gas phase, the proton affinity of methoxide is less than that of hydroxide.[1] This reverses the aqueous solution ordering which was consistent with the electron releasing hypothesis.

The purpose of this communication is to point out that, according to a simple molecular orbital theory, a methyl group is electron-attracting (relative to hydrogen) in amines, alcohols and ethers. Nevertheless, if the same theory is used to calculate total energies of the neutral, protonated and deprotonated systems, all experimental orderings of gas-phase proton affinities are reproduced.

The quantum mechanical method used was ab initio linear combination of atomic orbital theory, with a minimal basis of Slater-type orbitals (STO). Each STO is replaced by a least-squares fitted combination of three gaussian functions (STO-3G), and scaled by a standard set of molecular ζ-factors.[2] Molecular geometries for the neutral molecules were chosen according to a standard model used previously.[3] The same bond lengths and tetrahedral valence angles were also used in both positive and negative ions.

The STO-3G molecular orbital method was applied to the molecules listed in the table and to the cations and anions obtained by adding and removing single protons. The energies of proton addition and removal were obtained by taking differences of the corresponding total energies.. Also tabulated are the atomic charges (obtained from Mulliken gross populations) for the heavy atom X (nitrogen or oxygen) and the corresponding hydrogens in the neutral molecules.

The theoretical values for proton addition and removal energies are not in good agreement with experimental estimates which are numerically smaller. Thus the difference between the theoretical and experimental energy of proton removal for methanol is 150 kcal/mole.[4] Calculated absolute energies of proton addition are in somewhat better agreement with experiment, the theoretical values for water and methanol being too large by about 60 kcal/mole.[4,5] It might be noted that experimentally the difference in the energies of protonation of water and methanol is 11 kcal/mole in good agreement with our calculated quantity. Although little quantitative experimental information about the energies of proton addition and removal is available for comparison, it is significant that all known trends with methyl substitution are reproduced correctly. Replacement of a hydrogen by methyl increases acidity and basicity for both series of compounds.[6,7] The atomic charges on nitrogen and oxygen show a strong electron-withdrawing effect for methyl substitution, but those on hydrogen change only slightly.

These results suggest that energies of proton transfer reactions do not necessarily correlate with charge densities on the atom to which the proton is attached. For these series of compounds, it appears that methyl substitution stabilizes both positive and negative ions relative to neutral molecules. A more reasonable qualitative interpretation is that a methyl group provides an extended structure which can be polarized more effectively by both cationic and anionic centers.

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ENERGIES AND ATOMIC POPULATIONS

Molecule	E (hartrees)	ΔE(Proton Addition) (kcal/mole)	ΔE(Proton Removal) (kcal/mole)	q_X[a]	q_H[a]
NH_3	-55.45254	-258.3	555.3	-0.481	0.160
$MeNH_2$	-94.03005	-266.0	539.0	-0.405	0.157
Me_2NH	-132.60922	-271.2	523.8	-0.332	0.156
Me_3N	-171.18930	-274.7	--	-0.263	--
H_2O	-74.96072	-228.6	568.0	-0.372	0.186
MeOH	-113.54550	-235.8	535.4	-0.308	0.189
Me_2O	-152.13214	-239.7	--	-0.244	--

[a] q_X, q_H are Mulliken populations on the neutral molecules. q_X is the charge on the atom from which the proton is to be removed, q_H is the charge on the hydrogen to be removed.

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