

metal-hydrogen  $\sigma$  bonds are slightly stronger than metal-carbon  $\sigma$  bonds. The metal-ethylene complexes, while often described similarly to metal-carbonyl complexes, actually have far different electron distributions and formal oxidation states. The results of this study give direct evidence that these systems are best described as metallacyclopropanes with formal M(V) oxidation states, in agreement with conclusions drawn from other investigations.<sup>32</sup>

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## Experimental and Theoretical Studies of the Gas-Phase Protonation of Vinyl Ethers, Vinyl Sulfides, and Vinyl Selenides

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**Abstract:** A series of nine chalcogen-substituted ethylenes (chalcogen = O, S, Se) have been synthesized, and their gas-phase proton affinities (PA) were determined experimentally by measuring gas-phase basicities (GB) in an ion cyclotron resonance (ICR) spectrometer and theoretically by means of ab initio MO calculations at the STO-3G and 3-21G\* levels. A satisfactory correlation ( $r = 0.978$ , slope = 1.41) has been obtained between the experimental and calculated 3-21G(\*) values. In contrast with a number of previous reports, we consistently found that third- (SMe) and fourth-row (SeMe) substituents do not stabilize better the adjacent positive charge than does the second-row substituent OMe, even in the gas phase. In fact, comparison of experimental proton affinity value of ethylene with that of mono(methylchalcogen)ethylenes indicates that OMe, SMe, and SeMe groups stabilize the corresponding ethyl cations to very much the same extent. In 2-propyl cations the trend is O > S > Se, but the differences ( $\delta\Delta$  in Table III) are quite small: 1.2 kcal mol<sup>-1</sup> between O and S and 1.4 kcal mol<sup>-1</sup> between S and Se. The superior ability of oxygen in carbenium ion stabilization appears the most clearly in the protonation of bis(methylchalcogen)ethylenes: dimethoxyethyl cation is more stable than the corresponding thio species by  $\sim 5.5$  kcal mol<sup>-1</sup>, whereas dithio- and diselenocarbenium ions again have very similar stabilities. These conclusions are supported and extended by ab initio results on optimized geometries.

The effects of substituents on the stability of gas-phase ions are being increasingly studied in order to distinguish the intrinsic molecular properties from the effects of the surrounding medium (solvent, etc.). From an experimental point of view, the substituent effects can be evaluated by the determination of the gas-phase basicity (GB), and hence of the proton affinity (PA), in equilibrium proton-transfer reactions. The results of these studies have been recently reviewed.<sup>2</sup>

Another approach to the evaluation of the properties of isolated systems consists of the calculation of the total energy of the systems using molecular orbital methods. The results of the latter not only can be compared to experimental results but they also provide insights into the geometries of the ionized species. Furthermore, the energy-structure relationships of the less stable species can also be investigated by the MO methods.<sup>3</sup>

The present study addresses the problem of the stabilization of carbocations by substituents containing adjacent heteroatom(s). Except for the case of enamines,<sup>4</sup> these effects have been relatively

little studied in the gas phase,<sup>5</sup> unlike the well-documented substituent effects of alkyl groups on the stability of, e.g., carbenium, oxonium, and ammonium ions.<sup>2</sup> Regarding the stabilizations of carbenium ions by group VI substituents, it has been admitted, essentially on the basis of kinetic data in solution<sup>6</sup> on one hand and mass spectrometric and ion cyclotron resonance studies<sup>5</sup> on the other hand, that  $\alpha$ -oxygen-substituted carbenium ions are more stable in solution than their  $\alpha$ -thio analogues, whereas the reverse holds in the gas phase. While early theoretical calculations<sup>7</sup> seemed to confirm the latter conclusion, higher level ab initio results obtained recently<sup>8-10</sup> have shown that second- and third-row

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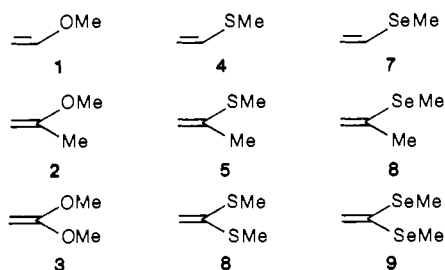
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substituents of the group VI (i.e., O- and S-moieties, respectively) possess very similar intrinsic cation-stabilizing abilities. Eventually, the ranking admitted earlier could be reversed so that the  $\alpha$ -oxocarbenium ions might be more stable than the  $\alpha$ -thio analogues even in the gas phase. This apparent discrepancy between theory and experiment has been analyzed and (at least partially) solved by Schleyer<sup>9</sup> and Apeloig<sup>10</sup> by quantitatively taking into account stabilization effects in the neutral molecules participating in some gas-phase equilibria that had been neglected before.

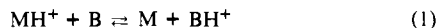
In order to enlarge the body of available data and to extend the stabilization considerations to more complex structures including fourth-row substituents, we report on measurements and calculations of proton affinity of a series of vinyl ethers (1–3), vinyl sulfides (4–6), and vinyl selenides (7–9). Experimental



results are thus provided for the first time showing that, indeed, O, S, and Se substituents display essentially the same stabilizing behavior in monohetero-substituted carbocations, whereas 1,1-dioxocarbenium ions appear significantly more stable than their thio and seleno analogues.

### Experimental Section

Gas-phase basicities were determined in an ion cyclotron resonance (ICR) spectrometer under conditions previously described,<sup>3</sup> from the equilibrium constant for the proton-transfer reactions between the compounds 1–9 (M) and the reference bases B, eq 1.  $GB(M) = GB(B) +$



$\Delta G_r$  is obtained from the measurements of the equilibrium constant for reaction 1,  $K_{eq}$ , and from the relationship  $\Delta G_r = -RT \ln K_{eq}$ , with  $T = 313$  K. At least three independent measurements were carried out for each couple M/B with pressure ratio varying in about a 5-fold range and a total pressure of about  $2-3 \times 10^{-6}$  Torr. The concentrations of the neutrals were determined from the pressure measurements of an ionization gauge. The correction for the gauge readings was estimated from the polarizability of the neutrals as explained in ref 3b.

With the exception of 2-(methylchalo)propenes 2, 5, and 8, all the compounds, i.e., 1, 3, 4, 6, 7, and 9, have been prepared by known procedures. 2-Methoxypropene (2) has been purchased from Jansen Chimica Co. (Beerse, Belgium) and distilled twice before use in the measurements.

Methyl vinyl ether<sup>11</sup> (1) has been prepared by adapting the method of McElvain and Walters described for the synthesis of ketene dimethyl acetal.<sup>12</sup> A total of 4.6 g (0.2 M) of sodium was heated and dispersed by vigorous stirring in 70 mL of dry refluxing toluene placed in a 250-mL two-necked flask equipped with a dropping funnel and fitted for distillation. A toluene (30 mL) solution of 16.9 g (0.1 M) of 1,1-dimethoxy-2-bromoethane was added dropwise through the funnel, and the distilling methyl vinyl ether was collected in a cooled ( $-78$  °C) flask. The crude product was cold-distilled from room temperature to  $-78$  °C to give 4.4 g (76%) of 1 as a colorless liquid. <sup>1</sup>H NMR ( $CCl_4$ ,  $\delta$ , TMS): 3.48 (s, 3 H), 3.77–4.17 (m, 2 H), 6.40 (dd,  $J = 7, 14$  Hz, 1 H).

Methyl vinyl sulfide<sup>13,14</sup> (4) and methyl vinyl selenide<sup>14</sup> (7) have been prepared by the method of Brown and Moggridge<sup>13</sup> except for the synthesis of the starting materials 2-bromoethyl methyl sulfide and 2-bromoethyl methyl selenide, which were obtained by addition of methylsulfenyl bromide or methylselenenyl bromide to ethylene.<sup>15</sup> <sup>1</sup>H

NMR ( $CCl_4$ ,  $\delta$ , TMS): (4) 2.20 (s, 3 H), 4.87 (d,  $J = 16$  Hz, 1 H), 5.10 (d,  $J = 10$  Hz, 1 H), 6.37 (dd,  $J = 10, 16$  Hz, 1 H); 2.08 (s, 3 H), 5.20 (d,  $J = 16$  Hz, 1 H), 5.60 (d,  $J = 10$  Hz, 1 H), 6.60 (dd,  $J = 10; 16$  Hz, 1 H).

2-(Methylthio)propene (5) and 2-(methylseleno)propene (8) have been prepared from the corresponding thio- and selenoacetals. To a cooled ( $-40$  °C) solution of 10.4 g (40 mM) of tin tetrachloride in 80 mL of dry dichloromethane were added slowly 4.08 g (40 mM) of triethylamine followed by 4.09 g (30 mM) of 2,2-bis(methylthio)propane dissolved in 10 mL of dichloromethane, also introduced slowly (15 min) by a syringe. After another 15 min of reaction the mixture was diluted with 100 mL of ether, warmed to room temperature and filtered through Celite. The solution was washed several times with aqueous copper sulfate, once with saturated bicarbonate, and once with brine and dried over potassium carbonate. The solvents were distilled off, and spinning band distillation of the residue gave 1.1 g (40%) of 5 as a pale yellow liquid (bp 69 °C at atmospheric pressure). <sup>1</sup>H NMR ( $CCl_4$ ,  $\delta$ , TMS): 1.97 (s, 3 H), 2.20 (s, 3 H), 4.47 (s, 1 H), 4.90 (bs, 1 H). In the same way, 6.9 g (30 mM) of 2,2-bis(methylseleno)propane gave 0.8 g (20%) of 8 (bp 98–101 °C at atmospheric pressure). <sup>1</sup>H NMR ( $CCl_4$ ,  $\delta$ , TMS): 2.10 (s, 6 H), 4.77 (s, 1 H), 5.30 (bs, 1 H).

1,1-Dimethoxyethylene (3) has been obtained according to McElvain and McKay,<sup>16</sup> whereas 1,1-bis(methylthio)ethylene<sup>17,18</sup> (6) and 1,1-bis(methylseleno)ethylene (9) have been synthesized by a method described recently.<sup>19</sup> <sup>1</sup>H NMR ( $CCl_4$ ,  $\delta$ , TMS): (3) 2.96 (s, 2 H), 3.55 (s, 6 H); (6) 2.30 (s, 6 H), 5.15 (s, 2 H); (9) 2.20 (s, 6 H), 5.74 (s, 2 H).

### Results

**A. Gas-Phase Basicity.** The GB values for compounds 1–9 determined in the equilibrium proton transfer, eq 1, are reported in Table I. Although no systematic determination of the forward and backward rate constants was attempted, we noticed that in some cases the protonation rate was too slow for the equilibrium to be attained during the observation time (usually 1 s). This was mainly due to the small amount of fragment ions (which act as efficient proton donors) formed in the ionization process by electron impact. In those cases, a small amount (ca.  $3 \times 10^{-6}$  Torr) of methane was added to serve as a source of protons via the secondary methane ions  $CH_5^+$  and  $C_2H_5^+$ . In the extreme case of compound 9, only bracketing experiments could be performed.

**B. Theory.** Hartree-Fock ab initio calculations were made for the neutral (1–9) and protonated ( $1H^+ - 9H^+$ ) compounds. All computations were performed with the GAUSSIAN 82 series of programs<sup>20</sup> adapted for an FPS-164 processor attached to an IBM 4341 computer. The standard threshold conditions of the GAUSSIAN 82 program have been kept:  $10^{-10}$  au for the two-electron integrals and  $10^{-9}$  for the requested convergence on the density matrices. Gradient optimization techniques<sup>21,22</sup> have been employed to optimize fully the geometries of the bases (1–9) and their corresponding protonated species ( $1H^+ - 9H^+$ ). To examine the dependence of the results upon the atomic basis, two different sets of calculations were performed: one with the minimal STO-3G basis<sup>23</sup> (hereafter referred to as basis set I) and the split-valence 3-21G(\*) basis<sup>24</sup> (II). The 3-21G(\*) basis is a flexible

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**Table I.** Gas-Phase Basicity (GB) of Vinyl Derivatives 1–9

M	B	GB(B) <sup>a</sup>	$\Delta G_r^b$	GB(M) <sup>c</sup>
		200.1	-1.4	198.8
		198.7	0.1	206.2 <sup>d</sup>
	<i>n</i> -Pr <sub>2</sub> NH	219.2	-0.3	
	Me <sub>2</sub> NEt piperidine	218.8 217.3	0.1 1.5	218.8
		200.1	-1.3	
		198.7	-0.1	198.6
		198.8	-0.3	
		206.2	-0.9	
		205.5 <sup>e</sup>	-1.0	205.0
		204.0	1.0	
		215.0	-1.5	
		212.9	0.2	
	<i>t</i> -BuNH <sub>2</sub>	212.9	0.4	
		212.6	0.4	
	<i>i</i> -Pr <sub>2</sub> O	198.7	-1.1	197.6
		197.5	0.1	
		204.0	-0.5	203.4
		202.7 <sup>f</sup>	0.6	
	<i>s</i> -BuNH <sub>2</sub>	212.1		211.60 ± 0.5 <sup>g</sup>
		212.0		
	<i>n</i> -C <sub>5</sub> H <sub>11</sub> NH <sub>2</sub>	211.2		
	<i>i</i> -BuNH <sub>2</sub>	211.1		
	<i>n</i> -PrNH <sub>2</sub>	210.1		

<sup>a</sup> Taken from ref 2 unless otherwise indicated. Reference value, GB(NH<sub>3</sub>) = 196.7 kcal mol<sup>-1</sup>. <sup>b</sup>  $\Delta G_r$  is the free energy change for reaction. <sup>c</sup> ±0.2 kcal mol<sup>-1</sup> unless otherwise indicated (deviation on the experimental determination of  $\Delta G_r$ ). <sup>d</sup> Value from: Maquestiau, A.; Jortay, C.; Beugnieux, D.; Flammang, R.; Houriet, R.; Rolli, E.; Bouchoux, G. *Origine et Structure d'Ions C<sub>4</sub>H<sub>9</sub>O<sup>+</sup>* Issus de la Méthylation de l'Acétone par l'Iodométhane Ionisé. *Int. J. Mass Spectrom. Ion Processes* **1988**, in press. <sup>e</sup> Value from: Houriet, R.; Rolli, E.; Bouchoux, G.; Hoppilliard, Y. *Helv. Chim. Acta* **1985**, *68*, 2037. <sup>f</sup> Taken from ref 28b. <sup>g</sup> The equilibrium was found to be extremely slow with this compound; its GB was thus bracketed using the reference bases quoted.

and convenient medium-sized basis, which incorporates d orbitals on third- and fourth-row atoms such as sulfur and selenium. Geometry optimizations have been conducted starting with unsymmetrical structures. Various conformers have been obtained, but in this work we only report on the most stable structures, which turn out to be the planar ones. It is beyond the scope of the present paper to consider the other (less stable) gauche structures that have been obtained during the optimization procedure. The neutral as well as the protonated systems considered in this work have very limited symmetry, and no attempt to use group theory has been made.

**Table II.** Total Energies  $E_T$  (au) and Theoretical (PA<sub>calcd</sub>) and Experimental (PA<sub>exptl</sub>) Proton Affinities (kcal mol<sup>-1</sup>)

molecule	$E_T$		PA <sub>calcd</sub>		PA <sub>exptl</sub>
	STO-3G	3-21G*	STO-3G	3-21G*	
<b>1</b>	-189.49700	-190.85530	265.4	215.1	207.2
<b>1H<sup>+</sup></b>	-189.91986	-191.19806			
<b>4</b>	-508.84194	-512.08832	264.3	211.2	207.0
<b>4H<sup>+</sup></b>	-509.26308	-512.42494			
<b>7</b>	-2489.22070	-2505.10975	256.0	211.4	206.0
<b>7H<sup>+</sup></b>	-2489.62868	-2505.44661			
<b>2</b>	-228.08444	-229.68207	276.0	225.6	214.6
<b>2H<sup>+</sup></b>	-228.52427	-230.04164			
<b>5</b>	-547.42595	-550.91126	273.36	219.63	213.4
<b>5H<sup>+</sup></b>	-547.86156	-551.26126			
<b>8</b>	-2527.80470	-2543.93253	265.12	219.07	211.8
<b>8H<sup>+</sup></b>	-2528.22720	-2544.28164			
<b>3</b>	-301.92311	-304.11603	293.56	243.94	227.2
<b>3H<sup>+</sup></b>	-302.39093	-304.50478			
<b>6</b>	-940.60476	-946.56902	290.2	229.7	221.6
<b>6H<sup>+</sup></b>	-941.06725	-946.93509			
<b>9</b>	-4901.36174	-4932.61560	278.17	229.64	220.0
<b>9H<sup>+</sup></b>	-4901.80504	-4932.98155			

Due to the complexity of the systems and computer limitations, we have not attempted in this study to take into account correlation and zero-point vibrational energy corrections. On the basis of other results in the context of proton affinity and gas-phase basicity calculations,<sup>3b</sup> we tend to believe that the above-mentioned corrections will not impair the trends and the resulting conclusions. In the case of the zero-point vibrational energy corrections, it is generally observed that they are reasonably constant for similar bonds. As will be argued later on in this work, the protonation takes place on the  $\beta$ -carbon, and thus, in the case of our series of compounds, the zero-point vibrational energy corrections should mainly arise from the  $\beta$ -C(sp<sup>2</sup>)  $\rightarrow$   $\beta$ -C(sp<sup>3</sup>) change. As estimated from the harmonic vibration model, these corrections fall in the range of 5–10 kcal mol<sup>-1</sup>. Since they generally tend to decrease the PA values, they would in fact improve the agreement between theoretical and experimental data reported in this work. The question is not as clearcut for correlation energy corrections since it is not possible to predict their sign and magnitude on the basis of simple arguments, and thus the question remains open.

The most relevant geometrical parameters of the SCF-optimized molecular structures of the neutral and protonated species obtained with the two basis sets are given in Figures 1 and 2, respectively.<sup>25</sup> Corresponding total energies and theoretical proton affinities PA<sub>calcd</sub>, estimated as the difference between total energies of the protonated and the neutral molecule, are given in Table II. Also given in this table are the experimental proton affinities PA<sub>exptl</sub>. They are deduced from the measured GB values (Table I) corrected for the translational entropy of the free proton (7.9 kcal mol<sup>-1</sup>) and for free rotation appearing on protonation of the double bond (0.5 kcal mol<sup>-1</sup>).<sup>26</sup> Figure 3 shows the correlation between experimental and theoretical proton affinities.

In a preliminary note,<sup>27</sup> STO-3G-optimized geometries of the neutral and protonated oxygen- and sulfur-containing systems **1–6** have been reported. A reasonable agreement was noticed with existing theoretical and experimental data on related molecular structures. It can be observed in Figures 1 and 2 that the trends in the 3-21G(\*) equilibrium geometries remain similar to those predicted with the STO-3G basis. However there are differences worth pointing out. For instance, in the case of the neutral systems the C<sub>1</sub>–C<sub>2</sub> bond distance obtained with STO-3G is more dependent on the substitution than 3-21G(\*). This is particularly true for the sequence of compounds substituted with two XMe groups, i.e., **3**, **6**, and **9**. Nevertheless, the predicted relative orientation

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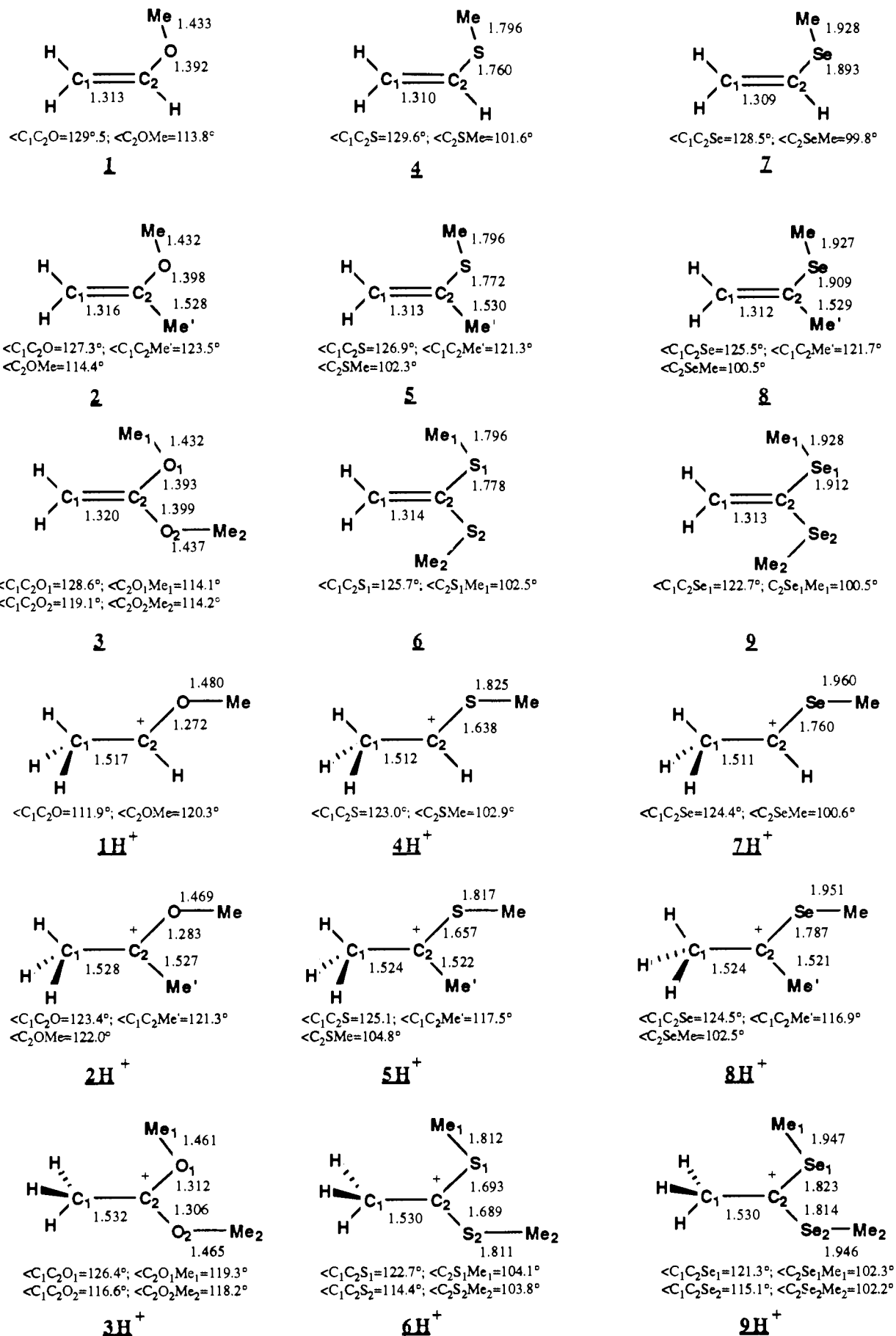


Figure 1. Bond lengths and bond angles of the STO-3G equilibrium geometry of the neutral and protonated species.

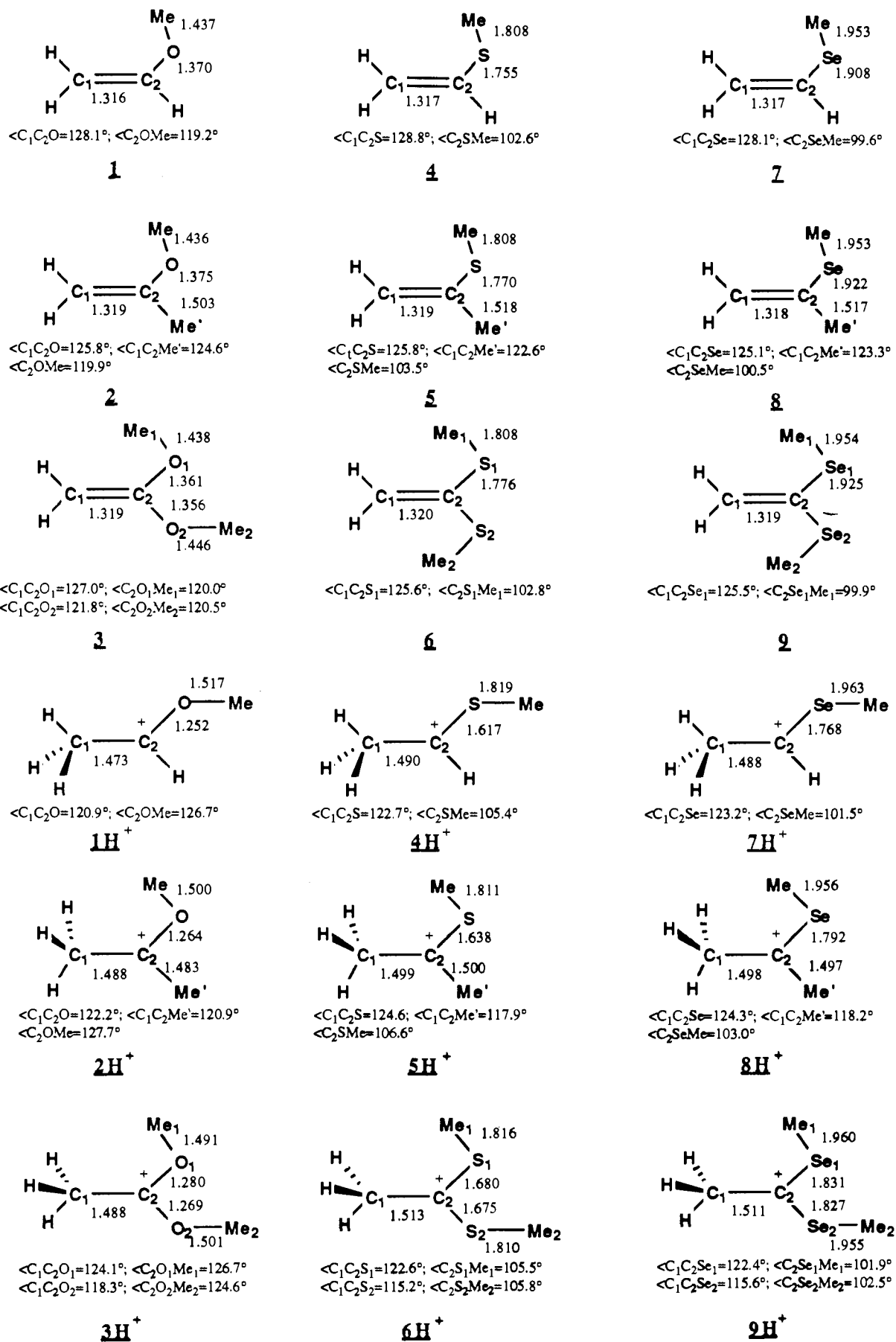


Figure 2. Bond lengths and bond angles of the 3-21G\* equilibrium geometry of the neutral and protonated species.

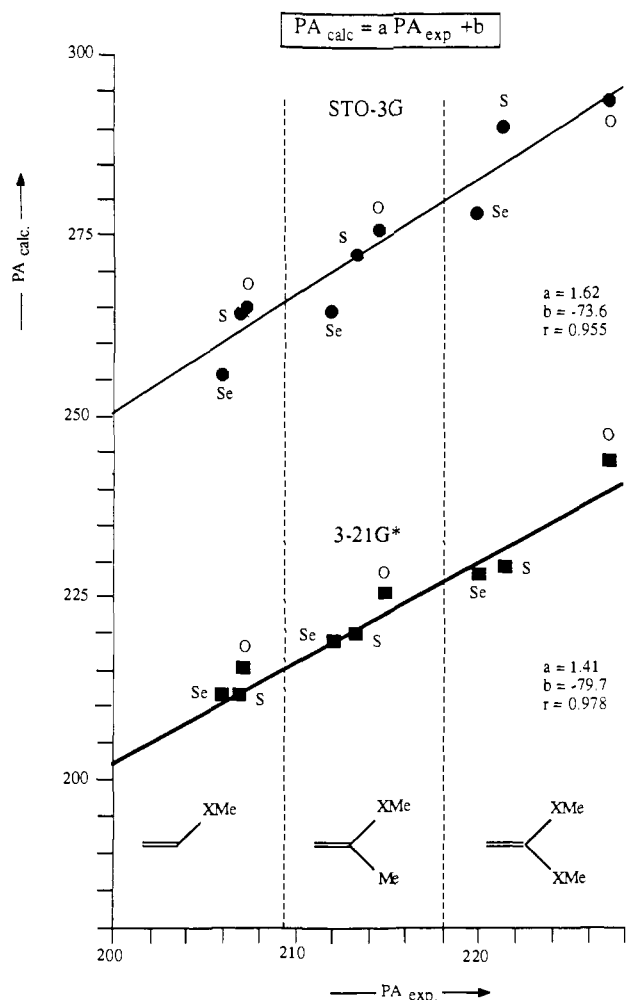


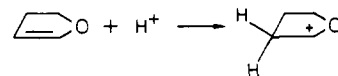
Figure 3. Linear least-squares fit between theoretical ( $PA_{\text{calc}}$ ) and experimental ( $PA_{\text{expt}}$ ) proton affinities ( $\text{kcal mol}^{-1}$ ).  $r$  is the correlation coefficient.

in space and bond angles of the substituents on the  $C_2$  atom are totally similar in both bases. In the case of the carbocations, the spatial orientation of the substituents on the  $C_2$  atom is also very similar in both bases with the exception of  $8H^+$ . Most important deviations occur for the  $C_1$ - $C_2$  bond distance of oxygen-containing compounds; the 3-21G(\*) value is shorter than that of STO-3G by 0.04 Å. In spite of these differences, it is justified to conclude that both basis sets yield similar trends, and thus qualitatively consistent predictions on the relative stability are expected for the carbocations considered.

In order to ascertain that the calculated energy values do indeed correspond to the measured species and thus that considerations about geometries are pertinent, it is important to address first of all the question of the site of protonation in the ethylenic derivatives 1-9. A priori gas-phase protonation may occur either on the heteroatoms of 1-9 or on the  $\beta$ -carbon atom of the olefinic double bonds ( $C_1$  in Figures 1 and 2). As a matter of fact, we do not have any direct experimental evidence regarding the site of protonation. Nevertheless, it is reasonable to admit that this takes place at  $C_1$  of 1-9 for the following reasons:

(i) Previous work on the basicity of enamines<sup>4</sup> has established that protonation occurs at the  $\beta$ -C atom. These conclusions are supported by the effect of methyl substituent, i.e., substitution on the  $\alpha$ -C increases the PA by about 7  $\text{kcal mol}^{-1}$ , whereas the effect is minor ( $\leq 2 \text{ kcal mol}^{-1}$ ) for Me substitution on the  $\beta$ -C atom. This is in accordance with the structure of the carbenium ion formed after  $\beta$ -protonation (the charge resides in the  $\alpha$ -position where the stabilizing effect of the methyl group is largest).

(ii) Similarly, gas-phase protonation of 1,2-dihydrofuran has been proved experimentally to occur on  $C_3$ , i.e., in  $\beta$ -position.<sup>28</sup>



(iii) We have checked theoretically that  $C_1$  is indeed the preferred site of protonation by comparing the total energies of the fully optimized structures performed both at the STO-3G and 3-21G(\*) levels on methyl vinyl ether (1), methyl vinyl sulfide (4), and methyl vinyl selenide (7) protonated on the heteroatom and on  $C_1$ . The relevant geometrical parameters and the total energies corresponding to fully optimized structures are given in Figure 4. In the case of 3-21G(\*) geometry optimizations for methyl vinyl sulfide (4) and methyl vinyl selenide (7), it has been impossible to obtain a minimum for torsion angles (their related eigenvalues in the Hessian matrix being negative). Accordingly, an asterisk has been added to their total energy symbol,  $E_{\text{T}}^*$ , in Figure 4. First to notice is that all the  $C_1$ -protonated molecules are significantly more stable than the corresponding ones protonated on the heteroatom. The predicted energy difference between the  $C_1$  and the corresponding heteroatom protonated compounds is 23.8, 51.6, and 51.4  $\text{kcal mol}^{-1}$  [STO-3G] and 12.0, 41.7, and 43.8  $\text{kcal mol}^{-1}$  [3-21G(\*)] for methyl vinyl ether (1), methyl vinyl sulfide (4), and methyl vinyl selenide (7), respectively. Compared to the neutral forms, the optimized geometry of the molecules protonated on the heteroatom shows less stabilizing interaction in the  $[\text{C}_1\text{C}_2\text{XHM}e]^+$  skeleton between the double bond and the heteroatom: on the one hand the  $C_1$ - $C_2$  distance is shorter than that in the neutral form and, on the other hand, the  $C_2$ -X distance has increased quite substantially.

In the case of available crystalline analogues of  $3H^+$ ,  $6H^+$ , and  $9H^+$ , for which X-ray crystal structure determinations have been made, the excellent agreement observed between experimentally<sup>29</sup> and theoretically derived geometries also supports the view that protonation occurs at the  $\beta$ -carbon atom. Finally, the good correlation (Figure 3) existing between experimental,  $PA_{\text{expt}}$  and theoretical,  $PA_{\text{calc}}$ , proton affinities increases not only the confidence in  $C_1$  as the preferred site of protonation but also the validity of the theoretical prediction of the relative stability of the carbocations  $1H^+$ - $9H^+$ .

It is interesting to point out that, because of the drastic structural changes occurring in the carbocations  $1H^+$ - $9H^+$  compared to those of the neutral form 1-9, electrostatic potential maps are not appropriate for predicting the site of protonation. As observed in Figure 5, at a distance of 1.60 Å from the molecular plane the electrostatic potential contours suggest that the heteroatom is the preferred protonation site. In practice, away from the molecule the path followed by the proton is mainly determined by the electrostatic interactions with the heteroatom, but closer to the molecule geometry relaxation takes place to ensure better stability and drive the proton to  $C_1$ .

## Discussion

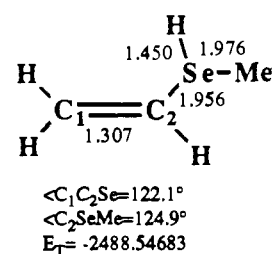
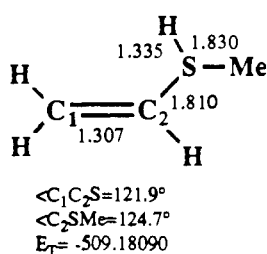
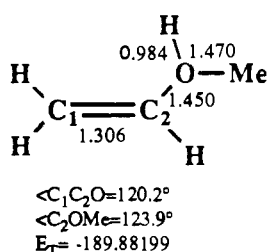
In this section we analyze the experimental and theoretical results to understand the effects of substituents on the stability of the protonated species  $1H^+$ - $9H^+$ . In order to limit the discussion and because they correlate somewhat better with experimental results, we only consider the 3-21G\* data in the following, unless otherwise indicated. The values of the proton affinities are taken from Table II.

**A. Vinyl Oxo-, Thio-, and Selenoethers.** The experimental basicity of these three analogues differs only slightly, the oxo compound 1 being more basic than the thio compound 4 by 0.2  $\text{kcal mol}^{-1}$  only, whereas vinyl selenoether 7 is less basic by about 1  $\text{kcal mol}^{-1}$ . 3-21G(\*) results also yield small basicity differences, with 1 being more basic than both 4 and 7 by 3.9  $\text{kcal mol}^{-1}$ ; the thio and seleno analogues 4 and 7 have nearly identical proton affinities. Thus theory exaggerates somewhat the relative basicity

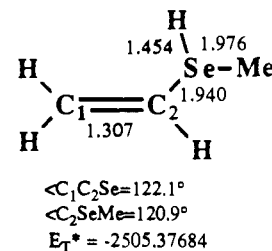
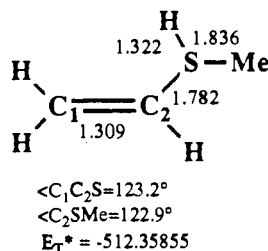
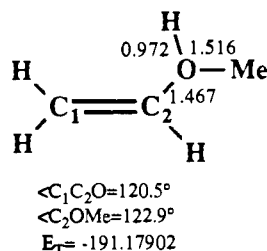
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## a) STO-3G



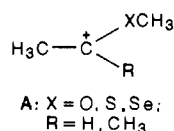
## b) 3-21G(\*)



**Figure 4.** Relevant fully optimized, STO-3G and 3-21G(\*), structural parameters for **1**, **4**, and **7** protonated on the heteroatom. Total energies  $E_T$  in atomic units.

of the oxo compound and does not distinguish between the thio and seleno derivatives.

Considering that protonation of the vinyl derivatives occurs on the  $\beta$ -carbon atom to form ethyl cations A, our results stand in



apparent contrast with those of the existing reports<sup>5</sup> on the relative abilities of oxygen and sulfur substituents to stabilize an adjacent positive charge in the gas phase. However, this divergence almost completely disappears if we consider that (i) due to the uncertainties in stabilization energies of  $\text{HOCH}_2^+$ ,  $\text{HSCH}_2^+$ ,  $\text{MeOCH}_2^+$ , and  $\text{MeSCH}_2^+$  measured by Taft et al.<sup>5a</sup>, the observed differences of 4–5 kcal mol<sup>-1</sup> between oxo and thio species might in fact be reduced by as much as 2–3 kcal mol<sup>-1</sup> and thus come to close agreement with our values, (ii) the higher intensities of thiocarbenium ions compared to those of oxocarbenium ions observed in mass spectrometric studies<sup>5c,d</sup> most probably arise from factors other than better stabilization of the formers compared to the latters (see discussion in ref 5d and 10), and (iii) the exothermicity of the equilibrium favoring  $\text{CH}_3\text{SCH}_2^+$  over  $\text{CH}_3\text{OCH}_2^+$  observed in chloride ion transfer reactions measured by ICR<sup>5e</sup> has been shown<sup>9,10</sup> to be due to differences in anomeric stabilization between the neutrals  $\text{CH}_3\text{SCH}_2\text{Cl}$  and  $\text{CH}_3\text{OCH}_2\text{Cl}$ .

It may therefore be proposed that, in contrast with previous interpretations, carbenium ion stabilization by group VI substituents in the gas phase is roughly the same when only one heteroatomic substituent such as OMe, SMe, or SeMe is attached to the positive carbon. This is further visualized in Table III where proton affinities of ethylene and propene are compared to those of heterosubstituted ethylenes and propenes. One can see that replacement of an  $\alpha$ -hydrogen atom in ethyl cation by an XMe group brings about an extra stabilization ( $\Delta$ ) of 48.2, 48.0, and 47.0 kcal mol<sup>-1</sup> when X = O, S, and Se, respectively. It seems unrealistic to assign definite significance to the small differences between these values.

**B. 2-Methoxy-, 2-(Methylthio)-, and 2-(Methylseleno)propenes.** Theoretically, compounds **2**, **5**, and **8** having a methyl substituent on the  $\alpha$ -carbon are predicted to be more basic than **1**, **4**, and **7**. The corresponding stabilization energies are calculated as 10.5, 8.25, and 7.7 kcal mol<sup>-1</sup>, in agreement with the ICR measure-

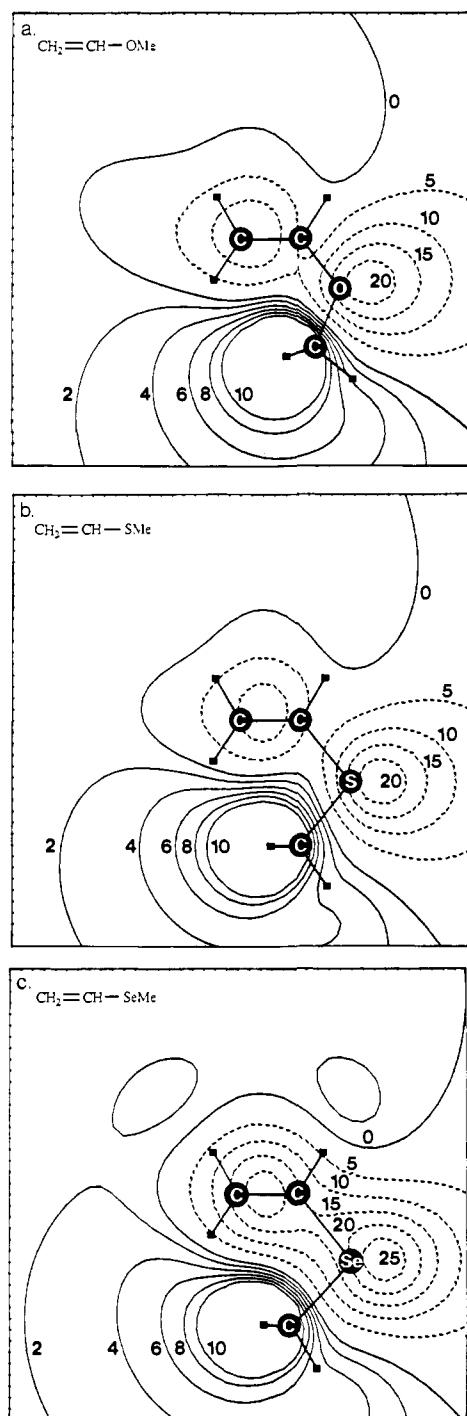
**Table III.** Proton Affinities (PA, kcal mol<sup>-1</sup>) of Ethylenes  $\text{CH}_2=\text{CH}_n(\text{XMe})_{2-n}$  and Propenes  $\text{CH}_2=\text{C}(\text{Me})\text{XMe}$

compd	X					
	O		S		Se	
	PA	$\Delta$	PA	$\Delta$	PA	$\Delta$
$\text{CH}_2=\text{CH}_2^a$	159		159		159	
$\text{CH}_2=\text{CHXMe}$	207.2	48.2	207	48	206	47
$\text{CH}_2=\text{C}(\text{XMe})_2$	227.2	20	221.6	14.6	220	14
$\text{CH}_2=\text{CHMe}^a$	182		182		182	
		32.6		31.4		30
$\text{CH}_2=\text{C}(\text{Me})\text{XMe}$	214.6		213.4		212	

<sup>a</sup> Taken from: Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Heron, J. T.; Draxl, K.; Field, F. H. *Ionisation Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions*; NSRDS-NBS, U.S. Government Printing Office: Washington DC, 1969. Quoted by: Long, J.; Mason, B. *J. Am. Chem. Soc.* **1973**, *95*, 2427.

ments, which show that the introduction of a methyl substituent on the  $\alpha$ -carbon as in **2**, **5**, and **8** stabilizes the resulting carbenium ions by 7 kcal mol<sup>-1</sup>, approximately. This difference is close to the effect of  $\alpha$ -methyl substitution in the enamine series,  $\text{GB}[\text{CH}_2=\text{C}(\text{Me})\text{NH}_2] - \text{GB}[\text{CH}_2=\text{CHNH}_2] = 6.3$  kcal mol<sup>-1</sup>.<sup>4b</sup> Concerning the effect of the heteroatom, the same trend in the evolution of the GB values of **2**, **5**, and **8** is observed as with compounds **1**, **4**, and **7**. However, an increased difference in GB can be noted, methoxypropene (**2**) being more basic than the methylthio compound **5** by 1.2 kcal mol<sup>-1</sup> and **5** being more basic than seleno analogue **8** by 1.4 kcal mol<sup>-1</sup>. Notice that theory again predicts a significantly larger basicity for the oxo compound and closer values for the thio and seleno derivatives.

**C. 1,1-Dimethoxy-, 1,1-Bis(methylthio)-, and 1,1-Bis(methylseleno)ethenes.** The  $\alpha$ -substitution by an additional XMe group as in **3**, **6**, and **9** shows a dramatic increase in GB. This effect is particularly spectacular in the dimethoxy compound **3**, the ICR measurements giving it to be more basic than the thio and seleno analogues **6** and **9** by 5.6 and 7.2 kcal mol<sup>-1</sup>, respectively. Thus the effects in the thio and seleno compounds are seen to be unchanged when going from the methyl-substituted systems **5** and **8** to the **6** and **9** analogues. Here again, theory predicts the same effects: **3**, **6**, and **9** are the most basic entities of the nine molecules studied in this work. The dimethoxy compound **3** is calculated to be more basic than the thio and seleno analogues



**Figure 5.** 3-21G\* molecular electrostatic maps for **1** (a), **4** (b), and **7** (c) at a distance of 1.6 Å from the molecular plane. Energies are in kilocalories per mole. Positive (negative) contours are indicated by a solid (dashed) line.

**6** and **9** by 14.2 and 14.3 kcal mol<sup>-1</sup>, respectively.

As seen in Table III, replacement of two  $\alpha$ -hydrogen atoms by two XMe groups does not lead to similar stabilization energies for the three heteroatoms. When X = S and Se, the additional stabilizing effect of the second XMe group is 14.6 and 14.0 kcal mol<sup>-1</sup>, respectively. It is interesting to observe that in the oxo derivative the second methoxy group leads to a significantly higher additional stabilization energy, 20 kcal mol<sup>-1</sup>. Our calculational results, which are in the line with these conclusions for **1**, **4**, and **7** and **2**, **5**, and **8**, suggest that the level of theoretical description chosen here is adequate to interpret the differences in the behavior of **3** compared to **6** and **9**. Also, since theoretical and experimental results obtained in this work are generally well correlated (Figure 3), we feel confident in using other aspects of the calculations to

analyze the origin of this more efficient stabilization of the di-substituted carbocation. In contrast, we note that previously published theoretical calculations<sup>7,8</sup> on the stabilization of  $\alpha$ -substituted methyl cations have shown that the differences between the stabilization energies of oxygen and sulfur are small.

It was already pointed out that protonation on C<sub>1</sub> leads to drastic changes in the geometries. The most important is in the C<sub>1</sub>-C<sub>2</sub> bond, initially a double bond, which tends to increase in length to a distance typical of a C-C single bond. The oxygen substituents turn out to be quite effective in keeping this bond length shorter. In 3H<sup>+</sup> the C<sub>1</sub>-C<sub>2</sub> bond length is identical with that in 2H<sup>+</sup>. Compared to their neutral parents, the C<sub>2</sub>-XMe distance shrinks the most in the monosubstituted compounds (1H<sup>+</sup>, 4H<sup>+</sup>, 7H<sup>+</sup>), the less in those containing two heteroatoms (3H<sup>+</sup>, 6H<sup>+</sup>), 9H<sup>+</sup>, while the C<sub>1</sub>-C<sub>2</sub> bonds in the carbocations with a methyl group on the C<sub>2</sub> atom (2H<sup>+</sup>, 5H<sup>+</sup>, 8H<sup>+</sup>) have intermediate lengths. This situation prevails irrespective of the nature of the heteroatom. However, the X-Me bond is, comparatively to the thio and seleno compounds, more affected in the oxygen series upon going from the neutral molecule to the protonated form. This pattern of geometry relaxations suggests that oxygen compounds make a better use of the methyl part of the methoxy group to redistribute the extra charge brought by the proton. In other words one could argue that stabilizing hyperconjugation effects are still mediated through the oxygens while sulfur and selenium atoms interrupt that effect. In 3H<sup>+</sup> the coupling of the two methoxy groups and the methyl group formed by the protonation enhances the stabilization of the carbocation. The theoretical results show that geometry relaxation plays a significant role in ultimate stability of the cation. They also stress that it may be too naive to explain the stabilization effects of heteroatoms by only considering their nature, since other groups (here the methyl group) can participate in the whole stabilization process. Therefore, the structural changes cannot be overlooked. This interpretation of the cooperative role of oxygen and methyl fragments of the methoxy groups in 3H<sup>+</sup> also finds support in the data provided by Lossing.<sup>30</sup> Figure 2 of ref 30 shows indeed that the replacement of a hydroxy by methoxy and ethoxy groups in various oxygen-stabilized alkyl cations brings about additional stabilizations of 7–12 kcal mol<sup>-1</sup> for each step (i.e., OH → OMe and OMe → OEt), whereas the extra stabilization gained on extending by one CH<sub>2</sub> unit the alkyl chain of 1-hydroxy-1-ethyl and 2-hydroxy-2-propyl cations is only 7 and 5 kcal mol<sup>-1</sup>, respectively. Our observations fit with the warning already made by Bernardi et al.<sup>7</sup> in 1975 on the danger of interpreting the relative stabilization of a reactive center by different adjacent heteroatoms only in terms of their  $\pi$ -donating abilities.

### Conclusion

Experimental and theoretical determinations of gas-phase basicities of the nine vinyl ethers, vinyl sulfides, and vinyl selenides **1–9** show that protonation occurs on the  $\beta$ -carbon. Except in the case of **3**, and in remarkable parallel with condensed-phase properties,<sup>29</sup> the differences in the cation stabilization energies (gas-phase basicities) by the three heteroatoms O, S, and Se are small. The classical interpretation of the basicity (hence of carbenium ion stabilization) in terms of the  $\pi$ -donating ability is not really appropriate; it is necessary to take into account other contributions such as the possibility for the molecular structure to relax.

Further studies, both experimental and theoretical, along these lines are in progress on the mixed (O, S; O, Se; S, Se) compounds to search for further demonstration of these conclusions.

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tional Suisse is also gratefully acknowledged. We express our appreciation to G. Baudoux and Dr. D. Vercauteren for their help in obtaining the electrostatic potential energy maps.

**Registry No.** 1, 107-25-5; 1H<sup>+</sup>, 51624-53-4; 2, 116-11-0; 2H<sup>+</sup>, 41798-19-0; 3, 922-69-0; 3H<sup>+</sup>, 81876-12-2; 4, 1822-74-8; 4H<sup>+</sup>, 64840-96-6; 5, 7594-44-7; 5H<sup>+</sup>, 85838-78-4; 6, 51102-74-0; 6H<sup>+</sup>, 105384-19-8;

7, 76573-19-8; 7H<sup>+</sup>, 120991-14-2; 8, 114659-08-4; 8H<sup>+</sup>, 120991-15-3; 9, 99030-02-1; 9H<sup>+</sup>, 90195-92-9.

**Supplementary Material Available:** The full set of 3-21G(\*)-optimized geometrical parameters for compounds 1-9 and 1H<sup>+</sup>-9H<sup>+</sup> (4 pages). Ordering information is given on any current masthead page.

## Production of Hydrated Metal Ions by Fast Ion or Atom Beam Sputtering. Collision-Induced Dissociation and Successive Hydration Energies of Gaseous Cu<sup>+</sup> with 1-4 Water Molecules<sup>1</sup>

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Contribution from the Center for Structure and Reactivity, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712-1167. Received September 8, 1988

**Abstract:** Low-temperature sputtering of frozen aqueous solutions of metal salts, of hydrated crystalline transition-metal salts, of frosted metal surfaces, and of frosted metal salts with kiloelectronvolt energy rare gas atoms or ions produces copious amounts of cluster ions, among which M<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> and/or M<sup>+</sup>OH(H<sub>2</sub>O)<sub>n</sub> frequently dominate. Variable-energy collision-induced dissociation of these ions in a triple quadrupole mass spectrometer yields the successive gas-phase solvation energies. Several known hydration and bond energies have been reproduced, and the first and second hydration energies of the Cu<sup>+</sup> ion have been determined as 35 ± 3 and 39 ± 3 kcal/mol, respectively. It is concluded that gaseous Cu<sup>+</sup> prefers dicoordination.

In recent years many ligand-metal ion bond dissociation energies and enthalpies have been measured by thermodynamic equilibrium,<sup>2-4</sup> ion beam,<sup>5,6</sup> FT-ICR collision-induced dissociation,<sup>7</sup> and photodissociation methods.<sup>8</sup> However, reported energies of

weak inorganic ligand-metal ion bonds remain relatively scarce and are limited to the hydrates<sup>2</sup> and ammoniates<sup>3a</sup> of alkali-metal cations and their complexes with sulfur dioxide,<sup>3b,4a</sup> hydrates of Ca<sup>+</sup>,<sup>3c</sup> Sr<sup>+</sup>,<sup>3d</sup> and Pb<sup>+</sup>,<sup>3f</sup> and some of the hydrates and ammoniates of Bi<sup>+</sup>,<sup>3a,3e</sup> Cu<sup>+</sup>, and Ag<sup>+</sup>.<sup>4</sup> These ligated metal cations were generated by thermionic metal ion sources<sup>4c</sup> in high-pressure mass spectrometers. Recently, sputtered ions have been used in place of the thermionic metal ion sources in high-pressure mass spectrometers under conditions suitable for making weak ligand-metal ion complexes.<sup>9</sup> For applications where a continuous metal ion source is not necessary, other techniques, notably pulsed laser desorption and ionization,<sup>10,11</sup> produce a wide variety of metal ions and metal clusters.

In the present paper, we describe the use of fast atom or fast ion bombardment of selected substrates for the production of copious amounts of hydrated and/or hydroxylated transition-metal ions and cluster ions. The use of these sources is a logical extension of prior reports of large cluster ion formation upon ion bombardment of frozen ammonia<sup>12</sup> and water,<sup>12,13</sup> as well as other

(1) Much of the work was performed in the Chemistry Department of the University of Utah in Salt Lake City, UT. The results were reported in part at: *Book of Abstracts*; 30th ASMS Annual Conference, Honolulu, June 1982; p 695. 19th National Meeting of the American Chemical Society, New York, NY, April 13-18, 1986; American Chemical Society: Washington, DC, Abstract No. PHYS 93.

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