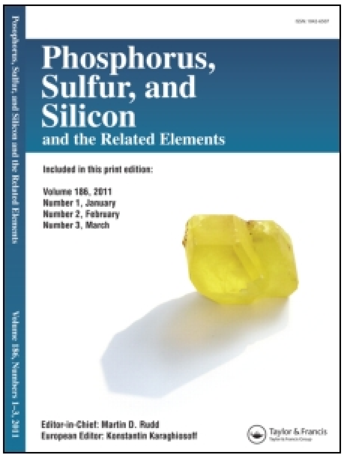

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CNDO/2-CALCULATIONS ON THE STABILIZATION OF CARBANIONS BY σ-BIVALENT SULFUR†

by

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ABSTRACT

The significantly enhanced acidity of C–H bonds attached to a σ-bivalent sulfur atom can be explained without taking into account the octet expansion of sulfur. The higher carbanion stabilization effect of sulfur in comparison to oxygen has been related to the greater capability of the σ-bivalent sulfur to take up excess charge into the *sp*-valence shell.

I. Introduction

It is well known that the CH-acidity of aliphatic sulfides at the α-position is relatively high.[1–3] By measurements of the deuterium exchange rates[4] Oae and coworker established that the RS-groups exert a larger acidifying effect than the RO-groups. The generally accepted explanation resorts to the empty 3*d* orbitals of the sulfur which should be partially filled by the excess charge of the adjacent carbanion.

However, according to more recent quantum-chemical studies this explanation is again open to question. Investigating the stereochemistry of α-sulfinyl- and α-sulfonyl carbanions, Csizmadia and coworkers found only negligible *d*-orbital effects.[5] The participation of the *d*-orbitals can also be neglected in structures as **1** and **2**.[6] The *d*-orbitals act rather as polarization functions as getting occupied valence orbitals.[7]

$$\underset{\mathbf{1}}{H_2\bar{C} - SH^-} \qquad \underset{\mathbf{2}}{H_2\bar{C} - S - \bar{C}H_2^{--}}$$

Ab initio calculations have clearly shown the carbanion **1** to be stabilized by the sulfur substituent.[8] However, the significance of the *d*-orbitals was not discussed in ref. 8. Later Streitwieser *et al.*[9] questioned the mechanism of the stabilization, considering the deprotonation of methanthiole compared to that of ethane. The calculations confirmed the marked carbanion stabilizing effect of sulfur and showed that the *d*-orbitals have essentially no effect.

This conclusion has most recently also been established by Csizmadia and coworkers.[10] According to them the gas-phase acidity of a C–H bond adjacent to sulfur is greater than that of a C–H bond adjacent to oxygen, whether or not *d* functions are employed on the heteroatom.

These results encouraged us to communicate some results we achieved on the semi-empirical all-valence electron level.[11] Employing the CNDO/2 approximation, we have computed the energy ΔE which is necessary to remove a proton from the carbon atom adjacent to sulfur and oxygen, respectively.

$$\underset{\mathbf{3}}{H - CH_2 - XH} \rightarrow \underset{\mathbf{4}}{\bar{C}H_2 - XH^-} + H^+$$

a: $X = O$
b: $X = S$

$$\Delta E = E\,(\mathbf{4}) - E\,(\mathbf{3})$$

II. Theoretical Method and Choice of Model Structures

The all-valence electron calculations have been performed within the CNDO/2 approximation described in ref. 12. This method, which completely neglects differential overlap and employs empirical parameters, has found a wide range of application in sulfur quantum chemistry.[13] Except for the neglected *d*-orbital our calculations involve the same parameterization as formerly described.[12]

To attain better insight into the electronic effects the energy was examined by an energy-partitioning analysis.[14] The overall binding energy has been separated into contributions by the nuclei E^n and by the electrons E^{el}. Furthermore, the electronic energy has been considered to consist of atomic and bond energy terms. Thus, the gain in energy by chemical bonding may tentatively be explained by contributions due to electrostatic attraction between electron

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† Part XXXVII in a series "MO-LCAO Calculations on Sulfur-containing π-Electron Systems" (for Part XXXVI see R. Mayer, J. Sühnel, H. Hartmann, and J. Fabian, *Z. physikal. Chem.* [Leipzig], **256**, 792 (1975).

and nuclei E_{AB} and by contributions arising from the orbital overlap E^R_{AB} ("resonance term"). This energy partitioning technique was described in detail by Kollmar and Fischer.[14]

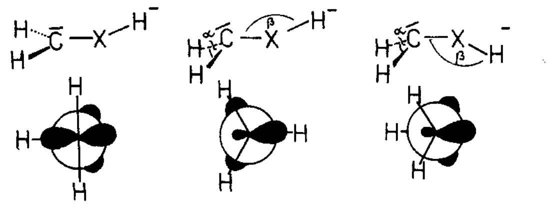
The calculated energy for deprotonation following eq. 1 depends upon the molecular geometry of 3 and 4. As experimental data were only available for 4 a standard geometry has been employed (Table I). To find the preferred configurations CNDO/2 calculations were performed on 4a-4c (*cf.* Figure I). In accord with *ab initio* results[6] the pyramidal arrangement 4c presents the energetically most favored structure.

TABLE I

Bond Lengths (in Å) and Bond Angles

Bonds	Calculated Structures CH_3OH/CH_2OH^-	 CH_3SH/CH_2SH^-
R_{C-H}	1.09	1.09
R_{C-X}	1.43	1.82
R_{X-H}	0.96	1.34
α^a	115° or 120°	115° or 120°
β^a	104° 52′	100°

[a] *cf.* Figure I.



4a **4b** **4c**

FIGURE I

III. Results and Discussion

The calculated deprotonation energies of 3 are listed in Table II. In spite of the neglect of the sulfur *d*-orbitals, a higher acidity of the α-CH bond of sulfides in comparison to the oxygen isologues has been found. Within the semi-empirical approach used the change of bonding and the relative stabilization can be explained as follows: The C–O as well as the C–S bond is weakened upon deprotonization, but the latter one less strongly. The energy-partitioning analysis reveals that the energy difference arises mainly from the atomic energy terms of the hetero atoms. This result cannot be interpreted in straight-forward terms. However, the energy difference of atomic terms is evidently related to the change of electron densities upon deprotonation. Whereas the electronegative oxygen 3a carries already a pronounced negative charge before deprotonation which upon deprotonization hardly changes, the sulfur shows striking pecularities: As the valence shell of sulfur is less occupied by electrons the electron density can significantly be enhanced upon deprotonation. In other words, the different C–H acidity can be related to the differences in atomic polarizabilities.

TABLE II

Change of deprotonation energy (in a.u.) of CH_3XH

Heteroatoms X	ΔE_{total}	ΔE_X	ΔE_{C-X}
O	1.011	−0.036	0.115
S	0.982	−0.061	0.109
ΔE^a	−0.029	−0.025	−0.006

[a] $\Delta E = E(CH_2SH^-) - E(CH_3OH^-)$

The structurally determined difference in C–H acidity between 3a and 3b ought to be strongly influenced by solvent effects. Thorough calculations of the solvent effect are very cumbersome and hard to tackle within the framework of the theoretical model used. Therefore, we simplified our estimation by using the rough continuum solvent model. Solvent

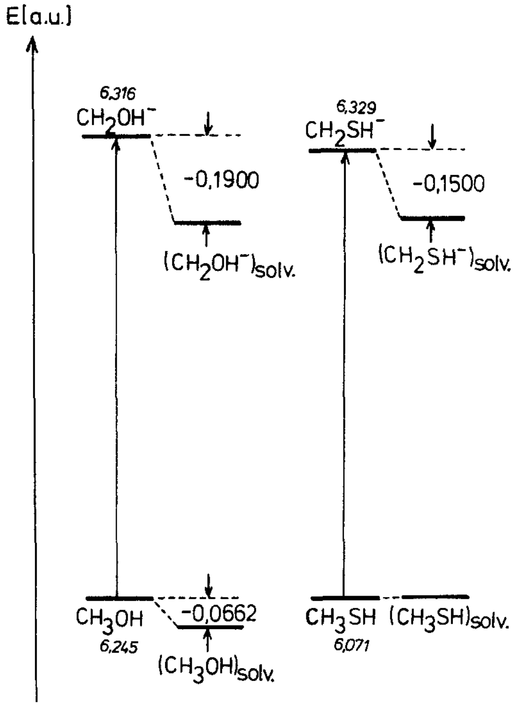


FIGURE II

stabilization energies of **3a** and **3b** have been computed employing the János equation:[15]

$$E_{\text{Solv.}} = -\left(1 - \frac{1}{D}\right)\left[\frac{1}{2}\sum_i q_i{}^2\gamma_{ii} + \sum_{i\neq j} q_iq_j\gamma_{ij}\right]$$

Where D denotes the dielectric constant and q_i the net charges of the atoms. The q_i-values as well as the electron repulsion integrals are taken from the CNDO/2-calculations. The results of this calculation is illustrated in Figure II. Accordingly the preferred deprotonation of sulfides in comparison to ethers may be reinforced by polar solvents.

IV. Conclusions

The convenient explanation of the sulfur stabilization effect on carbanions seems to be ambiguous. According to the CNDO/2 calculation this effect is due to the higher capability of the sulfur to accept electrons into the *sp*-valence shell and to the preferred solvent-carbanion stabilization rather than to 3*d*-orbital participation. This conclusion is in good agreement with results of most recent *ab initio* calculations.[9,10]

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