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The Phenylsulfenium Cation: Electronic Structure and Gas-Phase Reactivity

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Abstract: The energies and the geometries of the phenylsulfenium cation (PhS^+) in the singlet and triplet states have been optimized *ab initio* at the MP2/6-31G*//MP2/6-31G* level. The (^1A) PhS^+ state is more stable by 63.0 kJ mol^{-1} than the (^3A) PhS^+ state. The PhS^+ ion reacts in the gas-phase with ethylene and carbon monoxide affording the addition products $[PhS+CO]^+$ and $[PhS+CH_2CH_2]^+$ respectively. *Ab initio* calculations and MS/MS spectra suggest that the additions of CH_2CH_2 and CO occur at the sulfur center.

Keywords: phenylsulfenium cation; sulfenium ions; *ab initio* calculations; mass spectrometry

Sulfenium cations, that are expected to be very strong electrophiles, have never been observed in solution phase as isolated species, but have always been associated with a "carrier".[1,2] Sulfenyl chlorides are converted by silver tetrafluoroborate to chlorosulfonium salts,[3] which may be considered as sulfenium ions supported by the sulfenyl chloride carrier. Furthermore, the one electron oxidation of disulfides gives rise to disulfide radical cations, with no evidence for the formation of a free sulfenium cation.[4] However, sulfenium cations are observed in the gas phase. Thus aryl sulfenium ions are easily produced in mass spectrometry experiments from different precursors.[5,6] On the other hand, alkyl sulfenium ions are also formed in the gas-phase, but not observed as they readily rearrange by H or alkyl migration to the more stable thiocarbonyl ions.[7] Theoretical and experimental studies[8-13] have shown that the CH_3S^+ ion has the ground triplet state and that it rearranges to the more stable protonated thioformaldehyde (CH_2SH^+) with almost no activation barrier.

We report in this communication an investigation on the electronic states of the phenylsulfenium ion[14] (as prototype of arylsulfenium ions) by *ab initio* calculations at MP2/6-31G*//MP2/6-31G* level. We also report preliminary experimental studies on the gas-phase reactivity of PhS^+ toward ethylene, carbon monoxide and nitrogen as nucleophiles.

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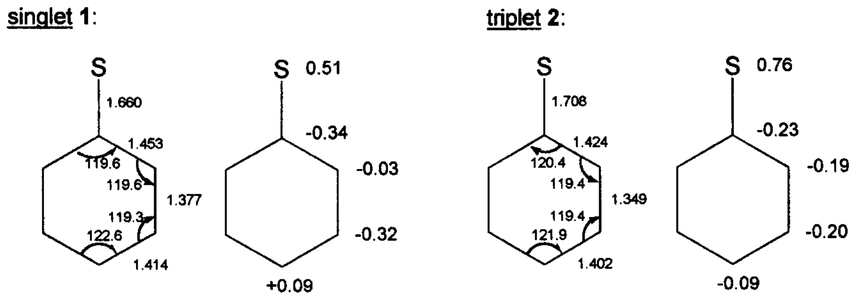
Ab initio calculations[15] of the singlet and triplet states of the PhS^+ ion at the MP2/6-31G*//MP2-6-31G* level show that the singlet state **1** is 63.0 kJ mol^{-1} more stable than the triplet state **2**. The optimized structures of **1** and **2**, together with the natural charges at the carbon and sulfur atoms are reported in Figure 1. The singlet state **1** is characterized, with respect to the triplet state **2**, by a shorter S-C bond length and by a greater charge transfer from the formally positive sulfur atom. Both features are indicative of a resonance interaction between the sulfur and the aromatic ring which is stronger in the singlet state than in the triplet state. The reciprocally orthogonal p orbitals at the sulfur atom do interact in a different manner with the orbitals of the aromatic ring. It is precisely this interaction difference that removes the degeneracy of the p orbitals and makes the singlet state more stable than the triplet state. This removal is correctly predicted at the MP2/6-31G* level, on structures optimized at the same level. The RHF/6-31G* and the MP2/6-31G*//RHF/6-31G* levels give, incorrectly, the triplet state as being more stable than the singlet state.



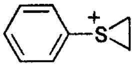
Energy: -628.1839605 hartree (0.0 kJ mol^{-1}); -628.1599989 hartree (63.0 kJ mol^{-1})

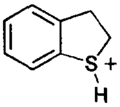
Figure 1. Optimized geometries, energies and natural atomic charges (MP2/6-31G*//MP2/6-31G*) of singlet and triplet PhS^+ configurations.

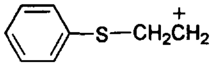
The phenylsulfenium ion has been obtained in the gas-phase from the MS/MS ionization of PhSSPh, taking advantage of the high ion abundance and easy mass selection.

The reaction of the PhS^+ ion with ethylene gives a single reaction product corresponding to the intact ion-molecule adduct $[PhS+C_2H_4]^+$ at m/z 137. The collision-induced dissociation (CID) mass spectrum of the addition product consists of a major decomposition to $[C_7H_7]^+$ (m/z 91), formally due to the expulsion of a neutral thioformaldehyde molecule, and of a second fragmentation at m/z 123, which may be associated with the loss of a CH_2 moiety.[16]

Different structures may be proposed for the adduct at m/z 137. The most plausible structure is that of thiiranium ion **3**, which is known to be more stable in the condensed phase than the open β-thiocarbenium ion.[17] Thiiraniium ion **3** is not, however, the most stable isomer with m/z 137, as shown by the series of isomers **3-6**, optimized at the RHF/6-31G*//RHF/6-31G* computational level. The loss of the CH_2 moiety may occur from any of these structures, while the loss of thioformaldehyde is best accounted for by structure **5**.



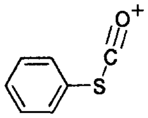




	3	**4**	**5**	**6**
Energy (hartree):	-705.4297181	-705.4495990	-705.4050292	-705.4050292
($kJ\ mol^{-1}$):	52.2	0.0	117.1	229.9

The reaction of PhS^+ with carbon monoxide affords a new ionic species at m/z 137 corresponding to the intact ion-molecule adduct $[PhS+CO]^+$. The CID mass spectrum of the addition product indicates facile CO loss, corresponding to the reverse of the addition reaction.

The structures and energies of some possible isomers of $PhSCO^+$ have been computed at the RHF/6-31G*//RHF/6-31G* level. Of the investigated isomers, only the linear isomer **7** is stable. The S-CO bond (1.682 Å) is shorter than a pure single S-C bond indicating that this is a covalent bond and not an interaction between the sulfur atom and the π electrons of the CO molecule.



7

Energy (hartree): -740.0820370

The $[PhSCO]^+$ ion was independently generated from PhSC(O)Cl[18] under electron impact conditions, isolated and fragmented by application of a tickling voltage of 110 mV. In agreement with the precedent experiment, the loss of CO was the sole decomposition channel observed, suggesting, also in the light of the similar supplementary (tickling) voltages employed, the identification of the pre-formed $PhSCO^+$ ion with the isobaric ion resulting from the ion-molecule reaction.

When the sulfenium cation PhS^+ was allowed to react with molecular nitrogen, no products derived from the ion-molecule reaction were observed, even after 0.9 s reaction time and different partial pressures of the analytes. *Ab initio* calculations carried out to establish the process energetics confirmed the instability of the hypothetical $PhS\text{-}N_2^+$ addition product. At the RHF/6-31G*//RHF/6-31G* level $PhS\text{-}N_2^+$ dissociates into PhS^+ ion and N_2 molecule. Our results contrast with those observed in solution under ordinary conditions, where the incorporation of nitrogen by arylsulfenium ion was claimed.[19] However, the effect of the solvent stabilization on these cations is not known.

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