Different Approaching Directions of σ and π Nucleophiles to the Sulfur Atom of Thiiranium and Thiirenium Ions

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The nucleophilic attack to the charged sulfur of thiiranium and thiirenium ions has been since long postulated[1, 2] as the reverse reaction of the electrophilic addition of sulfenyl halides to alkenes and alkynes and occasionally reported.[3] Only recently this reaction has been thoroughly studied and kinetically characterized.[4, 5]

In a recent paper[6] Radom et al. have reported a theoretical investigation on the nucleophilic attack of ethylene and acetylene to the sulfur atom of unsubstituted thiiranium ($C_2H_5S^+$) and thiirenium ($C_2H_3S^+$) ions. Two transition states have been localized, corresponding to the addition of the double or triple bond along the *x* direction (pathway A) or along the *z* direction (pathway B). Pathway A is energetically favored over pathway B.

On the other hand, we have demonstrated[5] that the attack of the nucleophile dialkyl disulfide to the sulfur atom of *trans* and *cis* disubstituted thiiranium ions and of disubstituted thiirenium ion is sensitive to the substitution pattern both at sulfur and at ring carbons, and it will therefore occur along the *y* direction (shown in Figure 1), rather than along the orthogonal *x* or *z* directions. The approach along the *y* direction also assures the greatest overlap between the appropriate occupied orbital of the nucleophile and the LUMO of thiiranium or thiirenium ions (determined by ab initio calculations at the 3–21G* level): The LUMO is a Walsh-type orbital with the greatest expansion along the y direction.

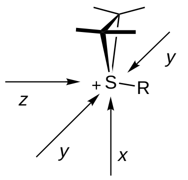

Figure 1. Orthogonal approaching directions of a nucleophile to the sulfonium sulfur of a thiiranium ion.

The results of our investigation and Radom's are only apparently at odds, and can be conciliated when we consider that disulfide is a monocentric nucleophile (interacting with σ orbitals localized at a single sulfur atom), while ethylene or acetylene are bicentric nucleophiles (interacting with π orbitals delocalized at the two unsaturated carbon atoms). The interaction diagram in Figure 2 makes the point.

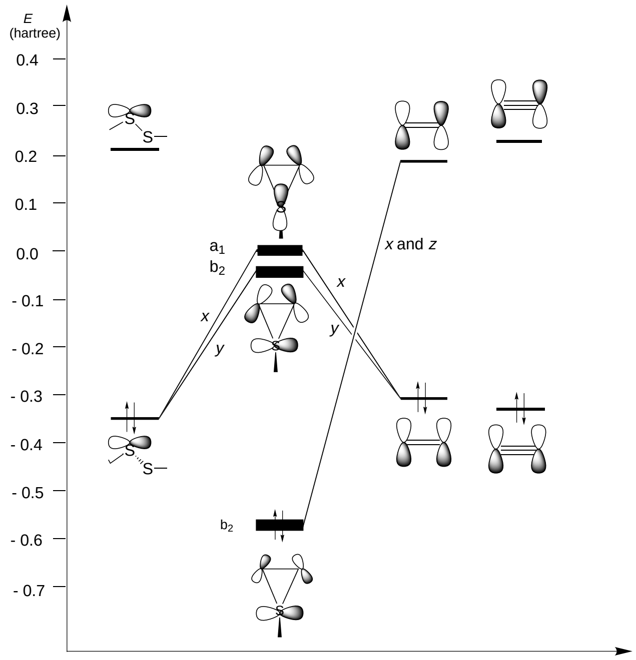

Figure 2. Interaction diagram for the attack of σ (disulfide) and π (double and triple bonds) nucleophiles to the sulfur of thiiranium and thiirenium ions. The orbital energies have been calculated on disubstituted di-*tert*-butyl-*S*-metylthiiranium and thiirenium ions. The solid bars indicate the orbital energy range of these ions.

The LUMOs of *cis* and *trans* di-*tert*-butylthiiranium ions and of di-*tert*-butylthiirenium ion (with b_2 symmetry) are similar as for shape and energy. The same is valid for the NLUMOs (LUMO+1) of thiiranium ions and for the LUMO+2 of thiirenium ion (with a_1 symmetry), as well as for the HOMOs of thiiranium ions and the SHOMO (HOMO – 1) of thiirenium ion (with b_2 symmetry). The

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HOMO and LUMO+1 of thiirenium ion are the π and π* orbitals of the endocyclic C-C double bond.

The HOMO of disulfide may interact with the b_2 LUMO of thiiranium or thiirenium ions (under energy-gap control) when the nucleophile approaches along the y direction, or with the vacant a_1 orbital (orbital-overlap control) when the nucleophile approaches along the x direction. The approach along the z direction does offer only a limited possibility of overlap. The experimental evidence points to the approach along the y direction, that is to the energy-gap control.

The case of bicentric nucleophiles represented by the π system of double and triple C–C bonds is different. The approach along the x direction is now favored by the possibility of a double interaction, between the HOMO of the nucleophile and the vacant a_1 orbital, but also between the LUMO of the nucleophile and the occupied b_2 orbital. This latter interaction is minimized, or even cancelled, in the disulfide monocentric nucleophile, because in the LUMO the atomic p orbital is almost totally engaged in the interaction with the orbitals at the adjacent atoms.

The interaction between the LUMO of the π system and the occupied b_2 orbital is possible also along the z direction. This is, however, the only interaction along this direction, and this may explain the energy difference found by Radom for A and B pathways.

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[1] a) U. Zoller, in *Small Ring Heterocycles* (Ed. A. Hassner), Wiley, New York, **1983**, p. 333; b) G. H. Schmid, D. G. Garratt in *The Chemistry of Double-bonded Functional Groups, Supplement A, Part 2* (Ed. S. Patai), Wiley, London, **1977**, p. 828.
[2] G. Capozzi, G. Modena, L. Pasquato in *The Chemistry of Sulfenic Acids and Their Derivatives* (Ed. S. Patai), Wiley, London, **1990**, p. 403.
[3] For example: a) G. H. Smidt, P. H. Fitzgerald, *J. Am. Chem. Soc.* **1971**, *93*, 2547; b) G. Capozzi, V. Lucchini, G. Modena, *Rev. Chem. Intermed.* **1979**, *4*, 347.
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[5] M. Fachini, V. Lucchini, G. Modena, M. Pasi, L. Pasquato, *J. Am. Chem. Soc.* **1999**, *121*, 3944.
[6] T. L. Solling, S. B. Wild, L. Radom, *Chem. Eur. J.* **1999**, *5*, 509.

Are the Approach Directions of σ and π Nucleophiles to the Sulfur Atom of Thiiranium and Thiirenium Ions Different?

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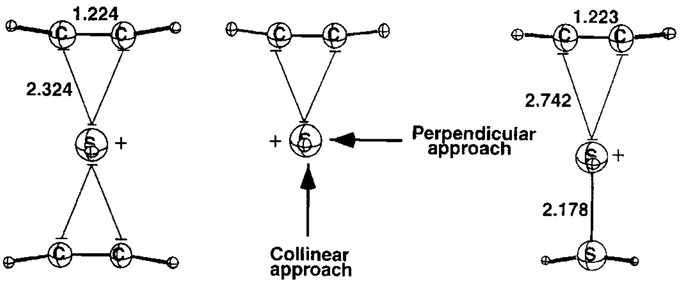
We have recently carried out a theoretical examination of nucleophilic substitution at the sulfur atom of thiiranium and thiirenium ions by the unsaturated hydrocarbons ethylene and acetylene using high-level ab initio molecular orbital calculations.[1] These reactions were found to result in π-ligand exchange and to proceed via transition structures that resemble the triple-ion configuration of the traditional S_N2 reaction at carbon ($X^- \cdots CH_3^+ \cdots X^-$), that is the transition structures are arranged so that the donor orbitals of the two π ligands and the vacant orbital at SH^+ are close to collinear (e. g. **1**). This transition structure description is consistent with that obtained from calculations for the analogous reactions of ethylene and acetylene with phosphiranium, phosphirenium, chloriranium and chlorirenium ions.[2, 3]

In an independent experimental study, Modena and co-workers examined the nucleophilic attack of dialkyl disulfides on the sulfur atom of substituted thiiranium and thiirenium ions.[4] They found that the reaction is sensitive to the substitution pattern both at sulfur and at the ring carbon atoms, from which they postulated that the nucleophile approaches in a perpendicular (rather than a near-collinear) direction (as illustrated in **2**).



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In an attempt to reconcile the apparently conflicting conclusions from the theoretical and experimental studies, Modena and co-workers have noted in the accompanying comment[5] that the theoretical study was concerned with bicentric nucleophiles whereas the experimental study was concerned with a monocentric nucleophile. From a consideration of orbital interactions in the two cases, they made the interesting observation that there is an additional interaction in the bicentric case that favors a collinear approach. Thus they concluded that the apparently different directions of nucleophilic attack could be associated with a difference in behavior between monocentric and bicentric nucleophiles.

We have, in fact, very recently carried out explicit high-level ab initio calculations on the exchange reactions of prototypical monocentric nucleophiles (specifically NH_3, H_2O, HF,

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