Photochemistry of Sulfide Dimer Cations in Clusters of Dimethyl Sulfide

J. A. Syage,* J. E. Pollard, and R. B. Cohen

The Aerospace Corporation, P.O. Box 92957/M5-754, Los Angeles, California 90009
(Received: May 21, 1991)

We report on wavelength-dependent photochemistry in dimethyl sulfide (DMS) cluster ions formed by resonance-enhanced multiphoton ionization and by electron-impact ionization. DMS cluster ionization leads to a stable dimer cation three-electron sulfur–sulfur bond with strong visible absorptions. Excitation in this spectral region promotes photoreaction to a cyclic $C_2H_3S^+$ structure (thiirenium ion). Excitation at shorter wavelengths produces entirely different products. The photoreactions resemble solution-phase chemistry, whereas the electron-impact-induced cluster reactions are similar to gas-phase ion–molecule chemistry.

Introduction

Photoinduced reactions in molecular clusters provide interesting parallels with analogous bimolecular reactions in solution and gas phase.[1-8] In previous work we have investigated cluster photochemistry for a variety of solute excitation conditions (bound and repulsive state excitation) and solute–solvent bonding interactions (van der Waals, hydrogen bonding, ion-induced dipole attraction).[4-6] Here we report on the photoexcitation of organosulfide (thioether) cluster ions. These systems are unusual because the bond for the dimer ion core is "covalent" due to a three-electron, two-center interaction (3e,2c)[9-16] represented by

Odd-electron bonds have a prominent role in radical chemistry, yet they are poorly understood compared with conventional two-electron neutral bonds. The three-electron σ-like bond in thioether dimer cations derives from the overlap between an open-shell p orbital of the cation with the corresponding closed-shell p orbital of the proximate neutral molecule. Dimer cation stability has been confirmed in solution and in gas-phase ion–molecule studies; the bond energy for dimethyl sulfide (DMS)

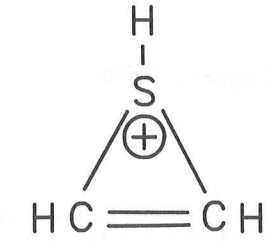
(1) (a) Echt, O.; Dao, P. D.; Morgan, S.; Castleman, A. W., Jr. *J. Chem. Phys.* **1985**, *82*, 4076.
(2) (a) Cheshnovsky, O.; Leutwyler, S. *J. Chem. Phys.* **1988**, *88*, 4127. (b) Droz, T.; Knochenmuss, R.; Leutwyler, S. *J. Chem. Phys.* **1990**, *93*, 4520.
(3) (a) Jouvet, C.; Lardeux-Dedonder, C.; Richard-Viard, M.; Solgadi, D.; Tramer, A. *J. Phys. Chem.* **1990**, *94*, 5041.
(4) (a) Syage, J. A. *J. Chem. Phys.*, **1990**, *92*, 1804. (b) Syage, J. A. *J. Phys. Chem.* **1989**, *93*, 107.
(5) (a) Steadman, J.; Syage, J. A. *J. Chem. Phys.* **1990**, *92*, 4630. (b) Syage, J. A.; Steadman, J. *Chem. Phys. Lett.* **1990**, *166*, 159.
(6) (a) Syage, J. A.; Steadman, J. *J. Chem. Phys.* **1991**, *95*, 2497. (b) Steadman, J.; Syage, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6786. (c) Steadman, J.; Syage, J. A. *J. Phys. Chem.* **1991**, in press.
(7) (a) Breen, J. J.; Peng, L. W.; Willberg, D. M.; Heikal, A.; Cong, P.; Zewail, A. H. *J. Chem. Phys.* **1990**, *92*, 805. (b) Breen, J. J.; Willberg, D. M.; Gutman, M.; Zewail, A. H. *J. Chem. Phys.* **1990**, *93*, 9180.
(8) Maier, J. P., Ed. *Ion and Cluster Ion Spectroscopy and Structure*; Elsevier: New York, 1989.
(9) (a) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672. (b) Baird, N. C. *J. Chem. Educ.* **1977**, *54*, 291.
(10) Illies, A. J.; Livant, P.; McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 7980.
(11) Naito, A.; Akasaka, K.; Hatano, H. *Mol. Phys.* **1981**, *44*, 427.
(12) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.
(13) (a) Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322. (b) Asmus, K.-D.; Gillis, H. A.; Teather, G. G. *J. Phys. Chem.* **1978**, *82*, 2677.
(14) Bonifacic, M.; Möckel, H.; Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 675.
(15) Meissner, G.; Henglein, A.; Beck, G. *Z. Naturforsch. B* **1967**, *22*, 13.
(16) Belloni, J.; Marignier, J. L.; Katsumura, Y.; Tabata, Y. *J. Phys. Chem.* **1986**, *90*, 4014.

0022-3654/91/2095-8560$02.50/0

is about 25 kcal/mol (~1 eV).[12] DMS is the simplest sulfide molecule for studying this interaction. H_2S is less favorable because it forms a strong intermolecular S···H bond that competes with the 3e,2c bond formation.

The study of reactions in cluster ions has direct correspondence to solution-phase chemistry, particularly nucleophilic displacements for which the formation of carbocations constitutes the central reactive site. Reaction intermediates for nucleophilic displacement with sulfides and halogenated sulfides often involve electropositive sulfur atoms. The stable S–S^+ bond and the alkylating nature of sulfides, which we observe in the cluster ions, are responsible for such adverse effects as the blistering action of mustard gas [2,2′-bis(chloroethyl)sulfide] or in a controlled environment are capable of beneficial effects such as the selective destruction of tumor cells in cancer treatment.[17] The formation and stability of dimeric thioether cations has other biological implications. ESR has confirmed that radiolysis of certain enzymes (e.g., those with methionine residues) can form cross-linkages of the type $[R_2SSR_2]^+$.[18] Sulfur–sulfur cross-linkages also have commercial applications such as the vulcanization process used in the manufacture of rubber.

The 3e,2c sulfide dimer cation has strong visible absorptions that are well separated from the far-ultraviolet absorptions of the neutral monomer and the near-ultraviolet absorptions of the monomer cation.[11-16] These properties allow us to study the wavelength-specific photochemistry from the dimer cation species in molecular clusters. In particular, the sulfide dimer cation complex is observed to decay almost exclusively to the cyclic thirenium ion



This species has been postulated as a critical intermediate or transition state in certain solution-phase rearrangement and addition reactions involving organosulfide molecules.[17]

We show that cluster chemistry can be very specific to the mode of excitation. The range of cluster sizes studied here (2–10 molecules) permits reactions characteristic of both the gas-phase and the solution-phase. The ability to study reactions in small clusters provides information on solution-phase chemistry at the molecular level.

Experimental Section

The present work employs pulsed molecular beam time-of-flight (TOF) mass spectrometry. Two different machines were used for these studies, both of which have been described before.[4,19,20] The DMS sample was contained in a bubbler cooled with dry ice/acetone or ice water baths and entrained in a flow of He or Ar at a pressure of 15–25 psi. The DMS was degassed by vacuum–freeze–thaw cycles. Electron-impact (EI) ionization served as a diagnostic for measuring and optimizing the extent of cluster formation.[19]

Excitation wavelengths were generated either by mixing visible output of a Nd:YAG-pumped dye laser with the Nd:YAG fundamental, by frequency doubling the visible output, or by mixing the frequency-doubled output with the Nd:YAG fundamental. Pulse energies were varied in the range 0.01–10 mJ by using a wedge prism attenuator. The laser beam diameter at the intersection of the molecular beam was typically 0.1–0.3 mm.

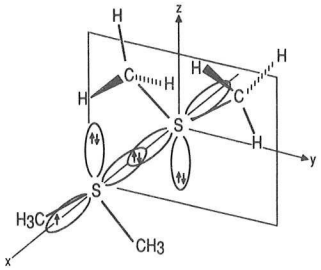


Figure 1. Geometry and coordinate system for DMS monomer and dimer cation. Structural parameters are C–H, 1.1 Å; C–S, 1.8 Å; CSC, 99° (refs 25 and 26).

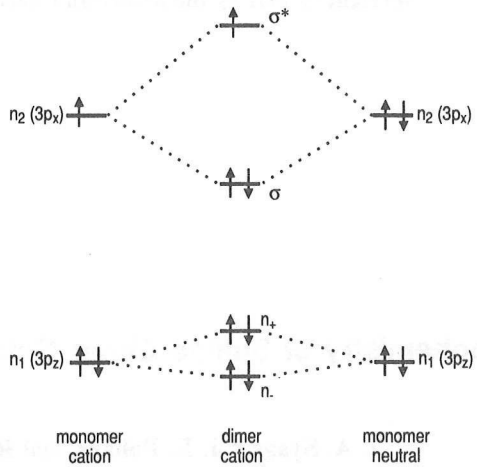


Figure 2. Energy level diagram for the sulfide dimer cation. The $3p_x$ is a pure p orbital, whereas $3p_z$ is actually a hybrid orbital with about 25% 3s admixture.

Background

The geometry of neutral DMS is known from spectroscopy,[21-25] electron diffraction,[26] and theory.[27] The structure and coordinate system of DMS monomer and dimer cation are given in Figure 1. The sulfur atom has 16 electrons; 10 electrons are assigned to the core $(1s)^2(2s)^2(2p)^6$, and 6 electrons are in valence orbitals. For DMS, two of these electrons are involved in bonding to the methyl groups and four are nonbonding. The bonding electrons fill 3s–3p hybridized orbitals (we ignore 3d and 4s admixture for simplicity). The calculated HOMO is a sulfur $3p_x$ orbital occupied by a nonbonding lone pair of electrons.[21] The second lone pair resides in a hybrid MO composed mostly of $3p_z$ and lesser amounts of 3s and methyl sp^3 (σ^*), respectively. These two nonbonding orbitals are calculated to differ in energy by 5.4 eV (compared with 3.3 eV for the analogous orbitals in H_2S).[21] The first ionization potential in DMS is, therefore, clearly from the $3p_x$ orbital.

A correlation diagram for the dimer ion was presented by Naito et al.[11] We modify their diagram to better represent reported MO calculations[21] and the measured dimer bond energy.[10] We also use the coordinate system of Thompson et al.[21] Although an energy scale is not attached to the qualitative picture in Figure 2, we assume that (1) the $n_2 - n_2$ splitting (i.e., the $\sigma - \sigma^*$ energy separation) is about 2 eV on the basis of the measured dimer bond energy of 1 eV,[10] (2) the n_1 orbitals and, therefore, the $n_\pm$ orbitals lie well below the n_2 orbitals, and (3) the n_1 splitting is small since

(17) Block, E. *Reactions of Organosulfur Compounds*; Academic: New York, 1978; Chapter 4.
(18) Hoffman, B. M.; Roberts, J. E.; Brown, T. G.; Kang, C. H.; Margoliash, E. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6132.
(19) (a) Pollard, J. E.; Cohen, R. B. *Rev. Sci. Instrum.* **1987**, *58*, 32. (b) Syage, J. A. *Chem. Phys. Lett.* **1988**, *143*, 19.
(20) Syage, J. A.; Pollard, J. E.; Cohen, R. B. *Appl. Opt.* **1987**, *26*, 3516.
(21) Thompson, S. D.; Carroll, D. G.; Watson, F.; O'Donnell, M.; McGlynn, S. P. *J. Chem. Phys.* **1966**, *45*, 1367.
(22) Scott, J. D.; Causley, G. C.; Russell, B. R. *J. Chem. Phys.* **1973**, *59*, 6577. These authors begin their Rydberg series assignments at $n = 3$. However, the highest occupied orbitals in sulfur are 3p, and therefore the lowest energy transitions should be to 3d, 4s, and 4p.
(23) Tokue, I.; Hiraya, A.; Shobatake, K. *Chem. Phys.* **1989**, *130*, 401.
(24) Clark, L. B.; Simpson, W. T. *J. Chem. Phys.* **1965**, *43*, 1965.
(25) Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479.
(26) Iijima, T.; Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2564.
(27) Ohsaku, M.; Imamura, A. *Mol. Phys.* **1985**, *55*, 331.

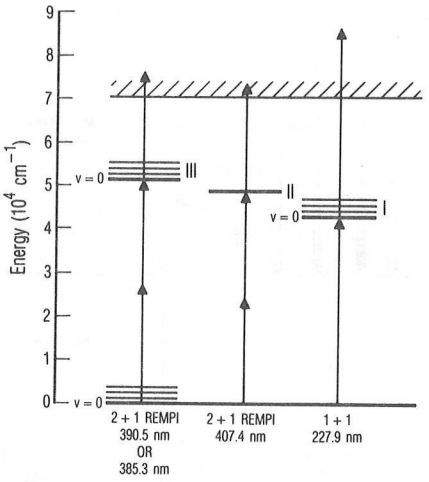


Figure 3. REMPI excitation schemes employed in the study of dimethyl sulfide.

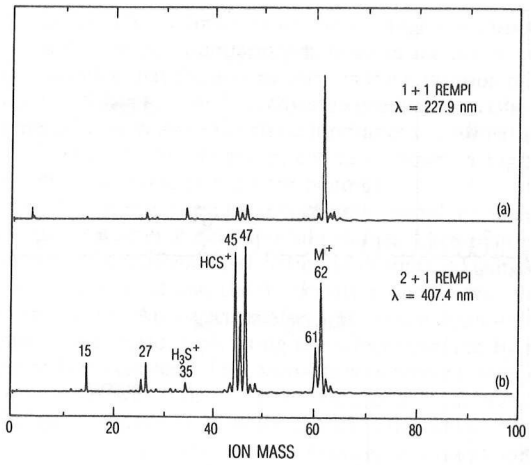


Figure 4. Molecular beam mass spectra of DMS: (a) 1+1 REMPI via the Rydberg state I at 227.9 nm; (b) 2+1 REMPI via the featureless state II at 203.7 nm.

they have little overlap in the dimer structure (Figure 1). Our diagram differs from Naito et al. in that they treat n_1 and n_2 as nearly degenerate, which causes σ to be the lowest energy dimer orbital of the four shown.[11]

Sulfide dimer cations absorb strongly in the 400–500-nm region ($\epsilon \sim 5 \times 10^3$ L/mol·cm).[11-16] Another band at around 300 nm has been assigned to the monomer cation;[14,15] however, more recent studies argue that this band may also be a dimer cation absorption.[11,16] The visible absorption is either a $n \rightarrow \sigma^*$ or a $\sigma \rightarrow \sigma^*$ transition. Naito et al. assign the two lowest energy transitions to $n_+ \rightarrow \sigma^*$ and $n_- \rightarrow \sigma^*$,[11] whereas Asmus and co-workers prefer $\sigma \rightarrow \sigma^*$.[12,13] If the MO calculations that predict a large $n_1 - n_2$ monomer energy difference are accurate,[21] then the visible transition must be $\sigma \rightarrow \sigma^*$. This assignment is also in reasonable accord with the $\sigma \rightarrow \sigma^*$ splitting predicted from the dimer cation bond energy. In any case, there is agreement that the upper state is σ^*, and hence, one might expect photochemistry to ensue for such cluster ion excitation.

Monomer Ionization/Dissociation

To study photochemistry in the cluster ions, it was first necessary to establish the monomer cation dissociation mechanisms. We used resonance-enhanced multiphoton ionization (REMPI) and electron-impact (EI) ionization on DMS. Several REMPI schemes were used to study the effects of intermediate neutral electronic states, vibrational excitation, excess ionization energy, and ion absorption on the ion dissociation pathways.[20] The three lowest lying one photon allowed transitions in DMS are given in Figure 3 along with our excitation schemes. Our results indicate that the two higher energy transitions also have two-photon activity.[20] The transitions in Figure 3 have been assigned differently by various authors. Thompson et al.[21] assign these transitions to Rydberg excitations from the $3p_x$ orbital to 3d, 4s, and 3d orbitals, respectively, whereas Scott et al.[22] assign the final states to 4s, valence, and 4p orbitals, respectively. Tokue et al.[23] assign them to valence, 4s, and 4p orbitals, respectively. We will simply refer to these states as I, II, and III. States I and III have distinct vibrational structure, and state II is diffuse. The values of log ϵ (molar extinction coefficient) are about 2.9, 3.7, and 4.0, respectively.[21]

The 1 + 1 REMPI mass spectrum through the origin of state I is given in Figure 4a. The predominant ion is the parent at mass 62, even though the excess photon energy above the ionization potential energy E_{IP} is greater than 2 eV. This result is consistent with a Rydberg intermediate state which should have nearly vertical Franck–Condon overlap with the ion potential surface, thus minimizing ion vibrational excitation. Excitation into the diffuse state II produced extensive fragmentation (Figure 4b). It was necessary to use two-photon resonance (2+1 REMPI) because of the high energy of this state. Since the three-photon ionization can produce low-energy parent ions (Figure 3), the ion

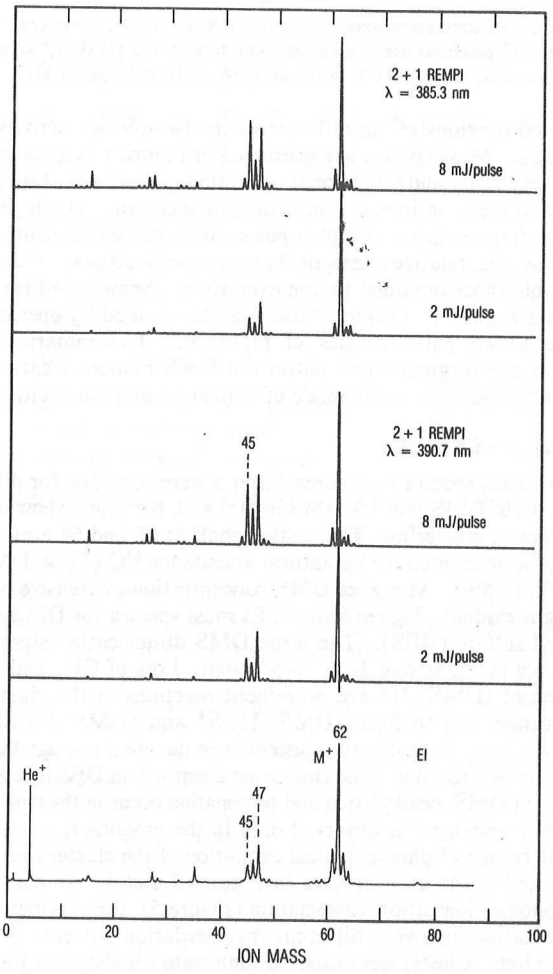


Figure 5. 2+1 REMPI mass spectra recorded via the vibrationless (390.7 nm) and the 704-cm^{-1} vibrational level (385.3 nm) of the Rydberg state III. EI ionization is shown to give similar results.

fragmentation must be due to ion absorption and dissociation from a fourth photon.[28] The ions can dissociate to an H atom or CH_3 group as well as rearrange to form $HCSH^+$ and HCS^+.

State III at 195.3 nm was excited and ionized by 2+1 REMPI. This Rydberg state is assigned either to a 4s or 4p excitation.[21-23] A vibrationally resolved 2+1 REMPI excitation spectrum has been

(28) Fragment ions may also result from neutral excited-state dissociation followed by fragment ionization. However, this mechanism is expected to be much less important than ion dissociation because it requires more total photons and a neutral state that dissociates on a time scale less than the laser pulse duration of 5 ns.

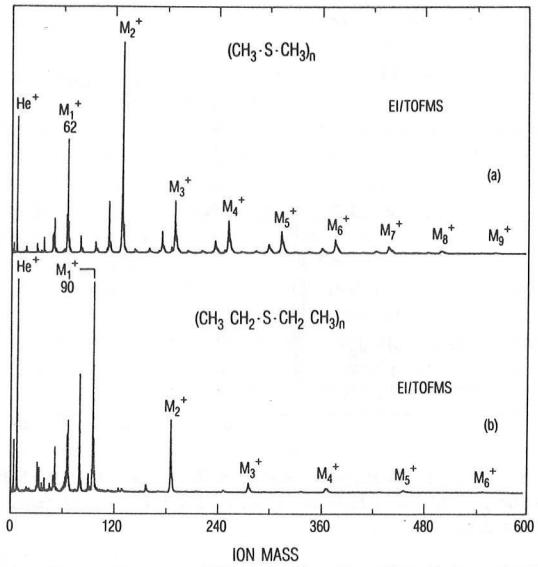


Figure 6. EI ionization mass spectra of DMS and DES clusters. The $(DMS)_nH^+$ products are evident as shoulders on the $(DMS)_n^+$ signals. Beam conditions were 4.0% DMS or 1.0% DES in 50 psi of He.

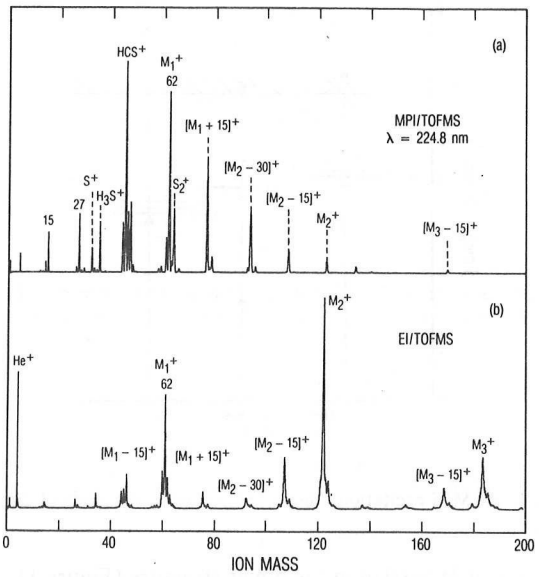


Figure 7. Mass spectra of DMS clusters: (a) REMPI excitation at a wavelength off-resonant from the monomer state I; (b) EI excitation showing different fragmentation behavior.

reported previously[20] and illustrates the two-photon activity of this state. Mass spectra are presented in Figure 5 as a function of pulse energy and vibrational excitation. These are also compared to electron-impact ionization/dissociation. Aside from greater fragmentation at higher pulse energies, the fragmentation patterns (i.e., relative intensities) are similar in all cases and also resemble those obtained by the excitation schemes used for recording Figure 4. Fragmentation can be avoided by operating at much lower pulse energies (cf. Figure 8a). To summarize this section, the fragmentation pattern of DMS monomer cation is basically invariant to the mode of ionization and ion excitation.

Cluster Ion Chemistry

The mass spectra in Figures 4 and 5 were recorded for dilute mixtures of DMS (<0.5% DMS in He) and, therefore, show little evidence of clustering. The weak signals at 63 and 64 amu can partly be accounted for by natural abundance ^{13}C (2% in DMS) and ^{34}S (4.5%). At higher DMS concentrations, extensive clustering is evident. Figure 6 shows EI mass spectra for DMS and diethyl sulfide (DES). The large DMS dimer cation signal is evidence of the strong 3e,2c $S–S^+$ bond. Loss of CH_3 and formation of $(DMS)_nH^+$ are prominent reactions in the clusters. Rearrangement to form $(DMS)_nHCS^+$ and $(DMS)_nHCSH^+$, however, is not evident in the clusters, even though it is a significant monomer ion reaction. The cluster ion chemistry in DES is similar to that in DMS; dealkylation and protonation occur in the clusters, but rearrangement is observed only in the monomer.

The results of photochemical excitation of the cluster ions are presented in the mass spectra in Figures 7 and 8. In contrast to monomer ionization/dissociation (Figure 5), the two methods of ionization give very different fragmentation patterns in the cluster ions. Cluster ionization through state I is shown in Figure 7a and compared with EI ionization in Figure 7b. Two-photon ionization of monomer DMS through state I produces a cation with insufficient energy to dissociate (Figures 3 and 4a). Fragmentation requires absorption of a third photon by the ion. Cluster ion photoexcitation (at 224.8 nm to avoid monomer excitation) at sufficiently high pulse energy to induce cluster ion absorption leads to products S_2^+, $(CH_3)_3S^+$, CS^+, and HCS^+ that are either absent or much weaker by EI excitation. It is also interesting that $(DMS)_2^+$ (and possibly larger clusters) readily loses one, two, and four CH_3 groups, but loss of three groups rarely occurs.

The mass spectra in Figure 8 were recorded by 2+1 REMPI through state III using wavelengths around 400 nm. At these wavelengths, monomer and cluster ions are formed with little excess energy. Fragmentation occurs by subsequent ion absorption. The cluster ions, because of the 3e,2c disulfide dimer cation bond,

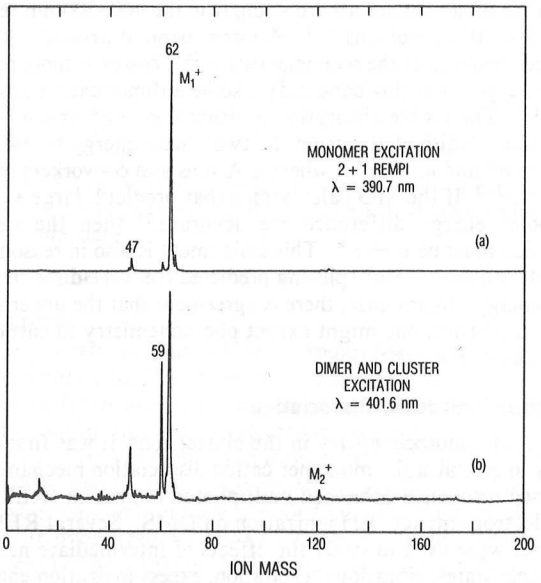


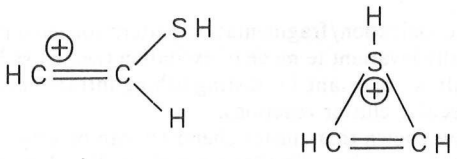
Figure 8. REMPI mass spectra for monomer vs dimer and cluster excitation in DMS: (a) 2+1 REMPI (390.7 nm, 0.02 mJ) excitation of monomer (v = 0) Rydberg state III; (b) 2+1 REMPI of dimer and cluster molecules using excitation to low-energy side of the monomer excitation (401.6 nm, 0.08 mJ).

absorb strongly at these wavelength, whereas the monomer cations absorb very weakly. The mass spectra in Figure 8 were recorded at very low pulse energies (0.02–0.08 mJ/pulse, 1-mm diameter) to avoid monomer cation dissociation. Excitation through the monomer origin of state III yields parent ion signal with very little dissociation (Figure 8a). The excitation wavelength was shifted to the red of the monomer origin to excite primarily clusters of DMS (Figure 8b). Some monomer excitation is possible through the weakly absorbing state II; however, at these low pulse energies minimal monomer ion dissociation should occur. Under the conditions of Figure 8b, a distinct enhancement is observed at mass 59 which can only be attributed to a cluster photochemical reaction (cf. Thiirenium Ion).

Our results reveal dramatic differences in the cluster ion chemistry induced by EI and by photochemical excitation. The principal cluster ion chemistry in EI ionization/dissociation is S–C bond cleavage leading to demethylation and hydride transfer, producing protonated DMS monomer and cluster ions. These results are similar to what is observed in bimolecular gas-phase reactions involving cation and neutral DMS.[10,29,30] Photochemical

excitation, however, produces distinct photoproducts that depend strongly on wavelength. Each of these reactions is considered in the following.

Thiirenium Ion. Mass 59 corresponding to $C_2H_3S^+$ can be assigned as a cluster photochemical product because it is absent in Figures 4 and 5 under nonclustering conditions and it is present under clustering conditions only when the wavelength is resonant with the strong absorption band of the 3e,2c disulfide dimer cation. (Mass 59 does not appear, for example, in Figure 7.) The structure of mass 59 could be either an open β-thiovinyl cation or a closed cyclic thiirenium cation:



Molecular orbital calculations indicate that the cyclic form is more stable by 1–14 kcal/mol with a barrier to interconversion of about 13 kcal/mol.[31]

The cyclic thiirenium structure was first proposed as an intermediate or transition state to explain the rearrangements in the solvolysis of some β-thiovinyl sulfonates and to explain the antistereospecificity of sulfenyl chloride addition to acetylenes.[32] Trimethylthiirenium has been observed by low-temperature NMR.[33] Mass 59 has only been observed as a trace component in gas-phase mass spectrometry of organosulfide molecules.[30,34]

Mass 59 appears as the dominant photoproduct following the dimer cation σ^* excitation in the clusters. There is also a weak methylthiirenium signal at mass 73. The mechanism for thiirenium formation in the clusters must involve a multiple bond rearrangement. If the reaction is intramolecular (with possible solvent stabilization), then the C···C separation in DMS of about 2.7 Å (Figure 1) must collapse to about 1.3 Å to form the C=C bond in either the open or closed structure of mass 59.[31] Further evidence for the formation of a C=C bond is the appearance of $CH_2{=}CH^+$ (mass 27) following monomer and cluster ionization. $CH_2{=}CH^+$ may form by elimination of S from the intermediate thiirenium structure. A three-center dissociation has been documented for high-energy electronic excitation of H_2S to produce $S + H_2$.[35] Apparently the observation of the thiirenium reactive intermediate derives from low-energy dimer cation excitation and energy dissipation to the surrounding cluster molecules. The energy is then released by evaporation.

Demethylation. The S–C bond energy in neutral DMS is 3.35 eV (the value in the cation is not known).[36] This compares to a C–H bond energy of about 3.7 eV (based on the value for $H{-}CH_2CH_3$).[36] Consequently, methyl loss dominates over hydrogen loss in the monomer cation mass spectra in Figures 4 and 5. The structures attributed to these species are $[H_2C{=}SH]^+$ and $[H_2C{=}SCH_3]^+$, respectively.[37] The efficient rupture of the S–C bond in the DMS cluster ions, as evidenced by the $(DMS)_nSCH_3^+$ series of peaks in Figure 6a, is consistent with a stable covalent S···S dimer cation bond. However, because the S···S bond is weaker than the S–C bond in the dimer cation, it seems plausible that the driving force is the formation of a much stronger S–S bond in the demethylated product ion. Dissociation of a methyl may remove the steric hindrance to internal rotation, thus allowing the hybridized p_z orbitals, shown in Figure 1, to rotate into favorable overlap for bonding.

The EI cluster ion results very closely resemble the reactions observed in gas-phase ion–molecule studies. Drewello et al. reported on the collisional dissociation of diisopropyl sulfide dimer cation and observed that the dealkylation dominated over $S{-}S^+$ bond breaking.[29] Also, a second dealkylation was observed to occur in much lower yield, replicating the effect observed by EI ionization of DMS clusters. This contrasts with photochemical cluster ion excitation, which shows increasing yields for subsequent demethylation (Figure 7). Finally, the EI ionization of dithioether chains, studied by Musker et al., resulted in cyclization due to S–S bond formation and dealkylation.[30] This cross-linkage reaction can be viewed as an "intramolecular" clustering and may have relevance for reactions in long-chain biological molecules.

Bimolecular gas-phase reactions involving DMS cation and neutral were reported by Illies et al.[10] However, they did not report a methyl loss fragment at mass 109 but instead cite the formation of protonated DMS at mass 63 via the mechanism

$$CH_2{=}SH^+ + (CH_3)_2S \rightarrow CH_2{=}S + (CH_3)_2SH^+ \quad (1)$$

If this mechanism holds for the cluster ions, then the formation of protonated clusters must be a sequential reaction requiring an initial demethylation.

Protonation by Hydride Transfer. DMS has a gas-phase basicity very similar to that of NH_3 (proton affinity of 8.7 vs 8.8 eV, respectively[38]). We assume that the gas-phase protonation occurs by the reaction

$$(CH_3)_2S^+ + (CH_3)_2S \rightarrow (CH_3)_2SH^+ + CH_2SCH_3 \quad (2)$$

even though reaction 1 may also occur. The gas-phase enthalpy for hydride transfer in reaction 2 can be calculated from a thermodynamic cycle[4b] that gives

$$\Delta H_g = E_{IP}(H) - E_{IP}(DMS) + D(C{-}H) - D(DMS{-}H^+)$$
$$= 13.60 - 8.68 + 3.70 - 8.70 \simeq 0 \text{ eV}$$

where E_{IP} values are ionization potentials and D values are bond energies, the latter value being a proton affinity. (The reported values are from refs 39, 39, 36, and 38, respectively.)

The occurrence of reaction 2 is supported by the observation of $C_2H_7S^+$ at mass 63 in gas-phase studies of ion–molecule reactions (although the mechanism is still in doubt).[10,34] The analogous reaction in a bound dimer cation is predicted to be endothermic by about 1.0 eV because of the strong dimer cation bond energy of about 1.1 eV, which stabilizes the reactant side of reaction 2. Indeed, the collisional dissociation of diisopropyl sulfide dimer cation failed to produce protonated monomer; only dealkylation product ions and unprotonated monomer ion were observed.[29] For larger clusters the enthalpy should progressively decrease (become less endothermic) with increasing cluster size because the complexation energy of DMS should be greater for a protonated ion (product side) than for an unprotonated ion (reactant side). This trend has been observed in the ionization of clusters containing molecules with large proton affinities,[40] such as the pure clusters $(NH_3)_n$[41] and $(CH_3OH)_n$[42] as well as the mixed

(29) Drewello, T.; Lebrilla, C. B.; Schwarz, H.; de Koning, L. J.; Fokkens, R. H.; Nibbering, N. M. M.; Anklam, E.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1987**, 1381.

(30) Musker, W. K.; Gorewit, B. V.; Roush, P. B.; Wolford, T. L. *J. Org. Chem.* **1978**, *43*, 3235.

(31) Csizmadia, I. G.; Duke, A. J.; Lucchini, V.; Modena, G. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1808.

(32) (a) Modena, G.; Tonellato, U. *Adv. Phys. Org. Chem.* **1971**, *9*, 185. (b) Modena, G.; Scorrano, G.; Tonellato, U. *J. Chem. Soc., Perkins Trans. 2* **1973**, 493.

(33) Capozzi, G.; DeLucchi, O.; Lucchini, V.; Modean, G. *Chem. Commun.* **1975**, 248.

(34) Möckel, H. J. *Fresenius' Z. Anal. Chem.* **1979**, *295*, 241.

(35) (a) Steadman, J.; Baer, T. *J. Chem. Phys.* **1989**, *91*, 6113. (b) Steadman, J.; Cole, S. K.; Baer, T. *J. Chem. Phys.* **1988**, *89*, 5498.

(36) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(37) (a) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 2774. (b) Pope, S. A.; Hillier, I. H.; Guest, M. F. *Chem. Phys. Lett.* **1984**, *104*, 191. (c) McLafferty, F. W.; Dill, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 6526. (d) McLafferty, F. W.; Dill, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 2907.

(38) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1.

(39) Weast, R. C., Ed. *Handbook of Chemistry and Physics*; 56th ed.; CRC Press: Cleveland, OH, 1975.

(40) (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. (b) Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939. (c) Payzant, J. D.; Cunningham, A. J.; Kebarle, P. *Can. J. Chem.* **1973**, *51*, 3242.

(41) (a) Echt, O. H.; Dao, P. D.; Morgan, S.; Castleman, A. W. *J. Chem. Phys.* **1985**, *82*, 4076. (b) Shinohara, H.; Nishi, N.; Washida, N. *J. Chem. Phys.* **1985**, *83*, 1939.

(42) (a) Shukla, A. K.; Stace, A. J. *J. Phys. Chem.* **1988**, *92*, 2579. (b) Morgan, S.; Castleman, A. W. *J. Am. Chem. Soc.* **1987**, *109*, 2867. (c) Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939.

cluster systems involving toluene,[43] aniline,[4b] and phenol[6] seeded in solvent clusters (e.g., NH_3, H_2O, and CH_3OH).

The mass spectra for DMS cluster ionization are consistent with the above trends. Very little dissociative hydride transfer to form $(DMS)H^+$ is observed by photochemical excitation of the dimer cation (cf. Figures 7a and 8). The dimer cation reaction is a little more evident for EI ionization than for MPI (compare parts a and b of Figure 7), perhaps because of the greater total energy of ionization by EI (70 eV of electron energy vs about 9–13 eV of photon energy). Hydride transfer is observed to occur more extensively in larger clusters. Although the EI mass spectrum in Figure 6a does not fully resolve unit masses, the shoulder corresponding to the protonated ion $(DMS)_nH^+$ does increase considerably relative to the parent ion signal $(DMS)_{n+1}^+$ with cluster size n. This result supports a reaction enthalpy that decreases with increasing cluster size.

Summary and Conclusion

The formation of a 3e,2c bond in the DMS dimer cation creates strongly absorbing bands in the visible region that are not present in the monomer cation. This has enabled us to study photochemistry in the cluster ions. The results of this work are summarized by the following:

(1) EI ionization/dissociation of DMS clusters promotes reactions that closely resemble those observed in gas-phase bimolecular ion–molecule reactions and collision-induced dissociation, namely, (i) dealkylation by S–C bond cleavage and (ii) hydride transfer to form protonated monomer and clusters.

(2) REMPI excitation followed by cluster ion absorption leads to reactions that are quite different from the EI results. The most distinct photochemistry occurred by exciting the dimer cation σ^* state at 400 nm. The strongest observed photoproduct, $C_2H_3S^+$, is believed to have the cyclic thiirenium structure, which has been implicated as an important intermediate in solution-phase sulfide chemistry.

(3) The ionization/fragmentation pattern for monomer DMS is essentially invariant to mode of excitation (i.e., EI vs REMPI). This result is important for distinguishing intramolecular from intermolecular cluster reactions.

We have shown that cluster chemistry can be very specific to the mode of excitation. The finite size of small molecular clusters has enabled us to selectively induce reactions associated with both the gas phase and the solution phase. The study of cluster ions has direct correspondence to solution-phase chemistry, particularly those involving nucleophilic displacement, for which the formation of carbocations and sulfur cations constitutes the central reactive site. The observation of analogous reactions in small clusters provides a bridge to understanding solution-phase chemistry on a molecular level.

(43) Brutschy, B.; Janes, C.; Eggert, J. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 74.