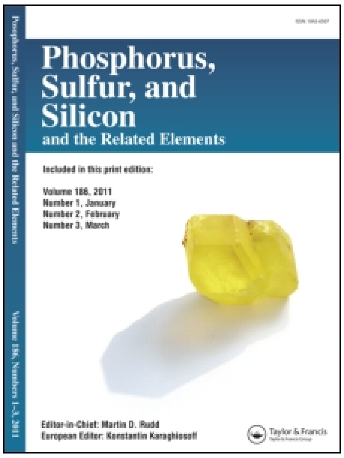

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Stability and Structure of Selenium Stabilized Carbenium Ions

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To cite this Article Hevesi, Laszlo(1992) 'Stability and Structure of Selenium Stabilized Carbenium Ions', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 155 — 168
To link to this Article: DOI: 10.1080/10426509208045833
URL: http://dx.doi.org/10.1080/10426509208045833

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 155–168

STABILITY AND STRUCTURE OF SELENIUM STABILIZED CARBENIUM IONS

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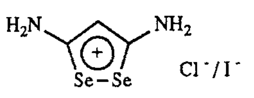
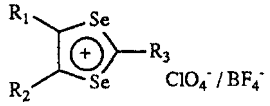
Abstract : The presently known data on reactivity, mechanistic and conformational aspects of the title species in solution are presented and discussed in relation with the corresponding oxo and thio- carbenium ions. Solid state (X-ray, XPS) as well as gas phase (ICR, ab initio MO) data of the chalcogen substituted carbocations are also compared .

While considerable effort has been devoted during the last half a century or so to the elucidation of the nature and extent of stabilization of carbocations by oxygen and sulfur substituents, the next chalcogen, selenium, has awaited untill recent years to be considered. This is most certainly due to the fact that, in contrast with oxo and thio derivatives, for longtime organoselenium compounds have not played an important role in everyday organic chemistry. It is only starting from the early 70's and following the pioneering work of a number of brilliant synthetic organic chemists that organoselenium chemistry underwent a spectacular mutation from an exotic area of science into a well mastered and highly potent methodology of organic synthesis.

The earliest examples of selenium stabilized cationic structures include 3,5-diamino-1,2-diselenolylium chloride and iodide [1] **A**, 1,3-diselenolylium salts [2-5] **B**, various methylseleno- and phenylselenocyclopropenylium salts [6-9] **C**, and 2-amino-1,3-diselenolan-2-ylium salts [10] **D** .



A



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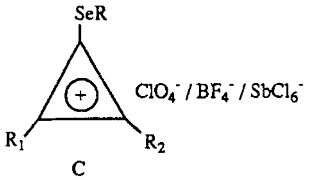

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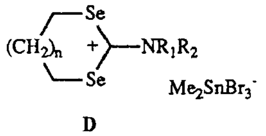


D

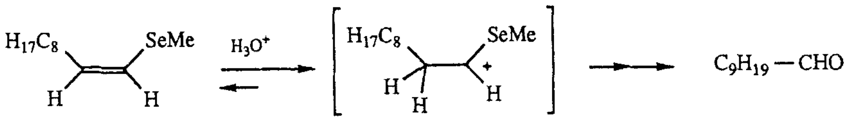
A number of Pummerer type rearrangements of aliphatic and alicyclic selenoxides have also been reported for which selenocarbenium ions have been postulated as intermediates [11-21].

Mechanistic and reactivity aspects in solution

We started to look at the latter type of species through a kinetic and mechanistic approach by investigating the acid catalyzed hydrolyses of a few vinylic selenium derivatives.

For all the methyl vinyl selenides studied [22,23] we have found i) kinetic solvent isotope effects, $k_{H_3O^+}/k_{D_3O^+}$, ranging from 1.4 to 1.8; ii) significant amount of deuterium incorporation into the unreacted vinyl selenides when the hydrolyses were carried out in the presence of heavy water; and iii) roughly the same degree of cis-trans isomerisation during hydrolysis as D incorporation [23] (Scheme 1)

Scheme 1



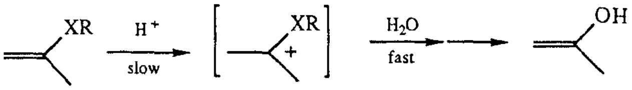
Partially reversible protonation : $k(H_2O)/k(D_2O) = 1.8$

25% D incorporation

25% cis ---> trans isomerisation

In contrast with the well established mechanism of hydrolysis of vinyl ethers [24], vinyl sulfides [25] and aryl vinyl selenides [26], the above results strongly suggest a change from rate determining irreversible protonation of the C,C double bond (Scheme 2) to a *partially reversible protonation in the case of methyl vinyl selenides and those aryl vinyl* selenides carrying a substitutent on the vinylic moiety [23].

Scheme 2



X = O, S

Se when R = Aryl

On the other hand, the following relative rates can be extracted from the existing data on the hydrolyses of vinyl chalcogenide derivatives [23,25b,26] : MeO/PhO = 133; MeS/PhS = 41; MeSe/PhSe = 15, and PhO : PhS : PhSe = 42 : 7 : 1; and their combination gives MeO : MeS : MeSe = 372 : 19 : 1. One would therefore be tempted to conclude in a logical manner that the order of stabilization of chalcogen substituted cations in solution is O > S > Se and MeX > PhX (X = O, S, Se).

As far as oxygen and sulfur are concerned, this conclusion is supported by rate data on the hydrolyses of several other types of compounds giving rise to oxo- and thiocarbenium ions as intermediates [27]. Nevertheless, exceptions to this generalization have been met with in the case of the acid catalyzed hydrolyses of dimethoxymethane and of methoxymethylthiomethane, where rate ratios less than unity have been found over a range of acid concentrations (Scheme 3), and have been rationalized by considering the differences in carbenium ion character of the transition states of the various reactions, and by taking into account the greater π-donor ability of sulfur as compared to oxygen [27].

Scheme 3

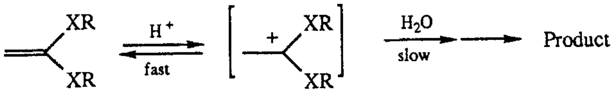
$$CH_3OCH_2-XCH_3 \xrightarrow{aq.\ H_2SO_4}$$

$$X = O, S \qquad k_O/k_S = 0.1$$

It appears thus that reactivity ratios do not necessarily reflect correctly the order of stabilization of carbocations in solution, and even if they do, the differences in stability should not exceed a few kcal/mole.

The change in mechanism examplified in Scheme 1 appears even more strikingly in the hydrolysis of ketene Se,Se-acetals which have shown inverse kinetic solvent isotope effects ($k_{H_3O^+}/k_{D_3O^+} = 0.4\text{-}0.7$), as well as essentially complete (~ 100 %) deuterium exchange at the β-position of the unreacted ketene acetals during hydrolysis [28]. These results undoubtedly point to fast preequilibrium protonation of the C,C double bond. Similar conclusions have been arrived at in the case of the hydrolyses of ketene S,S-acetals, detailed kinetic studies of which have established that the rate determining step is indeed hydration of the bis(thio)carbenium ion intermediates [29] (Scheme 4).

Scheme 4



X = S, Se

Again, this mechanism contrasts with that of the hydrolyses of ketene O,O-acetals which in turn have been shown to proceed, as vinyl ethers, [30] by the conventional A-S_E2 mechanism.

Bis(methylseleno)carbenium ions in condensed phase

We have found that trimethyl orthoselenophenylacetate reacts with triphenylcarbenium hexachloroantimonate (CH_2Cl_2/-20°C) to produce bis(methylseleno)benzylcarbenium hexachloroantimonate **E** as shiny pale yellow crystals in nearly quantitative yield. The corresponding bis(methylthio) derivative **F** could be prepared in a similar way, and it was therefore possible to carry out comparative solution NMR spectroscopic studies, as well as to determine their structures by X-ray crystallography [31].

$PhCH_2C(SeMe)_2SbCl_6$ $PhCH_2C(SMe)_2SbCl_6$

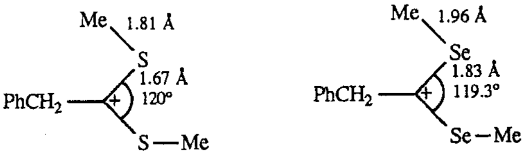
E **F**

^1H-NMR spectra of both compounds **E** and **F** (CD_3CN solution) appeared to be identical within a few hundredths of a ppm. Furthermore, the SMe and SeMe signals were found to be temperature dependent, which was attributed to hindered rotation around the C^+-SMe and C^+-SeMe bonds. The corresponding Arrhenius activation energies (14 and 13 kcal/mole, respectively) are within the range (8-15 kcal/mole) observed for various bis(methoxy)carbenium ions, suggesting significant and maybe comparable double bond characters in all three cases.

^{77}Se-NMR data of **E** and X-ray structural results of **E** and **F** quite satisfactorily corroborate this view. The broad band proton decoupled ^{77}Se NMR spectrum of **E** (CH_3CN solution at -40°C; 0.3 mol % of $Cr(acac)_3$; Me_2Se as external reference) shows two resonance lines located at 788 and 834 ppm [32] corresponding to the two selenium atoms in the unsymetrical conformation shown in Scheme 5. Comparison of these values to typical chemical shifts of selenonium salts and of selenocarbonyl derivatives [33] shows that they are compatible with partially positively charged and/or partially double bonded Se atoms as suggested for **E**.

The most important geometrical parameters of **E** and **F** as determined by X-ray diffraction are shown in Scheme 5.

Scheme 5



As expected, the atoms around the cationic carbon are arranged in planar trigonal geometry with bond angles not deviating significantly from the ideal value of 120°. Regarding the problem of cation stabilization by the neighbouring heteroatomic moieties the most relevant data are the C^+ -S and C^+-Se bond distances. Table 1 shows that these distances are very nearly halfway between C,S and C,Se single and double bond lengths.

Table 1. Bond Lenghts and Bond Orders in Oxo-, Thio-, and Selenocarbenium Ions.

bond	single	double	cation	π bond order
C—O	1.41	1.22	1.26	0.7—0.8
			1.29	
C—S	1.81	1.54	1.68	0.5
C—Se	1.98	1.67	1.84	0.5

These bond shortenings in the cations (as compared to single bonds) can be converted into bond-order changes, at least on an approximate level, by means of interpolation on bond length vs bond order plots, taken as straight lines for simplicity. In spite of all the uncertainties in the bond order values this procedure may give rise to, the data in Table 1 indicate strong interactions between the cationic carbon atom and each of the adjacent chalcogen atoms, the strongest being the C^+-oxygen interaction.

Stability and structure in the gas phase

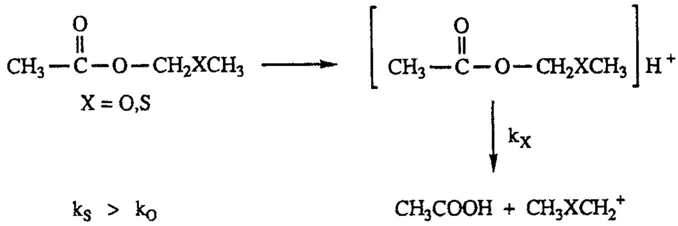
In 1965 Taft, Martin and Lampe have measured the appearance potentials of a series of substituted methyl cations, which allowed for the determination of the relative stabilization energies of these species with a precision of ± 3 kcal/mole [34]. The effects of substituents were found very large : a difference of 5 eV in the appearance potentials of $^+CH_2CN$ and $^+CH_2NMe_2$ corresponding to a difference in stabilization energies of ~ 115 kcal/mole was observed. Most remarkably, Taft et al. also found that the order of stabilization of the methyl cation by several substituents was reversed as compared to the cation stabilizing abilities of the same substituents in solution (as measured by the aromatic σ scales, for example). Among others it was found that relative to CH_3^+, $^+CH_2SH$ and $^+CH_2SCH_3$ were better stabilized than $^+CH_2OH$ and $^+CH_2OCH$ by 4 and 5 kcal/mole, respectively [34] (Scheme 6).

Scheme 6

	$^+CH_2$-X	S.E. (kcal)
X =	H	0
	OH	60
	SH	64
	OCH_3	69
	SCH_3	74

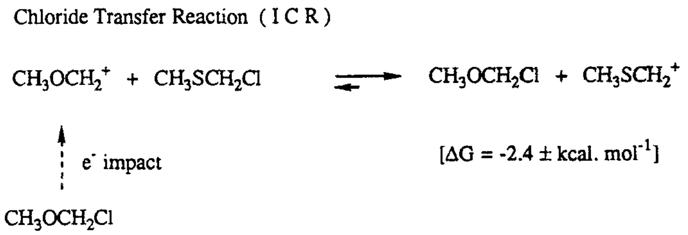
During the years, a number of other experimental, as well as computational results contributed to the establishment of the general belief that the inverse order of carbocation stabilization by chalcogen substituents (i.e. S > O) was prevailing in the gas phase as compared to the liquid phase (O > S). For example, Field and Weeks have observed that $CH_3SCH_2^+$ was formed faster than $CH_3OCH_2^+$ from the corresponding acetate or propionate precursors in a chemical ionisation mass spectrometer [35] (Scheme 7).

Scheme 7



The authors note, however, that this does not necessarily prove the greater stability of the methylthiomethyl cation [35]. While no unambiguous conclusions could be drawn from the comparison of the intensities of various $RXCH_2^+$ ions (R=H, CH_3 and X = O,S) arising from the mass spectrometric fragmentations of different precursors [36], ion cyclotron resonance measurements of chloride ion transfer equilibria by Caserio et al. were interpreted in terms of greater stability of thiocarbenium ions [37] (Scheme 8).

Scheme 8



Whereas the first, less sophisticated theoretical calculations agreed [38-41] with this conclusion, recent high level ab initio MO calculations have shown that oxygen and sulfur substituted methyl cations have very similar stabilization energies with the tendency of the formers to be even slightly more stable than the latters [42-44] (Scheme 9).

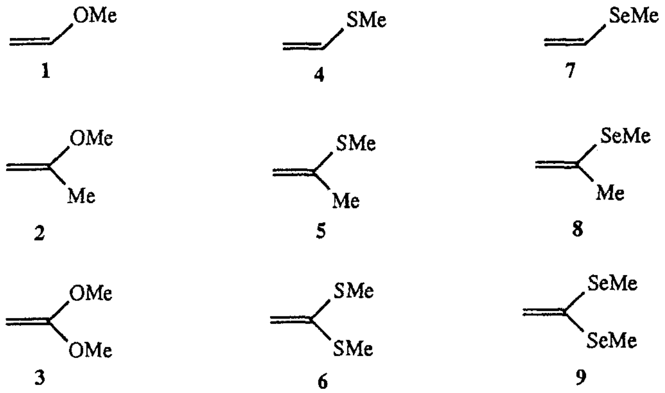
Scheme 9

$^{+}CH_2$—X	S. E. (kcal / mole)		
	a) MP2 / 6-31G*	b) MP3 / 6-31G*	c) MP4 SDTQ / 6-31G* // 6-31G*
H	0	0	0
OH	65.6	62.1	66.3
SH	63.8	59.7	64.9
OCH_3	-	72.7 (76.4)	-
SCH_3	-	73.4 (76.5)	-

a) ref. 42; b) ref. 44; c) ref. 43; d) values in parentheses include zero point energies.

In view of extending the above relative stability considerations in the gas phase to selenium substituted carbenium ions, and with the aim of contributing new data on the oxo and thio analogs, we have undertaken the determination of the gas phase basicities of a coherent set of O,S and Se substituted vinylic derivatives [45] (Scheme 10).

Scheme 10



The results of the experimentally (ion cyclotron resonance, ICR) vs. the computationally (ab initio MO, 3-21G*) derived proton affinities are represented in Figure 1.

Figure 1

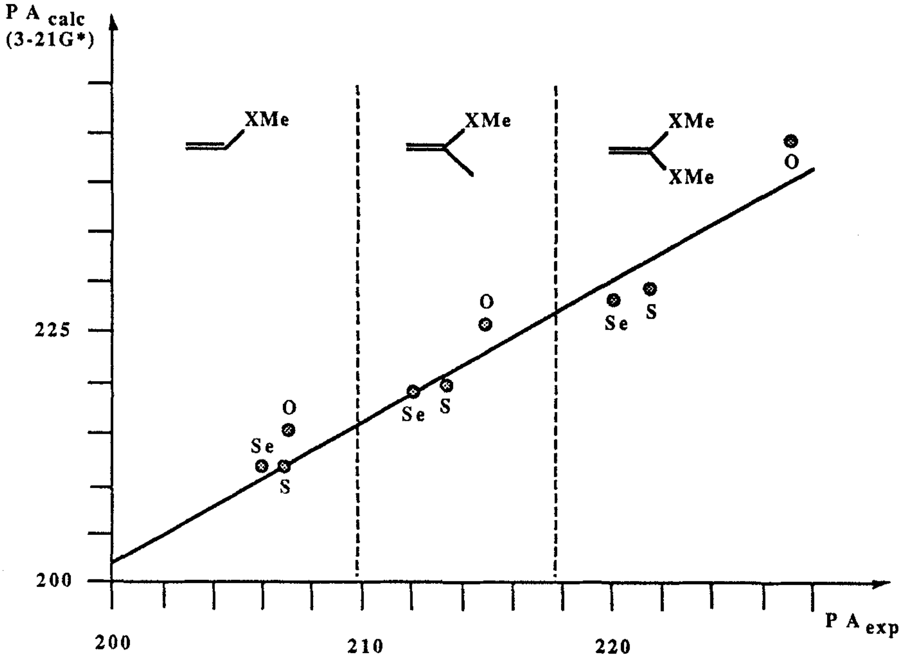


Figure 1. Correlation between experimental ($PA_{exp.}$) and theoretical (PA_{calc}) proton affinities of chalcogen-substituted vinylic derivatives.

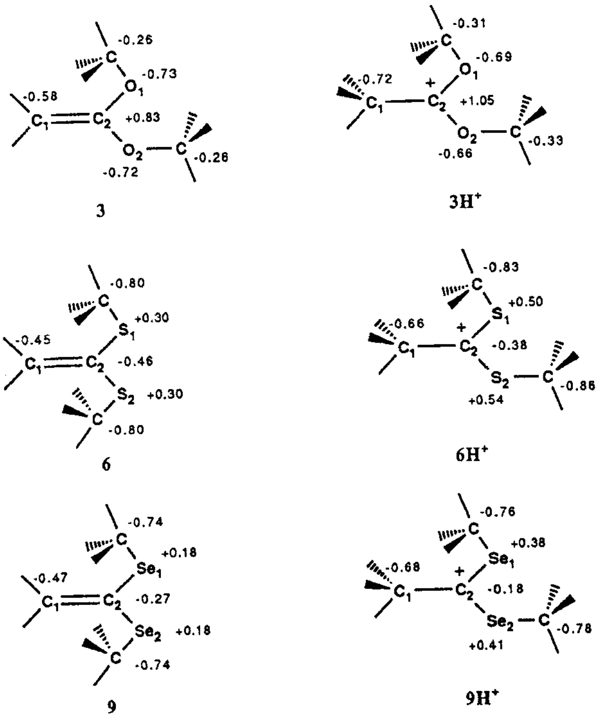
They demonstrate that i) the mono-heterosubstituted vinyl compounds **1**, **4**, **7** (Scheme 10) show very similar proton affinities, essentially indistinguishable experimentally. Therefore, the gas phase stabilization of the corresponding carbenium ions must also be comparable; ii) compounds **2**, **5** and **8**, bearing an additional α-methyl substituent, are somewhat more differentiated, so that here the oxocarbenium ion appears distinctly more stable than the corresponding S and Se species; iii) the superior cation stabilizing ability of oxygen substituents is clearly displayed in the series **3**, **6** and **9** where the bis-oxygenated cation is 5.6 kcal/mol more stable than the bis-sulfurated one, and 7.2 kcal/mol more stable than the bis-selenated species. The latter point is of particular importance since this is the first doubtless experimental evidence for oxygen substituents possessing higher intrinsic cation stabilizing ability in the gas phase than that of sulfur or selenium substituents.

In fact attention has been drawn recently to an alternative, more realistic interpretation of the I.C.R. results obtained by Caserio et al. [37] (Scheme 8) consisting of taking into account the stability of the neutral molecules which participate in the chloride transfer equilibrium [43,44]. Indeed, the well documented anomeric interaction between geminally disposed electronegative σ-acceptor and π-donnor atoms (groups) confers an extra stabilization [46] to the α-chloroether molecule on the right hand side which is much smaller or nil in the α-chlorosulfide on the left hand side. This leads to the conclusion that methoxymethyl cation should be more stable than methylthiomethyl cation [43,44].

In spite of all the necessary caution and restrictions that must be placed on the charge distributions which can be derived from MO theories, invaluable information on reactivity or spectroscopic behaviour of organic structures can often be obtained from the comparison of charge distribution patterns at least within homologous series of species.

We believe that such a comparison of the charge distribution patterns within chalcogen substituted cations can lead not only to interesting considerations about the reactivities and reaction mechanisms discussed above, but also to a novel view on the cation stabilizing abilities of and stabilization mechanism by chalcogen moieties. Charge densities on the heavy atoms as obtained by the Mulliken population analysis [47] for 1,1-dimethoxyethyl ($3H^+$), 1,1-bis(methylthio)ethyl ($6H^+$) and 1,1-bis(methylseleno)ethyl ($9H^+$) carbenium ions as well as for the corresponding ketene acetals **3**, **6** and **9** are given in Scheme 11.

Scheme 11



One can note that for all three couples of heteroatomic structures (**3**-**3H**$^+$, **6**-**6H**$^+$ and **9**-**9H**$^+$) and in an expected fashion, the C_2 charges in the cations are more positive (by 0.22, 0.18 and 0.11 charge units, respectively) than in the vinylic precursors **3**, **6** and **9**. However, because the calculated negative charges on the cationic C_2 carbon atoms of **6H**$^+$ and **9H**$^+$ are most puzzling, we thought X-ray photoelectron spectroscopic investigation of **3H**$^+$, **6H**$^+$ and **9H**$^+$ would be an appropriate means to obtain more realistic charge distribution patterns. We have therefore prepared these three carbenium ions as **3H**$^+BF_4^-$, **6H**$^+SbCl_6^-$ and **9H**$^+SbCl_6^-$ from the corresponding orthoesters. For practical reasons only the XPS spectra of the first two compounds (i.e. **3H**$^+BF_4^-$ and **6H**$^+SbCl_6^-$) could be recorded; the C1s portions of these spectra are displayed in Figures 2 and 3.

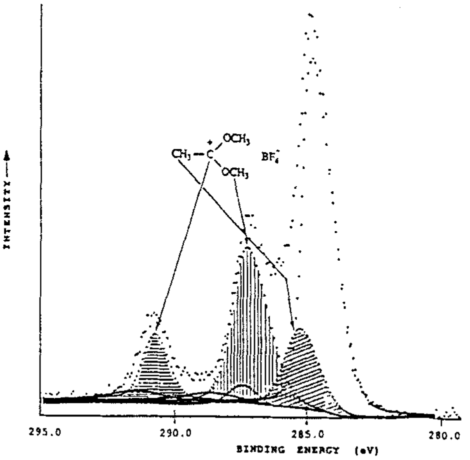


Fig 2. C 1s XPS spectrum of dimethoxy methyl carbenium tetrafluoroborate.

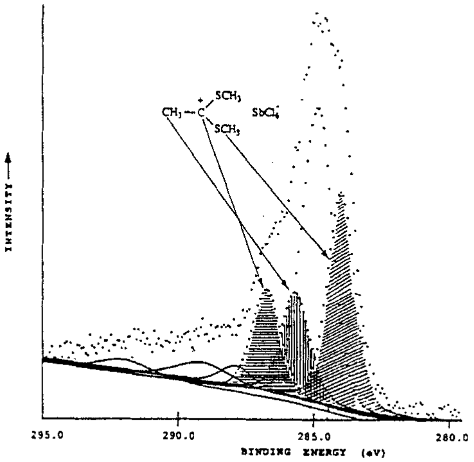
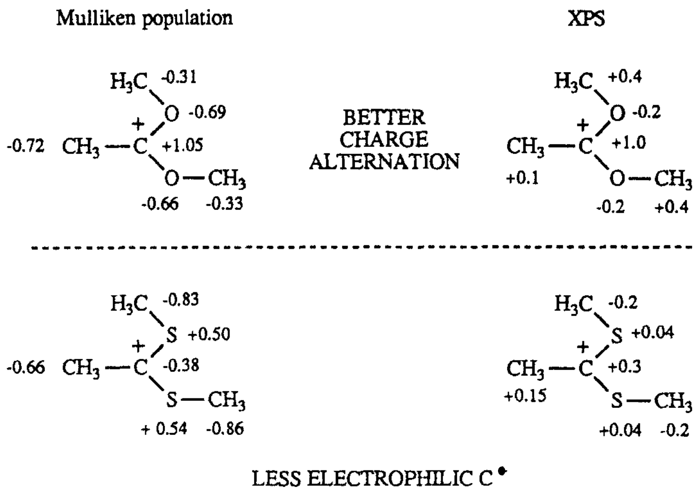


Fig 3. C 1s XPS spectrum of bis(methylthio) methyl carbenium hexachloroantimonate.

By means of the quantitative relationship which exists in the model potential approximation [48] between the binding energy of the core electrons of an atom and the electronic charge of this atom, the assigned E_b values can be converted into charge distributions [49] as shown in Scheme 12.

Scheme 12



In spite of the significant differences between the charges carried by certain atoms and determined by the Mulliken population analyses and by XPS, a great deal of convergence is also apparent : i) both methods give a unit positive charge on the C^+ of $3H^+$, whereas the C^+ of $6H^+$ carries a much smaller charge; ii) the oxygen atoms of $3H^+$ carry negative charges, while the sulfur atoms of $6H^+$ are positively charged; iii) almost perfect *charge alternation* is seen in $3H^+$, which is not at all present in $6H^+$, at least as found by XPS.

Although sulfur has a higher π-donating ability, and therefore brings about a higher degree of charge dispersal [38,39,44] than does oxygen, this factor alone is not enough to confer to sulfur a greater cation stabilizing ability [44]. The electrostatic stabilization resulting from a better charge alternation [50] in oxo-carbenium ions would compensate for the lack of charge dispersal, so that the overall stabilization of oxygen substituted cations appears to be higher (or eventually equal, depending on the actual structures) than that of sulfur (and by inference, selenium) substituted carbenium ions.

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