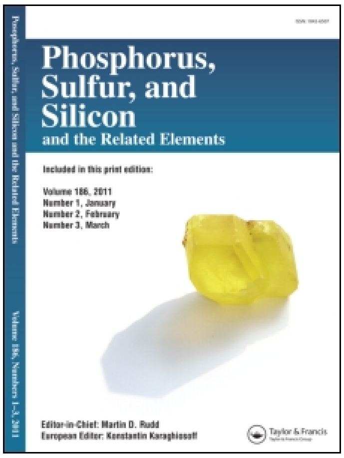

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CNDO/2-CALCULATIONS ON THE STABILIZATION OF CARBOCATIONS BY σ-BIVALENT SULFUR†

by

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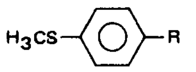
ABSTRACT

From the appearance potential measurements, groups with σ-bivalent sulfur are known to exert an unusual carbocation stabilization effect. In contrast to corresponding considerations on carbanions the 3*d* orbitals of sulfur can be invoked to rationalize this effect.

I. Introduction

As established by numerous experimental results with compounds of the type 1 the methylmercapto and mercapto group act as weaker donors than the methoxy and hydroxy group, respectively.[1] The feeble donor properties of the sulfur groups result from the low p_π-type overlap between the sulfur 3*p* and carbon 2*p*-orbitals.



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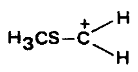

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Even solvolysis experiments on α-chlorethers and α-chlorthioethers,[2] respectively, seem to agree with the observations made above. The lower monomolecular hydrolysis rate constant of the sulfur containing compound can be interpreted by the formation of an energetically less favored carbocation, 2.

Gas phase studies, however, revealed a completely different substitutent effect.[3] From appearance potentials Taft and coworker derived an increase in carbocation stabilization following the sequence:

$$H < CH_3 < OH < SH < NH_2$$

Independently a similar conclusion has been achieved by Harrison and coworkers.[4] Also the substituent effect of halogens follows a similar pattern; the stabilization effect in the order F < Cl < Br deviates completely from the well-established donor capability found in appropriately substituted aromatic compounds.[5]

One way to rationalize these findings may consist in assuming different geometries for the carbocations of the type 2. The carbocation resulting by gas phase fragmentation may be formed by a vertical process (with geometrical relaxation). On the other hand, an adiabatic process (with geometrical relaxation) may be assumed by chemical reactions in solvents.[6] If, however, appearance potentials of sulfides determined by mass spectrometry and by photoelectron spectroscopy are compared[7] this argument seems to be dubious as the former values correspond to the adiabatic ionization potentials rather than to the vertical ones.[8]

Two other arguments seem to be more probable. Firstly, the gas phase cations are not stabilized by surrounding molecules and, consequently, contain the over-all charge completely distributed over a few atoms. It is well known that due to a 3*d* orbital contraction caused by charge effects, octet expansion is favoured. This may cause the intramolecular stabilization effect. Any solvation, however, strongly stabilizes the cations, simultaneously reducing the localized charges. In this case the condition for the *d*-orbital participation is no longer fulfilled.

Secondly, the different stabilization of the carbocations may arise completely from the solvent effect. In this case, intermolecular stabilization effects suggest peculiar electronic effects of the substituents, as sulfur-containing substituents should be less stabilized by solvent effects than oxygen-containing substituents.

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† Part XXXVIII in a series "MO-LCAO-calculations on Sulfur-containing π-Electron Systems" (for Part XXXVII see J. Fabian, P. Schönfeld and R. Mayer, following paper).

To get information about the significance of both phenomena, the following processes were investigated theoretically:

$$\underset{3}{H - CH_2 - X} \longrightarrow \underset{4}{\overset{+}{C}H_2 - X + H^-}$$

and

$$\underset{5}{Cl - CH_2 - X} \longrightarrow \underset{4}{\overset{+}{C}H_2 - X + Cl^-}$$

From the energy difference ΔE_x between the starting and final products the stabilization energy SE has been calculated by

$$SE = \Delta E_H - \Delta E_x$$

where ΔE_H denotes the energy to remove H^- and Cl^- from the unsubstituted compound 3 and 5, respectively (X = H) and ΔE_x for the substituted ones.

II. Theoretical Method and Choice of the Model Structures

For the all-valence electron calculation we employed the CNDO/2 approximation taking into account the *d*-orbitals as proposed by Santry and Segal.[9] This approach should be appropriate for order-of-magnitude calculations of sulfur-containing structures with strong 3*d*-orbital contraction as expected for sulfur atoms adjacent to positively charged carbon atoms. The preferred molecular geometry of **4** was derived by CNDO/2 calculations. Among the structures **4a**-**4c** the planar configuration **4b** is the more stable one with the C–X bond length being strongly shortened. The bond lengths and bond angles used in the calculations of stabilization energies are listed in Table I.

TABLE I

Bond lengths (in Å) and bond angles[a]

Bond	Substituent X H	CH_3	OH	SH	NH_2
R_{C-X}	1.09	1.54	1.43	1.82	1.47
R_{X-H}	1.09	1.09	0.96	1.34	1.04
R_{C^+-X}	1.09	1.48	1.30	1.76	1.30
∢HXC	109° 28′	109° 28′	104° 52′	100°	104° 52′

[a] R_{C-Cl} = 1.74 Å

III. Results and Discussion

If the *d*-orbitals are neglected, the substituent effect follows the commonly observed sequence $H < CH_3 < SH < OH < NH_2$. In spite of the strongly diminished C–S bond lengths the SH-group is a weaker donor in comparison to the OH-group. However, the donor effects of the sulfur exceed that of the oxygen if the *d*-orbitals are included.

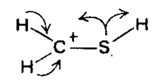
TABLE II

Calculated and experimental stabilization energies of heterosubstituted carbocations 4 (in kcal/mol^{-1})

	Substituents X in 4 H	CH_3	OH	SH	NH_2
calc.	0	22	87	60 (sp) 171 (spd)	142
exp.[a]	0	35	60	64	95

[a] Ref. 3

At the first glance this result is astonishing as empty *d*-orbitals should enlarge the acceptor rather than donor properties. A more detailed analysis of the electron occupation of the sulfur orbitals revealed that a higher electron population in the σ-type orbitals induces an increased p_π-donor effect. The overall change in the electron density may be illustrated as follows:



The increased migration of electrons to the carbon atom may be visualized in terms of the following limiting formulas:

$$\overset{+}{C}H_2 - SH \longleftrightarrow CH_2 = \overset{+}{S}H$$

However, the energy partitioning analysis of the stabilization energy reveals that the origin of the stabilization is more complicated as described by a change of charge distribution. The gain in stabilization energy arises mainly from the increase in the C–S bond energy due to the resonance term E^R_{CS} (see Table III).

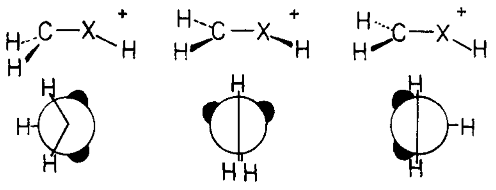
To estimate the solvent stabilization energies the equation of Jano[10] was used as described in the previous paper. The results illustrated in Figure II provided no arguments in favour of the solvent effects being responsible for the higher stabilization of the sulfur-containing cationic intermediate as compared to the oxygen-containing one. Consequently, for reasons outlined above the diminished *d*-orbital participation is considered to be responsible for the differences in reactivity in solvents compared to gas phase experiments.

TABLE III

Energy partitioning analyses

Energy contributions[a]	$\overset{+}{C}H_2SH$ [sp]	$\overset{+}{C}H_2SH$ [spd]	[spd]−[sp]
E_S^V	−16.7771	−16.3818	0.3953
E_S^J	7.5315	7.2415	−0.2900
E_S^K	−1.0283	−0.9620	0.0663
	−10.2739	−10.1023	0.1716
E_{CS}^R	−0.8039	−1.0466	−0.2427
E_{CS}^K	−0.2318	−0.2714	−0.0396
E_{CS}^J	6.2220	6.2826	0.0606
E_{CS}^V	−13.6692	−13.2669	−0.0674
E_{CS}^N	7.2160	7.2160	0.0000
	−0.7971	−1.0863	−0.2892

[a] One center contributions of sulfur E_S^U (atomic term), E_S^J (coulomb term), E_S^K (exchange term), two center contributions of the CS-bond E_{CS}^R (resonance term), E_{CS}^J (coulomb term), E_{CS} (exchange term), E_{CS}^V (electrostatic term), and E_{CS}^N (nuclear repulsion term).



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

FIGURE I

IV. Conclusions

The rough approximations and the oversimplified models used in this paper do not permit a reliable quantitative estimate on the various factors which are relevant for understanding the experimental findings. However, this theoretical study shows clearly that the relative substituent effects in carbocation stabilization in fact differ from the well-known pattern if the substituents are directly attached to the carbocation.

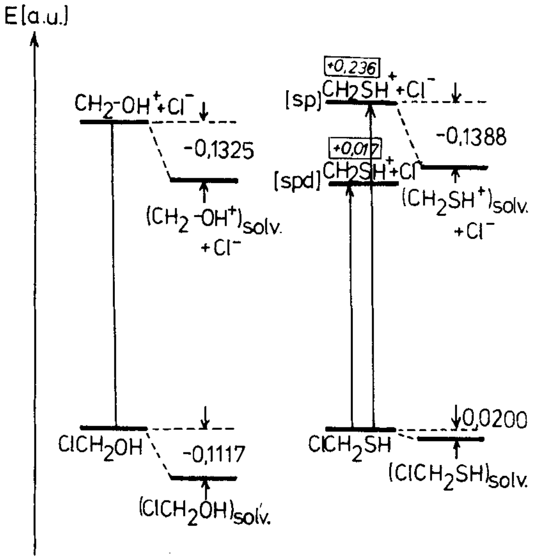


FIGURE II

The role of 3*d*-orbitals, generally negligible for σ-bivalent sulfur, may be of some importance, however, in cationic structures.

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