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Gas Phase Acidities of CH Bonds Adjacent to Oxygen and to Sulphur

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It has been shown, by double zeta quality *ab initio* MO calculations, that, in the gas phase, a CH bond adjacent to sulphur is more acidic than a CH bond adjacent to oxygen. This trend is in agreement with experimental observations in solution.

Key words: Gas phase acidity – Proton affinity – Carbanions

A hydrogen-containing molecule (AH) may undergo either protonation or deprotonation:

$$2\mathrm{H}^+ + \mathrm{M}^- \xleftarrow[\text{gas phase acidity}]{\text{deprotonation}} \mathrm{MH} + \mathrm{H}^+ \xrightarrow[\text{gas phase basicity}]{\text{protonation}} \mathrm{MH}_2^+$$

and the relative facilities of the two processes are measured, respectively, by the gas phase basicity and the gas phase acidity of the molecule. Since proton affinity (A_H^+) is defined, either in the thermodynamic convention:

$$\begin{aligned} \mathrm{A}_\mathrm{H}^+(\mathrm{MH}) &= \Delta H_f^0(\mathrm{MH}_2^+) - \{\Delta H_f^0(\mathrm{MH}) + \Delta H_f^0(\mathrm{H}^+)\} \\ \mathrm{A}_\mathrm{H}^+(\mathrm{M}^-) &= \Delta H_f^0(\mathrm{MH}) \quad - \{\Delta H_f^0(\mathrm{M}^-) + \Delta H_f^0(\mathrm{H}^+)\}, \end{aligned}$$

or in the quantum mechanical convention:

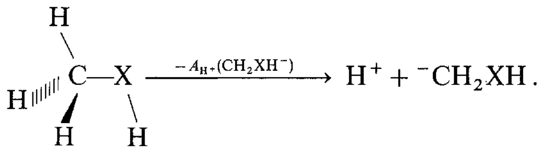
$$\begin{aligned} \mathrm{A}_\mathrm{H}^+(\mathrm{MH}) &= \mathrm{E}(\mathrm{MH}_2^+) - \mathrm{E}(\mathrm{MH}) \\ \mathrm{A}_\mathrm{H}^+(\mathrm{M}^-) &= \mathrm{E}(\mathrm{MH}) \quad - \mathrm{E}(\mathrm{M}^-), \end{aligned}$$

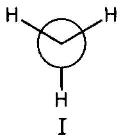
as a difference between protonated and deprotonated states, the gas phase basicity and acidity of the molecule may be defined as:

$$\begin{aligned} \text{gas phase basicity of MH} &= \quad \mathrm{A}_\mathrm{H}^+(\mathrm{MH}), \\ \text{gas phase acidity of MH} &= -\mathrm{A}_\mathrm{H}^+(\mathrm{M}^-). \end{aligned}$$

Introduction of a heteroatom into a hydrocarbon molecule leads to a change in the acidities of the remaining C–H bonds [1]. Because the quantitative effect of each heteroatom is different, a quantitative understanding of the effects of heteroatom substitution upon carbanion proton affinities is a necessary prerequisite to the understanding of experimental acidity differences. For example, it is an experimental fact [2] that the kinetic acidity of a proton at a carbon adjacent to sulphur is several orders of magnitude greater than that of a proton at carbon adjacent to oxygen. This has been attributed to d_π-p_π stabilization of the anion in the former case [2, 3]. However, it has not been necessary to postulate *d*-orbital conjugation to account for the *stereochemical* properties of sulphur-stabilized carbanions [4], and it seemed to us, therefore, that some, as yet unrecognized, non-conjugative explanation might also account for the *chemical* difference between the two systems.

The approach that is being taken involves double zeta quality computations of the energies of $HOCH_3$, $HOCH_2^-$, $HSCH_3$, and $HSCH_2^-$, with full optimization of the geometries, and with *s*, *sp*, and *spd* basis functions on the heteroatoms. In the first part of the work, geometry optimization of $HOCH_3$ [5] and $HOCH_2^-$ [6] was achieved for *sp* bases. This permits evaluation of the following gas phase acidity, for X=O:





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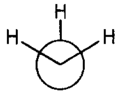

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In the present work, the gas phase acidity for X=S has been computed with an *spd* basis. Bond angles about the carbon atom in the carbanion have been assumed to be tetrahedral. Although full geometry optimization has not yet been performed, the trends in the gas phase acidities are already clear.

Table 1. Conformational energies of $HOCH_2^-$, $HOCH_3$, $HSCH_2^-$, and $HSCH_3$

Rotational angle[a]	0°	60°	120°	180°
$HOCH_2^-$	−114.30505	−114.29316	−114.28616	−114.29469
$HOCH_3$	−115.00875	−114.01105		
$HSCH_2^-$	−437.01398	−437.00044	−437.00131	−437.01555
$HSCH_3$	−437.68839	−437.69026		

[a] For definition of these angles, see Fig. 1.

The data are summarized in Table 1 and illustrated in Fig. 1. Two minima are found for each carbanion. These correspond to the *Y*(*I*) and *W*(*II*) conformations. In $HOCH_2^-$ the *Y conformation represents the lowest minimum, but in* $HSCH_2^-$ the *W* conformation has the lower energy (Fig. 1). The gas phase acidities, also shown in Fig. 1, are:

$$^{-}A_{\mathrm{H}}^{+}(\mathrm{HOCH_2^-}) = 0.70370\,\mathrm{hartree} = 441.7\,\mathrm{kcal/mole}\,,$$

$$^{-}A_{\mathrm{H}}^{+}(\mathrm{HSCH_2^-}) = 0.67284\,\mathrm{hartree} = 422.3\,\mathrm{kcal/mole}\,.$$

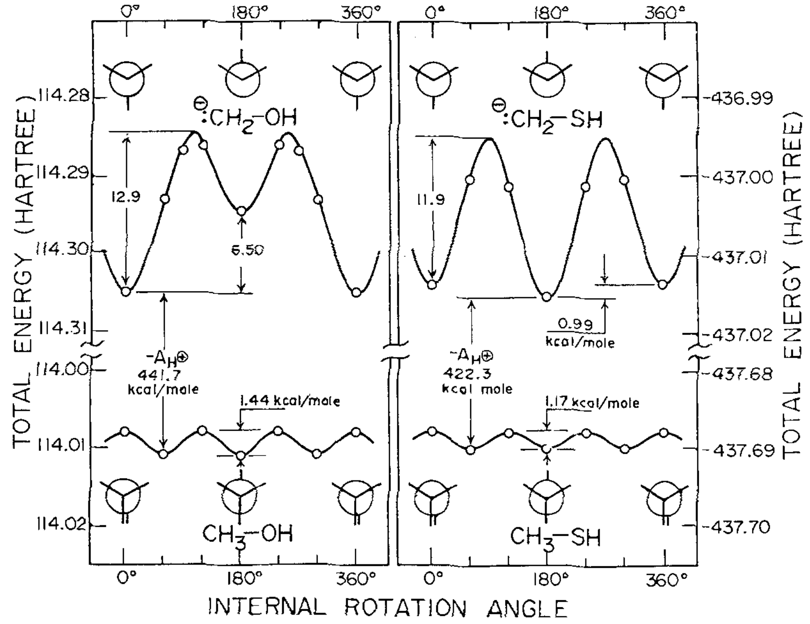

Fig. 1

These values indicate that a CH bond adjacent to sulphur is more acidic than a CH bond adjacent to oxygen. The final account of this work will contain the full geometry optimization of $HSCH_2^-$ and the comparative study of the gas phase acidities as a function of basis set.

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