smaller effect than E and C predicts. There very likely is a "window" of bond strengths in which the log of the stretching force constant changes in the adduct can be fit to E and C. For very weak adducts, E and C probably overestimates the covalent perturbation to the existing bonds, causing these systems to miss the predictions of the correlations. The calculated and experimental results in CCl_4 for the Et_2S adduct of 4-fluorophenol are also in conflict as the calculated entropy is $\sim$10 eu too large. This may be due to complexation of the solvent with this donor[8] as well as the effect described above.

The changes we have observed in the E and C fits of entropies and free energies are seen to be reasonable when compared to physical models for these effects. Furthermore, we have demonstrated that in order to obtain a free energy correlation with an E and C type of model the condition is that both the enthalpy and entropy fit an equation of the E and C form. It is not necessary that ΔS be a linear function of ΔH, for linearity would be require that ΔH and ΔS have the same C_A/E_A ratio. We emphasize that ΔG correlations should only be carried out with data from a given solvent that does not interact with the reagent being varied (donors in the above case). Even under these conditions the discussion given indicates why exceptions may still occur in ΔG fits.

Acknowledgment. We acknowledge the partial support of this research by the National Science Foundation.

Registry No. Iodine, 7553-56-2; 4-fluorophenol, 371-41-5.

Rearrangement and Fragmentation Processes in the Methanethiol and Dimethyl Sulfide Radical Cations

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Abstract: Ab initio molecular orbital calculations with large, polarization basis sets and incorporating electron correlation have been used to examine aspects of the CH_3S^+, $CH_4S^{+\cdot}$, and $C_2H_6S^{+\cdot}$ potential-energy surfaces. Detailed comparisons are drawn with corresponding CH_3O^+, $CH_4O^{+\cdot}$, and $C_2H_6O^{+\cdot}$ systems. The most stable CH_3S^+ ion is clearly the mercaptomethyl cation, CH_2SH^+ (**1**). Triplet thiomethoxy cation, CH_3S^+ (**2**), lies significantly higher in energy, while singlet thiomethoxy cation (**3**) is found to rearrange without activation energy to CH_2SH^+. For the $CH_4S^{+\cdot}$ system, the calculations reveal two stable isomeric ions, namely, the well-known methanethiol radical cation, $CH_3SH^{+\cdot}$ (**5**), and the recently discovered methylenesulfonium radical cation, $CH_2SH_2^{+\cdot}$ (**6**). The latter is calculated to lie 76 kJ mol^{-1} higher in energy than **5**, with a barrier to rearrangement to **5** of 114 kJ mol^{-1}. Both **5** and **6** will form CH_2SH^+ upon loss of H·. Examination of the relevant part of the $C_2H_6S^{+\cdot}$ potential-energy surface establishes a rearrangement–dissociation mechanism for the production of CH_3S^+ ions of structure CH_2SH^+ from ionized dimethyl sulfide, $CH_3SCH_3^{+\cdot}$ (**10**). This involves initial formation of a sulfonium ion intermediate, $CH_2SHCH_3^{+\cdot}$ (**11**), which subsequently undergoes simple bond cleavage. The CH_2SH^+ ion produced via this process has little excess energy. The intermediate sulfonium ion (**11**) lies 82 kJ mol^{-1} above $CH_3SCH_3^{+\cdot}$ (**10**), with a barrier to rearrangement to **10** of 120 kJ mol^{-1}, and represents a new, stable $C_2H_6S^{+\cdot}$ isomer.

Introduction

For many years, there has been considerable interest in the ionization and subsequent fragmentation of organosulfur compounds. The ion which has probably attracted most attention is CH_3S^+.[2-15] Earlier studies considered two structural isomers: CH_3S^+, thought to be generated[2-4,6-8] by ionization and fragmentation of alkyl methyl sulfides (CH_3S–R), and CH_2SH^+, thought to be generated[5-9] by ionization and fragmentation of alkane thiols (R–CH_2SH). In this way, CD_3SH was considered[6,7] to produce both ions, viz., CD_3S^+ and CD_2SH^+, by H· and D· loss, respectively. The heats of formation ($\Delta H_f{}^\circ{}_{298}$) of CH_3S^+ and CH_2SH^+ were reported[6] to be 895 and 920 kJ mol^{-1}, respectively.

However, recent studies[10-15] have cast doubt on the existence of an ion with the CH_3S^+ structure of energy similar to that of CH_2SH^+. The key observation was made by McLafferty and co-workers,[10,16] who combined the techniques of collisional-activation mass spectrometry and ab initio molecular orbital theory to investigate the CH_3S^+ and CH_3O^+ systems. Contrary to expectations, they found that, on fragmentation at low ionizing-electron energies, the dimethyl sulfide and dimethyl ether radical cations ($CH_3XCH_3^{+\cdot}$, X = S, O) yield the mercaptomethyl and

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Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) for Components of the $CH_4S^{+}\cdot$ and $C_2H_6S^{+}\cdot$ Systems[a]

	H·	CH_3^{+} $^1A'$ (D_{3h})	HS· $^2\Pi$ ($C_{\infty v}$)	$CH_2^{+}\cdot$ $^2A_1$ (C_{2v})	H_2S $^1A_1$ (C_{2v})	$CH_3\cdot$ $^2A_2''$ (D_{3h})
3-21G//3-21G	−0.496 20	−39.009 13	−396.118 46	−38.347 47	−396.704 67	−39.342 61
4-31G//4-31G	−0.498 23	−39.175 13	−397.617 87	−38.512 57	−398.204 12	−39.504 97
6-31G//4-31G	−0.498 23	−39.216 21	−398.040 25	−38.553 89	−398.627 54	−39.546 66
6-31G**//4-31G	−0.498 23	−39.236 27	−398.067 92	−38.570 52	−298.674 24	−39.564 44
MP2/6-31G//4-31G	−0.498 23	−39.280 76	−398.081 57	−38.598 04	−398.689 07	−39.621 71
MP3/6-31G//4-31G	−0.498 23	−39.293 80	−398.089 24	−38.608 80	−398.699 85	−39.634 46
ZPVE	0.0	87.0	15.5	45.0	39.6	78.1

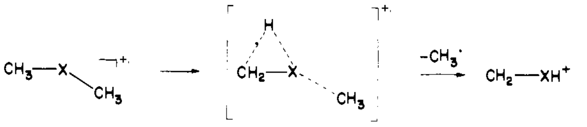
[a] 4-31G geometrical parameters are: CH_3^{+}, r(C–H) = 1.076; HS·, r(H–S) = 1.364; CH_2^{+}, r(C–H) = 1.078, ∠HCH = 141.7°; H_2S, r(H–S) = 1.353, ∠HSH = 95.7°; $CH_3\cdot$, r(C–H) = 1.070.

Table II. Experimental Heats of Formation ($\Delta H_f{}^{\circ}{}_0$, kJ mol^{-1}) for the CH_3S^{+}, $CH_4S^{+}\cdot$, and $C_2H_6S^{+}\cdot$ Ions and Component Systems

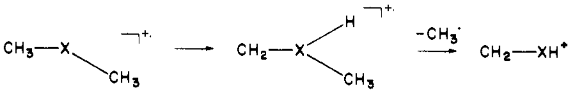
species	$\Delta H_f{}^{\circ}{}_0$	species	$\Delta H_f{}^{\circ}{}_0$
CH_2SH^{+}	870[a]	H·	216[b]
$CH_3SH^{+}\cdot$	899[b]	$CH_2^{+}\cdot$	1398[b]
$CH_2SH_2^{+}\cdot$	925[c]	H_2S	−18[b]
$CH_3SCH_3^{+}\cdot$	817[b]	CH_3^{+}	1095[b]
$CH_2{=}S$	99[d]	HS·	142[b]
H^{+}	1528[b]	$CH_3\cdot$	146[b]

[a] Reference 15. [b] Reference 51. [c] Based on $\Delta H_f{}^{\circ}{}_{298}$ = 916 kJ mol (ref 20c), corrected to 0 K by using calculaed vibrational frequencies (see text). [d] Based on a proton affinity for $CH_2{=}S$ of 757 kJ mol^{-1} (ref 14), and $\Delta H_f{}^{\circ}{}_0$ values for CH_2SH^{+} and H^{+} (ref 51).

hydroxymethyl cations (CH_2XH^{+}), respectively, rather than the thiomethoxy or methoxy cations (CH_3X^{+}). They proposed[10,16] that such a fragmentation occurs via an intramolecular displacement reaction:


(1)

In fact, recent ab initio calculations[17] have indicated that, in the case of the dimethyl ether radical cation, the fragmentation is likely to proceed by way of a closely related two-step mechanism (eq 2, X = O):


(2)

In the first step, a 1,2-hydrogen shift converts $CH_3OCH_3^{+}\cdot$ into an oxonium ion, $CH_2OHCH_3^{+}\cdot$. This oxonium ion was found to lie slightly lower in energy than $CH_3OCH_3^{+}\cdot$ and was proposed as a new, stable $C_2H_6O^{+}\cdot$ isomer. Loss of a methyl radical from $CH_2OHCH_3^{+}\cdot$ yields CH_2OH^{+}, the ion observed by McLafferty et al.[16]

The oxygen analogue of methanethiol is methanol, and recent ab initio calculations[18] have shown that for the ionized $CH_4O^{+}\cdot$ system there are two distinct stable isomers, viz., the methanol radical cation ($CH_3OH^{+}\cdot$) and the methylenoxonium radical cation ($CH_2OH_2^{+}\cdot$). The latter was predicted to be lower in energy by about 45 kJ mol^{-1}. Subsequent experimental studies[19,20] have verified the existence of the methylenoxonium ion as a stable isomer of the methanol radical cation. The experimental studies[20] also indicated the existence of the methylenesulfonium ion ($CH_2SH_2^{+}\cdot$) as a stable isomer of the methanethiol radical cation ($CH_3SH^{+}\cdot$).

In this paper, we report the results of moderately high-level ab initio calculations on the CH_3S^{+} ions and two radical-cation systems from which these ions may be produced, viz., $CH_4S^{+}\cdot$ and $C_2H_6S^{+}\cdot$. There have been a number of previous semiempirical[21] and ab initio[10,22-24] studies of the CH_3S^{+} system, although the latter have been restricted to the Hartree–Fock level with small, nonpolarization basis sets. To our knowledge, no theoretical studies of the $CH_4S^{+}\cdot$ and $C_2H_6S^{+}\cdot$ systems have yet been reported. In the calculations presented here, fully optimized geometries are used throughout, and, in order to ensure reliable energy comparisons, calculations using polarization basis sets and incorporating electron correlation have been performed. In particular, an attempt is made to answer the following questions: (i) Are the mercaptomethyl (CH_2SH^{+}) and thiomethoxy (CH_3S^{+}) cations likely to be observable, distinct ions, and do they have distinguishable heats of formation? (ii) What are the structures and relative energies of the methanethiol ($CH_3SH^{+}\cdot$) and methylenesulfonium ($CH_2SH_2^{+}\cdot$) radical cations, and what is the nature of the potential-energy surface linking these isomers and their fragmentation products? (iii) Is there a stable sulfonium ion in the $C_2H_6S^{+}\cdot$ system analogous to the $C_2H_6O^{+}\cdot$ oxonium ion $CH_2OHCH_3^{+}\cdot$? (iv) Can we provide a plausible mechanism to account both for the observation[10] of CH_2SH^{+} from dissociation of $CH_3SCH_3^{+}\cdot$ and for the observed thermochemistry[2,4,6,10] of this reaction?

Method and Results

Standard ab initio molecular orbital calculations have been carried out using a modified[25] version of the Gaussian 80 system of programs.[26] Geometries of equilibrium structures and transition structures have been determined at the Hartree–Fock (HF) level using analytical gradient procedures and the split-valence 4-31G basis set.[27] In order to characterize stationary points as minima (equilibrium structures) or saddle point (transition structures), and to allow for inclusion of the effects of zero-point vibrations in estimating relative energies, harmonic vibrational frequencies have been calculated[28] at the HF level with the 3-21G basis[29] using

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geometries optimized with this basis set. More reliable relative energies have been obtained from higher level calculations using the split-valence 6-31G[30,31] and split-valence plus dp-polarization 6-31G**[31,32] basis sets, and incorporating valence-electron correlation via Møller–Plesset perturbation theory terminated at third order (MP3).[33] All calculations on odd-electron species utilize the spin-unrestricted formalism.

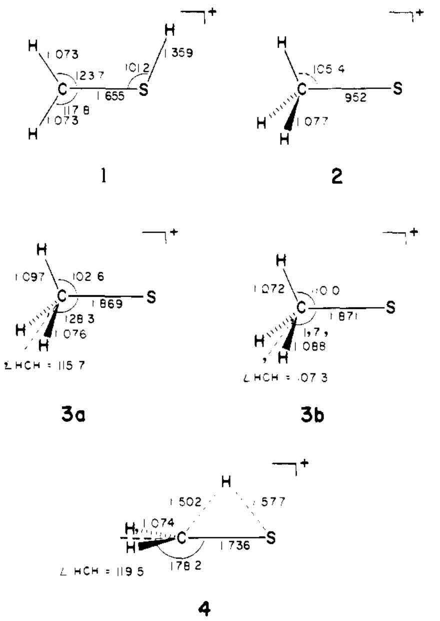
Energy comparisons for the CH_3S^+ system refer to MP3/6-31G** values with the addition of a contribution for zero-point vibrations. As HF/3-21G calculations are known to overestimate vibrational frequencies by ~10%,[34] the zero-point vibrational energy contributions have been scale by a factor of 0.9. For the $CH_4S^{+\cdot}$ and $C_2H_6S^{+\cdot}$ systems, computational expense precluded direct calculation of MP3/6-31G** energies. Instead, our best relative energies are MP3/6-31G** values estimated from the additivity relationship:[35]

$$\Delta E(\mathrm{MP3/6\text{-}31G^{**}}) \approx \Delta E(\mathrm{MP3/6\text{-}31G}) + \Delta E(\mathrm{HF/6\text{-}31G^{**}}) - \Delta E(\mathrm{HF/6\text{-}31G}) \quad (3)$$

Optimized HF/4-31G geometries are displayed in Figures 1, 2, and 4. Throughout this paper, bond lengths are given in ångströms and bond angles in degrees. Total energies for component systems, needed to calculate relative energies of fragmentation products, are given in Table I, and experimental heats of formation needed to allow comparison of our results with thermochemical data are listed in Table II. Calculated total energies, zero-point vibrational energies, and relative energies for the CH_3S^+, $CH_4S^{+\cdot}$, and $C_2H_6S^{+\cdot}$ systems are presented in Tables III to VIII, and calculated frequencies for equilibrium structures are listed in Table IX. Unless otherwise noted, relative energies quoted within the text correspond to MP3/6-31G**//4-31G values, evaluated directly (CH_3S^+ system) or via eq 3 ($CH_4S^{+\cdot}$ and $C_2H_6S^{+\cdot}$), together with zero-point vibrational contributions.[36]

Discussion

Structures and Stabilities of CH_3S^+ Ions. For the CH_3S^+ system, it was long thought[1-9] that there were two distinct isomers of comparable energies having the mercaptomethyl (CH_2SH^+) and thiomethoxy (CH_3S^+) cation structures. Only recently did a collisional activation study by Dill and McLafferty[10] reveal that, at low ionizing-electron energies, the fragment ion produced from the dimethyl sulfide radical cation is CH_2SH^+ and not CH_3S^+ as had been thought previously. Harrison,[11] in a kinetic-energy release study of H_2 elimination from ions with CH_3S^+ and CH_2SH^+ nominal structures, concluded that *either* both ions are of identical structure *or* the two (distinct) ions isomerize to a common structure prior to fragmentation *or* the two (distinct) ions fragment through a common transition structure. In a detailed photoionization study, accompanied by a thorough examination of the thermochemical evidence, Berkowitz and coworkers[13] have also considered the CH_2SH^+/CH_3S^+ problem, and their analysis suggests a unique ion structure unless the heats of formation for the two ions differ by less than 0.03 eV (3 kJ mol^{-1}). They also provide an elegant rationalization for the observed lower appearance energy for ions formed from CD_3SH of composition CD_3S^+ compared with CD_2SH^+ in terms of a unique mercaptomethyl cation structure and by taking into account differences in zero-point vibrational energy. A proton affinity study of thioformaldehyde ($CH_2{=}S$) by Roy and McMahon[14] led to observation of only one ion, judged to be CH_2SH^+ by its heat of formation. Baer and co-workers[15] in a photoionization study of dimethyl disulfide consider the fragment ion of composition CH_3S^+ to have the CH_2SH^+ structure, and report a heat of formation ($\Delta H_f{}^\circ{}_0$) of 870 kJ mol^{-1}. Finally, we note that Dill and McLafferty report[10] the formation at high ionizing energies of ions of structure CH_3S^+, in addition to CH_2SH^+, from precursors such as diethyl sulfide and dimethyl disulfide. Despite all this activity, even approximate relative energies of the CH_2SH^+ and CH_3S^+ ions are not yet known with any certainty.



1 2

3a 3b

4

Figure 1. Optimized geometries (HF/4-31G) for CH_3S^+ equilibrium structures **1**, **2**, and **3a**, and transition structures **3b** and **4**.

Ab initio studies of CH_3S^+ ions[10,22-24] have identified CH_2SH^+ as a stable species, and have indicated the possibility of the CH_3S^+ ion occurring in singlet and triplet electronic states.[10,23] A MINDO/3 study[21a] indicated several minima corresponding to CH_2SH^+, some hydrogen-bridged structures, and a carbene-substituted sulfonium ion, $CHSH_2^{+\cdot}$, while a recent MNDO study[21b] showed that CH_3S^+ rearranges to CH_2SH^+. However, none of these studies have been performed at a sufficiently high level of theory to be considered conclusive.

Recent ab initio calculations[16,17a,b,23,39-41] for the CH_3O^+ system have indicated that the most stable isomer is the hydroxymethyl cation, CH_2OH^+ ($^1A'$). The singlet methoxy cation CH_3O^+ ($^1A'$) collapses without activation energy to CH_2OH^+. The triplet methoxy cation, CH_3O^+ ($^3A_1$), is found to be a stable species,[16,17a,b,23] but is calculated to lie much higher in energy[17a,b] than CH_2OH^+ ($^1A'$). Similarly, the oxoniomethylene cation ($CHOH_2^+$), although stable with respect to rearrangement to CH_2OH^+, is found to have a relatively high energy.[41] Weak complexes (of composition CH_3O^+) between H_2 and HCO^+ and between H_2 and HOC^+ are predicted[40] to be bound by only 5 and 20 kJ mol^{-1}, respectively.

In the present study, we have considered the singlet mercaptomethyl cation, CH_2SH^+ ($^1A'$) (**1**), the triplet thiomethoxy cation, CH_3S^+ ($^3A_1$) (**2**), and two Jahn–Teller-distorted[42] structures for the singlet thiomethoxy cation, CH_3S^+ ($^1A'$) (**3a** and **3b**).[43,44] The

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Table III. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) of CH_3S^+ Structures and Thioformaldehyde

	CH_2SH^+ (1) $^1A'$ (C_s)	CH_3S^+ (2) $^3A_1$ (C_{3v})	CH_3S^+ (3a) $^1A'$ (C_s)	CH_3S^+ (3b) $^1A'$ (C_s)	TS:3a → 1 (4) $^1A'$ (C_s)	$CH_2{=}S^b$ $^1A_1$ (C_{2v})
3·21G//3·21G	−434.609 19	−434.638 73	−434.556 55	−434.556 38	−434.529 83	−434.336 25
4·31G//4·31G	−436.270 73	−436.300 08	−436.216 83	−436.216 67	−436.190 27	−435.993 17
6·31G//4·31G	−436.735 08	−436.761 47	−436.678 40		−436.654 94	−436.457 51
6·31G**//4·31G	−436.812 84	−436.801 13	−436.719 63		−436.729 76	−436.508 93
MP2/6·31G//4·31G	−436.885 36	−436.876 43	−436.808 49		−436.803 37	−436.611 24
MP2/6·31G**//4·31G	−437.081 10	−437.035 23	−436.972 43		−436.995 97	−436.781 39
MP3/6·31G//4·31G	−436.898 70	−436.891 61	−436.825 69		−436.817 42	−436.620 29
MP3/6·31G**//4·31G	−437.104 82	−437.063 87	−437.002 33		−437.021 16	−436.800 41
ZPVE	96.3	101.9	96.0	93.0^a	83.2	69.8

^{a} 3b has one imaginary frequency. ^{b} 4·31G geometrical parameters are: r(C–S) = 1.630, r(C–H) = 1.072, ∠HCS = 122.2°.

Table IV. Calculated and Experimental Relative Energies (kJ mol^{-1}) of CH_3S^+ Structures

	CH_2SH^+ (1)	CH_3S^+ (2)	CH_3S^+ (3a)	TS:3a → 1 (4)	$CH_2{=}S + H^+$
3·21G//3·21G	0	−78	138	208	717
4·31G//4·31G	0	−77	142	211	729
6·31G//4·31G	0	−69	149	210	729
6·31G**//4·31G	0	31	245	218	798
MP2/6·31G//4·31G	0	23	202	215	720
MP2/6·31G**//4·31G	0	120	285	224	787
MP3/6·31G//4·31G	0	19	192	213	731
MP3/6·31G**//4·31G^a	0	119	288	221	800
MP3/6·31G**//4·31G	0	108	269	220	799
MP3/6·31G**//4·31G^b	0	113	269	208	775
exptl^c	0				757

^{a} Values estimated using eq 3. See also ref 35a. ^{b} With zero-point vibrational energy contribution (see text). ^{c} Based on $\Delta H_f{}^\circ{}_0$ values of Table II.

calculated harmonic vibrational frequencies indicate that, at the HF/3-21G level, **1**, **2**, and **3a** are local minima while **3b** is a saddle point on the potential-energy surface. This last structure (**3b**) represents a transition structure for scrambling of the hydrogen atoms in **3a** and is not considered further. The transition structure (**4**) for the rearrangement of **3a** to the mercaptomethyl cation (**1**) via a 1,2-hydrogen shift, although optimized without symmetry constraints, was found to prefer C_s symmetry.

Our best direct calculations (MP3/6-31G**//HF/4-31G with zero-point vibrational contribution) indicate that the triplet CH_3S^+ ion (**2**) lies 113 kJ mol^{-1} above singlet CH_2SH^+ (**1**) although, on the basis of other singlet–triplet comparisons,[45] it is likely that this value *underestimates* the true energy difference. Our result may be compared with a previous value of −75 kJ mol^{-1} (i.e., favoring CH_3S^+!) at the HF/4-31G level,[23] and empirically corrected estimates[10] of +33 and +50 kJ mol^{-1}. The singlet CH_3S^+ ion (**3a**) is calculated to lie 269 kJ mol^{-1} above **1**. However, examination of Tables III and IV reveals that, although **4** is a true transition structure on the 3-21G potential surface, at the higher levels of theory (i.e., with inclusion of polarization functions in the basis set and incorporation of electron correlation), its energy drops below that of **3a**. This suggests that the 1,2-hydrogen shift **3a** → **1** may occur without activation energy; if the singlet thiomethoxy ion (**3a**) is formed as a result of fragmentation of a suitable precursor ion, it is likely to collapse spontaneously to the mercaptomethyl cation (**1**), which in this case would be formed with substantial excess energy.

The present study lends support to recent experimental results.[10,15] At low ionizing energies, CH_3SCH_3 and CH_3SSCH_3 are found to yield fragment ions of structure **1** (CH_2SH^+); these could be formed in a reaction similar to (1) or (2) (see below). At higher ionizing energies, both CH_2SH^+ and CH_3S^+ are observed as fragments from CH_3SSCH_3 and other dialkyl disulfides, with the maximum proportion of ions of structure CH_3S^+ occurring at an ionizing energy of 18 eV.[10] We would propose that this CH_3S^+ species is the triplet ion (**2**). Finally, at electron energies >18 eV, the abundance of CH_2SH^+ again increases at the expense of CH_3S^+. This was explained[10] in terms of isomerization of CH_3S^+ ions of sufficiently high internal energy to CH_2SH^+. Our results are consistent with this: formation of singlet CH_3S^+ (**3a**) at high energies either directly or via intersystem crossing from the triplet CH_3S^+ surface would lead to spontaneous collapse to CH_2SH^+ (**1**).

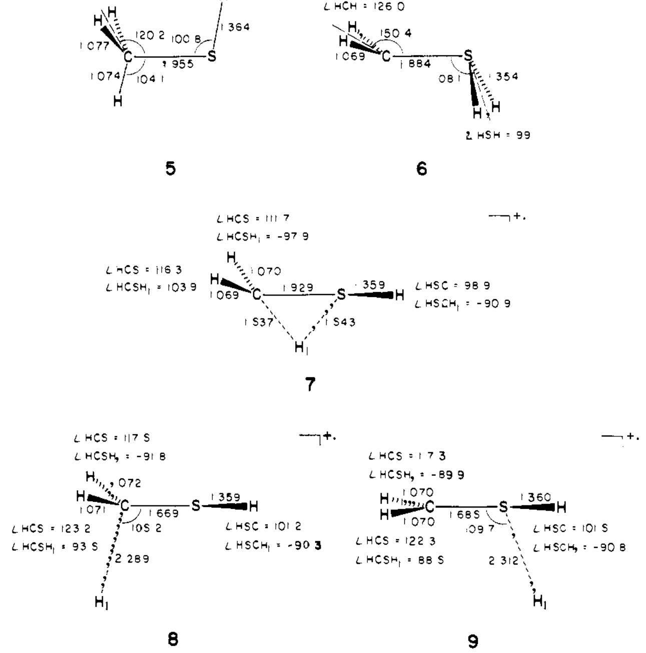

Figure 2. Optimized geometries (HF/4·31G) for $CH_4S^{+\cdot}$ equilibrium structures **5** and **6**, and transition structures **7**, **8**, and **9**.

The present results also provide insight into the thermochemistry of the CH_3S^+ ion. Earlier reports[1-8] which had indicated a heat

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(43) Preliminary results for some of these species were reported in ref 35a.

(44) Preliminary calculations carried out on triplet CH_2SH^+ and on singlet and triplet $CHSH_2^+$ suggest that these ions have relatively high energies.

(45) The energy difference at the MP3/6-31G**//HF/4-31G level between the $^1A_1$ and $^3B_1$ states of methylene is 74 kJ mol^{-1}. Better theoretical estimates yield a difference of ≈42–44 kJ mol^{-1}, e.g.: Meadows, J. H.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 4383. This may be compared with the HF/4-31G value of 156 kJ mol^{-1}.

Table V. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) of $CH_4S^{+}\cdot$ Structures

	$CH_3SH^{+}\cdot$ (5) $^2A''$ (C_s)	$CH_2SH_2^{+}\cdot$ (6) $^2A'$ (C_s)	TS:6 → 5 (7) ^2A (C_1)	TS:5 → 1 + H· (8) ^2A (C_1)	TS:6 → 1 + H· (9) ^2A (C_1)
3-21G//3-21G	−435.208 78	−435.157 84	−435.097 59	−435.105 94	−435.104 58
4-31G//4-31G	−436.870 30	−436.818 57	−436.759 01	−436.768 24	−436.765 78
6-31G//4-31G	−437.332 92	−437.284 03	−437.223 01	−437.232 88	−437.230 26
6-31G**//4-31G	−437.397 06	−437.366 64	−437.306 82	−437.309 88	−437.307 34
MP2/6-31G//4-31G	−437.468 11	−437.415 88	−437.369 54	−437.377 60	−437.368 52
MP3/6-31G//4-31G	−437.487 10	−437.436 68	−437.388 76	−437.392 78	−437.385 25
ZPVE	122.0	113.3	103.7	98.5	97.6

Table VI. Calculated and Experimental Relative Energies (kJ mol^{-1}) of $CH_4S^{+}\cdot$ Structures and Component Systems

	$CH_3SH^{+}\cdot$ (5)	$CH_2SH_2^{+}\cdot$ (6)	TS:6 → 5 (7)	TS:5 → 1 + H· (8)	TS:6 → 1 + H· (9)	1 + H·	CH_3^{+} + HS·	$CH_2^{+}\cdot$ + H_2S
3-21G//3-21G	0	134	292	270	274	271	213	411
4-31G//4-31G	0	136	292	268	274	266	203	403
6-31G//4-31G	0	128	289	263	270	262	201	398
6-31G**//4-31G	0	80	237	229	236	226	244	400
MP2/6-31G//4-31G	0	137	259	238	261	222	278	475
MP3/6-31G//4-31G	0	132	258	248	267	237	273	469
MP3/6-31G**//4-31G[a]	0	84	206	214	233	201	316	471
MP3/6-31G**//4-31G[a,b]	0	76	190	193	211	178	298	437
exptl[c]	0	26				187	338	481

[a] Values estimated using eq 3. [b] With zero-point energy contribution (see text). [c] Based on $\Delta H_f{}^{\circ}{}_0$ values of Table II.

of formation for CH_3S^+ similar to[8] or slightly lower than[6] that of CH_2SH^+ are clearly incompatible with our calculations. Indeed, our results support more recent conclusions[10,11,13-15] that at threshold there is a unique CH_3S^+ ion, namely, the mercaptomethyl cation, CH_2SH^+ (**1**), and allow us to discard the remote possibility[11,13] that there are two distinct ion structures with coincidentally indistinguishable heats of formation.

In order to provide some comparison with available experimental thermochemical data, we have carried out calculations of the proton affinity of thioformaldehyde ($CH_2{=}S$) to yield CH_2SH^+ (**1**). The calculated proton affinity of 775 kJ mol^{-1} (Table IV) may be compared with a recent experimental value[14] of 757 kJ mol^{-1}.

The $CH_4S^{+}\cdot$ System. Only recently have theoretical calculations[18] and experimental studies[19,20] established that there exists, in addition to the methanol radical cation ($CH_3OH^{+}\cdot$), another stable ion of composition $CH_4O^{+}\cdot$, namely, the methylenoxonium ion ($(CH_2OH_2)^{+}\cdot$). Indeed, there is accumulating evidence for the existence of many ions which, like the methylenoxonium ion, are striking in that they do not have stable, neutral counterparts.[17,18,20,46]

For the $CH_4S^{+}\cdot$ system, there have been many experimental studies of the methanethiol radical cation, $CH_3SH^{+}\cdot$ (**5**),[3,4,6-8,13,15,20,47-49] but to date only one experimental group[20] has studied the isomeric methylenesulfonium radical cation, $CH_2SH_2^{+}\cdot$ (**6**). Holmes and co-workers found that $CH_2SH_2^{+}\cdot$ could be distinguished from $CH_3SH^{+}\cdot$ by collisional-activation mass spectrometry, and measured its heat of formation ($\Delta H_f{}^{\circ}{}_{298}$) to be 916 kJ mol^{-1} (see Table II).[20c] We are unaware of any theoretical calculations on either **5** or **6**.

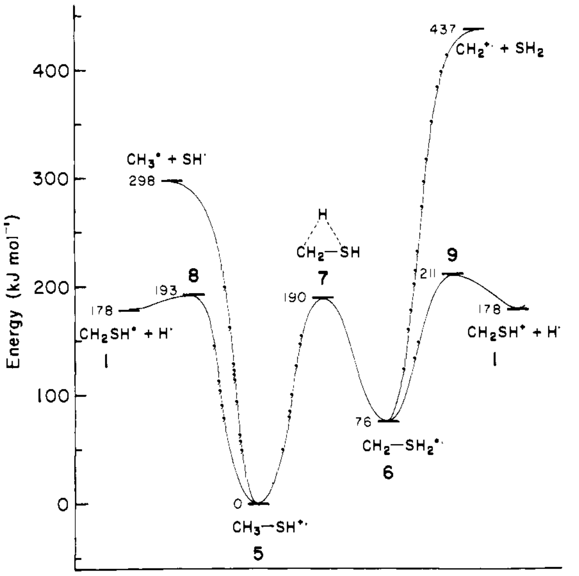

Figure 3. Schematic potential-energy profile for rearrangement and fragmentation reactions of $CH_3SH^{+}\cdot$ and $CH_2SH_2^{+}\cdot$.

In order to assess the stability of these ions with respect to rearrangement and fragmentation, we have examined the 1,2-hydrogen shift which interconverts **5** and **6** (via transition structure **7**) and the dissociation pathways from **5** and **6** leading to the mercaptomethyl cation (**1**) and H· (via transition structures **8** and **9**, respectively). Optimized geometries for structures **5**–**9** are shown in Figure 2.

The optimized structures for **5** and **6** may be compared with those of the corresponding neutral systems.[37,38] At the 4-31G level, the C–S bond in CH_3SH lengthens from 1.886 to 1.955 Å upon ionization; the C–S bond in the sulfonium ylide CH_2SH_2 likewise lengthens from 1.732 to 1.884 Å. The latter result contrasts with that found for the corresponding oxonium ylide,[50] where the (long) C–O bond in the neutral CH_2OH_2 species shortens upon ionization.[18]

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(46) In addition to the $CH_2OH_2^{+}\cdot/CH_3OH^{+}\cdot$ ions, additional related systems which have recently been theoretically predicted and/or experimentally observed include: $CH_2FH^{+}\cdot/CH_3F^{+}\cdot$, $CH_2NH_3^{+}\cdot/CH_3NH_2^{+}\cdot$, $CH_2OHCH_3^{+}\cdot/CH_3OCH_3^{+}\cdot$, $CH_2CH_2OH_2^{+}\cdot/CH_3CHOH_2^{+}\cdot/CH_3CH_2OH^{+}\cdot$, and $CH_2ClCH_3/CH_3CH_2Cl^{+}\cdot$. See: (a) Wagner, W.; Heimbach, H.; Levsen, K. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 125. (b) Terlouw, J. K.; Heerma, W.; Dijkstra, G. *Org. Mass Spectrom.* **1981**, *16*, 326. (c) Bouma, W. J.; Yates, B. F.; Radom, L. *Chem. Phys. Lett.* **1982**, *92*, 620. (d) Halim, H.; Ciommer, B.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 528. (e) Bouma, W. J.; Dawes, J. M.; Radom, L. *Org. Mass Spectrom.* **1983**, *18*, 12. (f) Hammerum, S.; Christensen, J. B.; Egsgaard, H.; Larsen, E.; Derrick, P. J.; Donchi, K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 351. (g) Apeloig, Y.; Ciommer, B.; Frenking, G.; Karni, M.; Mandelbaum, A.; Schwarz, H.; Weisz, A. *J. Am. Chem. Soc.* **1983**, *105*, 2186.

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Table VII. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) of $C_2H_6S^{+}\cdot$ Structures

	$CH_3SCH_3^{+}\cdot$ (10a) $^2B_1$ (C_{2v})	$CH_3SCH_3^{+}\cdot$ (10b) $^2A_1$ (C_{2v})	$CH_2SHCH_3^{+}\cdot$ (11) ^2A (C_1)	TS:11 → 10a (12) ^2A (C_1)
3-21G//3-21G	−474.059 11	−474.003 24	−474.005 56	−473.944 53
4-31G//4-31G	−475.878 77	−475.825 65	−475.824 67	−475.764 34
6-31G//4-31G	−476.381 67	−476.324 81	−476.329 58	−476.267 85
6-31G**//4-31G	−476.457 41	−476.382 02	−476.423 95	−476.361 85
MP2/6-31G//4-31G	−476.606 59	−476.538 95	−476.550 45	−476.503 56
MP3/6-31G//4-31G	−476.633 65	−476.565 78	−476.579 39	−476.530 65
ZPVE	209.7		197.1	187.7

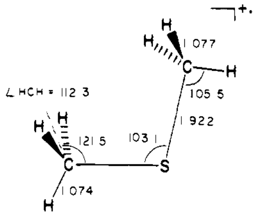
The calculated potential-energy profile for rearrangement and fragmentation processes involving $CH_3SH^{+}\cdot$ (**5**) and $CH_2SH_2^{+}\cdot$ (**6**) is displayed in Figure 3. Both $CH_3SH^{+}\cdot$ (**5**) and $CH_2SH_2^{+}\cdot$ (**6**) are indicated to be stable species, with **6** being 76 kJ mol^{-1} higher in energy than **5**. This result contrasts with that found for the $CH_3OH^{+}\cdot/CH_2OH_2^{+}\cdot$ system,[18] where the oxonium ion was calculated to be 45 kJ mol^{-1} *lower* in energy. However, the general observation that there is a large stabilization of CH_2XH_2 species relative to CH_3XH (X = O, S) upon ionization holds for both systems. Thus the relative energy of the onium ion drops from 365 to −45 kJ mol^{-1} for X = O,[18b] and from 326 to 76 kJ mol^{-1} for X = S.[36] Our conclusion that the methylenesulfonium radical cation (**6**) lies higher in energy than the methanethiol radical cation (**5**) does not support a recent suggestion to the contrary[15] but does agree qualitatively with thermochemical measurements[20c] which lead to an energy difference of 26 kJ mol^{-1} in favor of **5** (cf. Tables V and VI).

Our calculated barrier for **5** → **6** (via transition structure **7**) is 114 kJ mol^{-1}, and the barriers for **5** → **1** + H· (via **8**) and for **6** → **1** + H· (via **9**) are 193 and 135 kJ mol^{-1}, respectively. Dissociation of $CH_3SH^{+}\cdot$ to give CH_3^{+} + HS· and of $CH_2SH_2^{+}\cdot$ to give $CH_2^{+}\cdot$ + H_2S is found to occur without reverse activation energy. The energies, relative to **5**, of the dissociation products, CH_3^{+} + HS· and $CH_2^{+}\cdot$ + H_2S, are 298 and 437 kJ mol^{-1}, respectively. These values may be compared with 338 and 481 kJ mol^{-1} derived from experimental heats of formation.

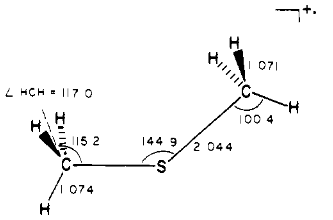
The potential-energy profile displayed in Figure 3 shows that **5** and **6** should be stable, noninterconverting isomeric ions at low internal energies. The similarity in barrier heights for the 1,2-hydrogen shift connecting **5** and **6** and for loss of H· from **5** and **6** suggests that, in practice, H· loss to give CH_2SH^{+} (**1**) may take place with hydrogen scrambling. This would explain the observed appearance energy[6,11,13] for ions of composition CD_3S^{+} formed by fragmentation of $CD_3SH^{+}\cdot$; the observed ions may have achieved the CD_2SD^{+} structure via intermediacy of the $CD_2SDH^{+}\cdot$ radical cation. The comparable magnitudes of the barriers to rearrangement and H· loss are consistent with the observation[20c] of identical shapes for the metastable peaks corresponding to H· loss from $CH_3SH^{+}\cdot$ and $CH_2SH_2^{+}\cdot$.

$CH_3SCH_3^{+}\cdot$ and $CH_2SHCH_3^{+}\cdot$. Experimental studies to date have concerned themselves only with the two known $C_2H_6S^{+}\cdot$ isomers, the dimethyl sulfide radical cation, $CH_3SCH_3^{+}\cdot$, and the ethanethiol radical cation, $CH_3CH_2SH^{+}\cdot$. Thermochemical measurements[51] indicate that the latter lies 50 kJ mol^{-1} higher in energy. This ion is not involved in the rearrangement and fragmentation reactions in which we are particularly interested and has therefore not been included in the present study. The dimethyl sulfide radical cation is experimentally well known through mass spectrometric studies; its ionization energy has been established,[3,4,11,47-49,51,52] and its collisional-activation spectrum has been reported.[46a]

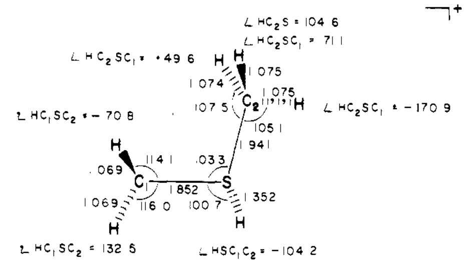
We have examined the dimethyl sulfide radical cation in its lowest $^2B_1$ and $^2A_1$ electronic states, yielding structures **10a** and **10b**, respectively. In contrast to results for the dimethyl ether radical cation, the methyl groups in both electronic states are found to stagger (rather than eclipse) the adjacent C–S bond. Our MP3/6-31G**//HF/4-31G calculations (eq 3) show that the $^2B_1$ state (**10a**) is 227 kJ mol^{-1} lower in energy than the $^2A_1$ state (**10b**).



10a



10b



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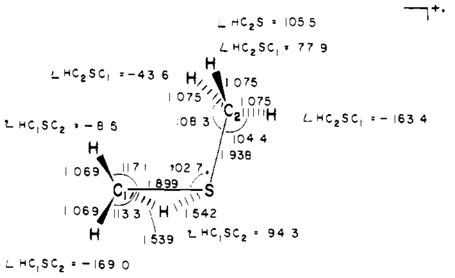

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Figure 4. Optimized geometries (HF/4-31G) for $C_2H_6S^{+}\cdot$ equilibrium structures **10a**, **10b**, and **11**, and transition structure **12**.

Like the analogous $C_2H_6O^{+}\cdot$ ion, $CH_2OHCH_3^{+}\cdot$,[17] the sulfonium ion, $CH_2SHCH_3^{+}\cdot$ (**11**), is found to be a stable structure on the potential energy surfaces and to have C_1 symmetry. Our best calculations (Tables VII and VIII) predict **11** to lie 82 kJ mol^{-1} above **10a**. By comparison, $CH_3OCH_3^{+}\cdot$ and $CH_2OHCH_3^{+}\cdot$ were calculated[17] to be almost equal in energy. A transition structure (**12**) was located for the 1,2-hydrogen shift interconverting **10a** and **11**. The barrier for the rearrangement **11** → **10a** is calculated to be 120 kJ mol^{-1}. Dissociation of **11** to give CH_2SH^{+} (**1**) + $CH_3\cdot$ is calculated to cost 98 kJ mol^{-1} and is found to occur without reverse activation energy. As $CH_2SHCH_3^{+}\cdot$ lies relatively low in energy, with a considerable barrier for rearrangement to the more stable dimethyl sulfide radical cation (**10a**), it offers a good prospect for experimental observation. It should be noted that a similar prediction[17] regarding the oxygen analogue, $CH_2OHCH_3^{+}\cdot$, has been verified by collisional activation mass spectrometry.[20a]

Fragmentation of the Dimethyl Sulfide Radical Cation. Whereas earlier studies[2-4,6-8] assumed that alkyl methyl sulfides yield ions of CH_3S^{+} structure upon ionization and fragmentation, recent

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Table **VIII**. Calculated and Experimental Relative Energies (kJ mol^{-1}) of $C_2H_6S^{+\cdot}$ Structures and Component System

	$CH_3SCH_3^{+\cdot}$ (10a)	$CH_3SCH_3^{+\cdot}$ (10b)	$CH_2SHCH_3^{+\cdot}$ (11)	TS: 11 → 10a (12)	$1 + CH_3\cdot$
3-21G//3-21G	0	147	141	301	282
4-31G//4-31G	0	139	142	300	271
6-31G//4-31G	0	149	137	299	262
6-31G**//4-31G	0	198	88	251	210
MP2/6-31G//4-31G	0	178	147	271	261
MP3/6-31G//4-31G	0	178	142	270	264
MP3/6-31G**//4-31G[a]	0	227	93	222	212
MP3/6-31G**//4-31G[a,b]	0		82	202	180
exptl[c]	0				199

[a] Values estimated using eq 3. [b] With zero-point energy contribution (see text). [c] Based on $\Delta H_f{}^\circ{}_0$ values of Table II.

Table **IX**. Calculated Vibrational Frequencies (cm^{-1}) for Equilibrium Structures[a]

CH_2SH^+ (1)	788 (a″)	828 (a′)	884 (a′)	1084 (a′)	1086 (a″)
	1427 (a′)	2324 (a′)	2977 (a′)	3089 (a′)	
CH_3S^+ (**2**)	433 (a_1)	929 (e)	929 (e)	1345 (a_1)	1407 (e)
	1407 (e)	2885 (a_1)	2998 (e)	2999 (e)	
$CH_3SH^{+\cdot}$ (**5**)	106 (a″)	275 (a′)	657 (a′)	955 (a″)	1007 (a′)
	1297 (a′)	1383 (a′)	1420 (a″)	2291 (a′)	2899 (a′)
	3016 (a″)	3045 (a′)			
$CH_2SH_2^{+\cdot}$ (**6**)	126 (a″)	490 (a′)	589 (a′)	724 (a″)	758 (a′)
	1030 (a″)	1194 (a′)	1320 (a′)	2347 (a′)	2355 (a″)
	2975 (a′)	3133 (a″)			
$CH_3SCH_3^{+\cdot}$ (10a)	52 (a_2)	104 (b_1)	216 (a_1)	485 (a_1)	522 (b_2)
	912 (b_1)	929 (a_2)	953 (b_2)	1051 (a_1)	1340 (b_2)
	1365 (a_1)	1418 (b_2)	1431 (a_2)	1435 (a_1)	1445 (b_1)
	2906 (b_2)	2908 (a_1)	3005 (b_1)	3007 (a_2)	3033 (b_2)
	3035 (a_1)				
$CH_2SHCH_3^{+\cdot}$ (11)	75	140	223	473	500
	604	681	811	990	1026
	1067	1324	1358	1436	1444
	2370	2927	2983	3040	3052
	3135				

[a] Values listed have been scaled by 0.9 (see text).

collisional-activation studies[10] have shown that, at threshold, this is incorrect; the ion produced is CH_2SH^+ (**1**). An important consequence of this discovery is that the reported[6] heat of formation of 895 kJ mol^{-1} ($\Delta H_f{}^\circ{}_{298}$), based upon appearance energies, cannot refer to ions of CH_3S^+ structure. The present study agrees with the collisional-activation results, as singlet CH_3S^+ (**3a**) is found to be unstable, and triplet CH_3S^+ (**2**) is predicted to be at least 113 kJ mol^{-1} higher in energy than CH_2SH^+ (**1**) (see above).

Our results also allow us to discuss the mechanism for the formation of CH_2SH^+ (**1**) from $CH_3SCH_3^{+\cdot}$ (**10a**). As shown in Figure 5, the mechanism is qualitatively the same as that found for the analogous oxygen system, $CH_3OCH_3^{+\cdot}$ (see eq 2). There is, however, a significant difference. For the oxygen system,[11] the height of the barrier for the 1,2-hydrogen shift connecting $CH_3OCH_3^{+\cdot}$ with $CH_2OHCH_3^{+\cdot}$ results in the fragments, CH_2OH^+ and $CH_3\cdot$, being produced with 110 kJ mol^{-1} excess energy. This compares well with the fact that the measured appearance potential for an ion of composition CH_3O^+ (now known[16] to be CH_2OH^+) leads to a heat of formation ~96 kJ mol^{-1} higher than that of CH_2OH^+. For the sulfur system considered here, we find the barrier for the 1,2-hydrogen shift, **10a** → **11**, to occur at an energy only slightly higher (by 22 kJ mol^{-1}) than the combined energy of the fragments CH_2SH^+ and $CH_3\cdot$. If the appearance energy for the ion of composition CH_3S^+ from dimethyl sulfide[6] (1069 kJ mol^{-1}) is combined with the experimental heats of formation ($\Delta H_f{}^\circ{}_0$) for CH_3SCH_3 (−37 kJ mol^{-1})[51] and $CH_3SCH_3^{+\cdot}$ (817 kJ mol^{-1}, Table II), the experimental barrier for the formation of CH_2SH^+ and $CH_3\cdot$ from $CH_3SCH_3^{+\cdot}$ is calculated to be 215 kJ mol^{-1}. This value is remarkably close to the 202 kJ mol^{-1} which follows from our proposed mechanism (see eq 2 and Figure 5).

Conclusions

The following conclusions emerge from this study.

(i) The singlet mercaptomethyl cation, CH_2SH^+ (**1**), is clearly the most stable CH_3S^+ isomer, lying substantially (≳113 kJ mol^{-1}) lower in energy than the triplet thiomethoxy cation, CH_3S^+ ($^3A_1$) (**2**).

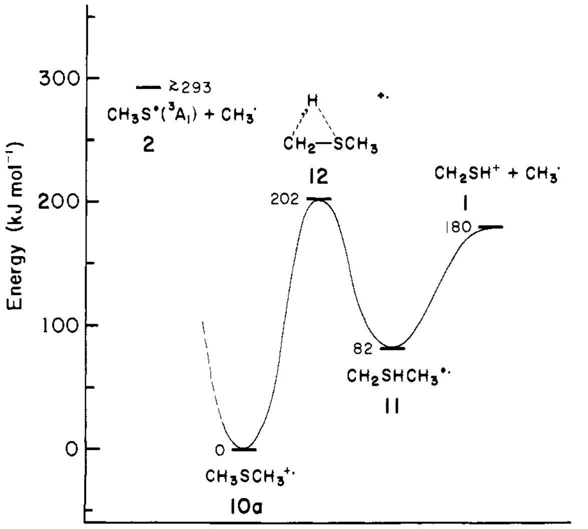

Figure 5. Schematic potential-energy profile for rearrangement and fragmentation of $CH_3SCH_3^{+\cdot}$ and $CH_2SHCH_3^{+\cdot}$.

(ii) Although the singlet thiomethoxy cation, CH_3S^+ ($^1A'$) (**3**), is found to be a local minimum on the HF/3-21G potential-energy surface, higher level calculations indicate that it is likely to collapse without activation energy via a 1,2-hydrogen shift to the mercaptomethyl cation, CH_2SH^+ (**1**).

(iii) In agreement with recent experimental results, we find that for the $CH_4S^{+\cdot}$ system there are two stable isomers, corresponding to the methanethiol radical cation, $CH_3SH^{+\cdot}$ (**5**), and the methylenesulfonium radical cation, $CH_2SH_2^{+\cdot}$ (**6**). The latter is calculated to be 76 kJ mol^{-1} higher in energy with a barrier for rearrangement (to give **5**) of 114 kJ mol^{-1}. As the barriers for
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loss of H· from **5** and **6** to give CH_2SH^+ (**1**) are calculated to be of similar magnitude to that for the intramolecular rearrangement, hydrogen scrambling may occur upon loss of H· or D· from $CD_3SH^{+}\cdot$.

(iv) In addition to the experimentally well-established dimethyl sulfide (**10**) and ethanethiol radical cations, the sulfonium ion $CH_2SHCH_3^{+}\cdot$ (**11**) is likely to be an observable $C_2H_6S^{+}\cdot$ isomer. This species is found to lie 82 kJ mol^{-1} above $CH_3SCH_3^{+}\cdot$, with a barrier to rearrangement to $CH_3SCH_3^{+}\cdot$ of 120 kJ mol^{-1}. The barrier to dissociation of **11** to give CH_2SH^+ and $CH_3\cdot$ is calculated to be 98 kJ mol^{-1}, with no reverse activation energy.

(v) The present results are consistent with the CH_2SH^+ (**1**) ion rather than CH_3S^+ (**2**) being formed by fragmentation of dimethyl sulfide at low ionizing energies. A two-step rearrangement–dissociation mechanism is found to lead to formation of CH_2SH^+. This mechanism yields a barrier for the formation of CH_2SH^+ from $CH_3SCH_3^{+}\cdot$ which agrees well with that derived from the experimentally observed appearance energy for formation of CH_2SH^+ from dimethyl sulfide.

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Overtone Spectral Investigation of Substituent-Induced Bond-Length Changes in Gas-Phase Fluorinated Benzenes and Their Correlation with ab Initio STO-3G and 4-21G Calculations

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Abstract: The gas-phase overtone spectra of eight fluorinated benzenes are measured in the CH-stretching regions corresponding to $\Delta v = 2$ to 5 and are analyzed in terms of the local mode model. Peaks corresponding to inequivalent CH bonds in monofluorobenzene and the three difluorobenzenes are partially resolved. The frequency shifts are compared to σ_I, and the peaks are assigned to the various CH bonds on the basis of the substitutent effect. CH bond lengths (r_{CH}^{LM}) are determined from the shift in the overtone peak frequency relative to benzene. These values are compared with bond lengths obtained from geometry-optimized ab initio molecular orbital calculations at the STO-3G ($r_{CH}^{STO\text{-}3G}$) and 4-21G ($r_{CH}^{4\text{-}21G}$) levels. There is excellent agreement between the values of r_{CH}^{LM} and $r_{CH}^{4\text{-}21G}$. In fact, the local mode analysis would appear to provide the best available technique for determining CH bond lengths in molecules of this size. The redistribution of electron population upon substitution is examined in terms of a bond-strength parameter, which is derived from the Mulliken population analysis. This parameter correlates well with the calculated and experimental bond lengths and provides a simple physical interpretation of the observed variation in r_{CH}.

I. Introduction

The understanding of the effect of substituents on the properties of a parent molecule is of primary importance in the organization of chemical knowledge. In particular, studies on benzene and its substituted derivatives have formed a considerable area of research for many years. In an earlier paper,[1] we examined the higher CH-stretching overtones of 20 substituted benzenes in the liquid phase, using the local mode model.[2] A given CH bond behaves as an uncoupled anharmonic diatomic oscillator whose overtone transition energies are given by

$$\Delta E_{0\to v}\ (\mathrm{cm}^{-1}) = \omega v + X v^2 \tag{1}$$

where ω is the local mode frequency, X is the diagonal local mode anharmonicity, and v is the CH-stretching vibrational quantum number. As ω is dependent on bond strength[3] and X is sensitive to steric hindrance,[4] unique CH bond types within a molecule can be spectrally resolved. In our liquid-phase study,[1] the lines were too broad to allow for resolution of inequivalent hydrogens, except in the case of nitrobenzene where a partially resolved doublet was observed. The assignment of the ortho hydrogens to the high-frequency peak was subsequently confirmed by partial deuteration.[5] We attempted to interpret the observed variation in the positions of the overtone frequencies of the substituted benzenes in terms of σ_I, the inductive part of the Hammett σ, after the work of Katayama et al.[6,7] The correlation of frequency shift with σ_I was only moderately successful, and the effect clearly ceased to be additive at higher levels of substitution.

In the present work, we investigate the overtone spectra of a series of fluorinated benzenes in the gas phase. Preliminary results for 1,3-difluorobenzene have already been presented.[8] Because of the decrease in intermolecular interactions in the gas phase, the overtone bands are narrower. Partially resolved peaks are observed corresponding to absorption from inequivalent CH bonds. This resolution leads to a greater understanding of the correlation of frequency shifts with σ_I.

McKean and his collaborators have investigated the fundamental CH-stretching transitions in molecules where all the hydrogens but one have been replaced by deuterium.[9] They have

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