overall potential energy functions. Halocioglu and White²⁵ and Garzón and Blaisten-Barojas²⁶ have shown that if they are sufficiently strong, three-body forces can cause immense changes in the nature and relative stabilities of different types of cluster structures. When the present work was undertaken, there existed no quantitative estimates of such terms for our mixed SF₆-(rare gas) systems, so the prevailing pairwise sum ansatz was adopted. However, it appears that such results are now becoming available.³⁹ This suggests that an important extension of the present work will be to examine the effect of such terms on our findings.

Another topic deserving further study is the effect of zero-point energies and other manifestations of quantum mechanics on our results. We have argued that they should not affect our conclusions regarding the unimportance of stacked structures for

 SF_6 -(Ne), and SF_6 -(He), clusters. However, it appears likely that quantum effects will have significant effects on the dynamics and phase-transition behavior of heterogeneous clusters formed from the lighter rare-gas atoms.

In any case, the present paper provides insight into the nature and dynamics of heterogeneous van der Waals clusters by delineating the effects of potential anisotropy and size compatibility on the nature of preferred structural forms. As a result, it makes an important contribution to our understanding of the bridge between molecular and macroscopic behavior provided by molecular clusters.

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Registry No. SF₆, 2551-62-4; Ar, 7440-37-1; Kr, 7439-90-9.

Dynamics of Metastable Dissociation and Photodissociation of the Gas-Phase Cluster Ion $(OCS:C_2H_2)^+$

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The dynamics of dissociation of $(OCS:C_2H_2)^+$ have been examined by using mass-analyzed ion kinetic energy spectrometry (MIKES). Kinetic energy release distributions for the dissociations were determined by analysis of the MIKES peak shapes. Metastable dissociation yields OCS^+ and $C_2H_2S^+$ as the ionic products of the cluster ion bond cleavage and a sulfur ion transfer reaction, respectively. The latter channel is exothermic by more than 25 kcal/mol, and the kinetic energy release distribution is highly nonstatistical. Ab initio calculations on the ground-state reactants and products of the S⁺-transfer reaction indicate that although the thicketene structure is the lowest energy isomer of C2H2S⁺, the alternative isomeric species, thirene molecular ion, is also permitted by the thermochemistry of the reaction. Photodissociation experiments were performed in the photon energy range 2.1-3.5 eV, using a crossed laser beam-ion beam geometry. The photodissociation cross section increases apparently smoothly from about 8×10^{-20} cm² at 2.1-eV photon energy to 4×10^{-18} cm² at 3.5 eV. The ionic products formed in this energy range are OCS⁺ and $C_2H_2^+$, which appear in an essentially constant ratio of 6:1. Analysis of the angular distributions of the OCS⁺ and $C_2H_2^+$ photoproducts indicates that both dissociation channels arise from excitation to a repulsive excited state. Analysis of the kinetic energy release distributions provides an upper limit to the cluster bond dissociation energy of about 1.15 eV and suggests a sulfur-carbon bonding interaction in the cluster ion. These results are supported by ab initio calculations, which indicate a bond dissociation energy of 0.875 eV, and that the most stable form of $(OCS:C_2H_2)^+$ is with near σ -bonding between the S atom of OCS and one of the carbons of C_2H_2 .

Introduction

The study of clusters and cluster ions has been an area of rapidly growing activity in recent years.¹⁻⁴ A fundamental goal of such studies is to elucidate the structural properties and molecular interactions of the cluster species. Among the many motivations that drive cluster ion research is the desire to understand dynamics and mechanisms of ion-molecule reactions. In favorable cases, cluster ions can act as models for the transient intermediate species in these reactions.⁵⁻⁷ As such, studies of the dissociation of cluster

ions can provide a valuable complement to full-collision experiments.

In an ongoing research program in this laboratory, the dynamics of photodissociation of numerous dimeric, trimeric, mixed, and homogeneous ion clusters have been examined.⁸ In these experiments, the disposal of the energy deposited by absorption of a photon into translational and internal modes of the product species is analyzed. It is possible thereby to deduce characteristics of the potential energy surfaces relevant to the dissociation and in certain cases to obtain information about cluster ion structure. From these studies has come a better understanding of the fun-

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In the present study, we examine the dynamics of metastable dissociation and photodissociation of the $(OCS:C_2H_2)^+$ cluster ion. Ion chemistry in the carbonyl sulfide-acetylene system has not been studied in depth and therefore is not well understood. A thermal energy reaction between OCS^+ and C_2H_2 produces $C_2H_2S^+$ and CO (eq 1).⁹ In the reaction of $C_2H_2^+$ with OCS,

$$OCS^+ + C_2H_2 \rightarrow C_2H_2S^+ + CO \tag{1}$$

two major channels are observed, corresponding to the exothermic charge-transfer reaction forming OCS⁺ and a sulfur-atom transfer that forms $C_2H_2S^+$ (eq 2).^{9,10} The structure of the $C_2H_2S^+$

$$C_2H_2^+ + OCS \rightarrow OCS^+ + C_2H_2$$
$$\rightarrow C_2H_2S^+ + CO$$
(2)

product in these reactions is not known. Theoretical calculations of the relative energies of isomers of neutral C_2H_2S indicate that the lowest energy species is thicketene,^{11,12} but information on isomers of the molecular ion is not available.

In recent studies by Anderson and co-workers, the OCS⁺ and $C_2H_2^+$ reactant species in eqs 1 and 2 were produced in specific vibrational states by means of multiphoton ionization of the neutral precursors.^{13,14} They observed mode-specific inhibitions or enhancements of the charge-transfer and sulfur-transfer reactions. Whereas the charge-transfer reaction may proceed by both direct and complex mechanisms, it is almost certain that the sulfurtransfer reactions involve complex mechanisms. In the sulfurtransfer reactions, the mode specificity observed was attributed to effects of a bottleneck in the complex formation step (first half of eq 3), rather than to a transition state associated with sulfur transfer (last half of eq 3).14

$$OCS^+ + C_2H_2 \rightleftharpoons (OCS:C_2H_2)^{+*} \rightarrow C_2H_2S^+ + CO \quad (3)$$

In a related study, Orlando et al. carried out photodissociation experiments on the (OCS:C2H2)+ cluster ions generated by ionization in an expansion of OCS and C₂H₂.¹⁵ They measured the photodissociation spectrum for the photon energy range 1.69-3.31 eV and observed three broad features. Three ionic products were observed, with an energy-dependent branching ratio. The OCS+ ion was observed throughout the entire energy range studied, and $C_2H_2^+$ was observed for all excitation energies above the apparent threshold of 1.69 eV. At energies above 2.74 eV, C₂H₂S⁺ could also be detected. They interpreted their results in terms of transitions to three repulsive excited-state surfaces and identified the $C_2H_2S^+$ product as arising from a photoinitiated reaction.

We have undertaken to examine the dynamics of dissociation of the $(OCS:C_2H_2)^+$ species in order to better understand the features of both the ground- and excited-state potential energy surfaces. Our experiments entail accurate measurements of the relative kinetic energy of the products formed by dissociation. We have also measured the photodissociation cross sections for the photon energy range 2.1-3.5 eV and have examined the angular distributions of the photoproducts. These experiments have been supplemented by ab initio calculations of the reactants and products in the ground-state reaction, including three isomeric forms of C₂H₂S⁺.

Experimental Section

The experiments described herein were carried out using a reverse-geometry (BE) double-focusing sector mass spectrometer (V.G. Instruments ZAB-2F) with an argon ion laser (Coherent,

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operated at about 270 K, with a total pressure of 0.04-0.10 Torr. The product ion peak shapes did not change measurably over this range of pressure, which suggests that the majority of the $(OCS:C_2H_2)^+$ ions exiting the source had internal energies close to thermal. Optimal intensities were obtained by using OCS in large excess over C₂H₂, i.e., about 2% C₂H₂ in OCS. Photodissociation was effected in the wavelength range 350-590 nm, corresponding to energies between 2.10 and 3.5 eV, using the all-UV-line laser output for excitation at 334, 351, and 364 nm, discrete argon ion laser lines from 458 to 529 nm, and the dye laser output at 590 nm (rhodamine 6G dye). For studies of the angular distribution of the ionic photoproducts, the orientation of the laser beam polarization was set to 0°, 54.7°, and 90° with respect to the ion beam direction, by using a polarization rotator (Spectra Physics 310A). Photodissociation cross sections were derived from integrated photoproduct yields for dissociation of $(OCS:C_2H_2)^+$ compared to $(N_2)_2^+$.

The product ions were analyzed by using mass-analyzed ion kinetic energy spectrometry (MIKES). This technique yields a peak shape that corresponds to the laboratory frame kinetic energy distribution for those product ions transmitted to the detector. The experimental peak shapes are fit by a linear combination of calculated peak shapes, each of which corresponds to a discrete kinetic energy release. These calculated peak shapes, or "basis functions", are derived from an analysis of the trajectories of product ions from the point of dissociation in the 2ndFFR to the detector.¹⁸ The coefficients of the basis functions are normalized to yield a probability distribution for kinetic energy release. This method is based on a peak-shape analysis program developed by Rumpf and Derrick¹⁹ and will be described in more detail in a future publication.20

Theoretical Calculations

Ab initio structure and energy calculations were carried out for each of the monomer species involved in the ground-state reaction of OCS⁺ with C_2H_2 . Three isomeric structures of $C_2H_2S^+$ were considered: thioketene (I), thiirene (II), and ethynethiol (III).



These calculations employed the 6-31+G(d) basis set, which includes a set of d-type polarization functions and diffuse s and p orbitals on the heavy (non-hydrogen) atoms.^{21,22} Diffuse

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Innova 20) and dye laser (Coherent, Model 599). The experimental method and instrument have been described in detail previously and will only be summarized briefly here.^{16,17}

Ions are generated in an electron impact/chemical ionization source, which can be cooled by circulating nitrogen through the source block. Subsequent to ionization, formation of cluster ions occurs through a sequence of ion-molecule reactions and termolecular association reactions. Clustering is facilitated by the low temperatures and relatively high pressures in the ion source. The ion source temperature is measured with a platinum resistor, and the pressure is monitored with an MKS Baratron capacitance manometer. Upon effusing from the source, the ions are accelerated to 8 keV, and the ion of interest is mass-selected at the magnetic sector. The ion beam is crossed at its spatial focal point in the second field-free region (2ndFFR, between the magnet and the electrostatic analyzer, ESA) by the output beam of the argon ion laser or dye laser. For collisional activation studies, helium gas is leaked into a collision cell in the second field-free region. To generate the $(OCS:C_2H_2)^+$ cluster ions, the ion source was

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TABLE I: Collisional Activation Spectrum of (OCS:C2H2)+

mass, amu	ion	rel int ^a	mass, amu	ion	rel int ^e
69	C ₁ HS ⁺	2.6	44	CS ⁺	12.1
68	C,S⁺	1.4	32	S+	23.2
60	OCS+	100.0	28	CO+	9.5
58	$C_2H_2S^+$	64.8	26	$C_{2}H_{2}^{+}$	42.0
57	C ₂ HS ⁺	61.1	25	C_2H^+	20.4
45	CHS+	15.6	24	C_{2}^{-+}	5.3

"Relative intensities normalized to 100. Intensities are taken at peak maxima and corrected for mass discrimination.

functions are known to be critical for a proper description of the electronic structure of anions.²³⁻²⁵ In the present system, we use a diffuse function to help improve the description of the lone pairs, which we expect to be intimately involved in the intermolecular interactions in the cluster ion. Full geometry optimerizations were carried out using the 6-31+G(d) basis set at the restricted Hartree-Fock (RHF) level for each of the neutral monomeric species and at the unrestricted Hartree-Fock level (UHF) for the open-shell systems. These optimizations were repeated with the 6-31+G(d) basis set, including electron correlation, by using Møller-Plesset theory to second order.²⁶ Zero-point vibrational energies were computed from frequency calculations carried out for the geometries optimized at the HF/6-31+G(d) level. Frequencies calculated by ab initio methods are often somewhat larger than the experimental values, and various schemes for scaling the frequencies have been suggested to correct for the errors.²⁷ For the computation of zero-point energies, the calculated frequencies were scaled by 0.89,26 and vibrations with scaled frequencies below 500 cm^{-1} were treated as classical rotations.

Preliminary searches for local minima for the $(OCS:C_2H_2)^+$ cluster ion were performed using the 3-21G(*) basis set, which includes d-type orbitals only for third-row atoms and beyond. Final optimizations were carried out at the UHF/6-31+G(d) level, and the correlation energy was computed by using second-order Møller-Plesset perturbation theory. These calculations are denoted UMP2/6-31+G(d)//6-31+G(d).

All calculations were performed using the GAUSSIAN90 sets of programs.28

Results

Ionization and subsequent ion-molecule reactions of OCS at pressures of 0.04-0.10 Torr and a source temperature of about 270 K result in the formation of $(OCS)_2^+$ as the most abundant species, along with the molecular ion OCS⁺, various fragment ions, and their clusters with OCS. Addition of C2H2 to the source gas leads to formation of $C_2H_2S^+$ (m/z 58) and (OCS: C_2H_2)⁺ (m/z 86) as major products of the ion-molecule reactions that take place. Production of the desired $(OCS:C_2H_2)^+$ cluster is maximized by using a mixture of about $2\% C_2H_2$ in OCS. The abundance of $(OCS:C_2H_2)^+$ is very sensitive to the partial pressure of C_2H_2 and is rapidly depleted if the pressure of C_2H_2 is increased beyond these optimal conditions. This is most likely a consequence of a rapid ion-molecule reaction of $(OCS \cdot C_2H_2)^+$ with C_2H_2 .

Supporting evidence for the assignment of a cluster ion structure to the m/z 86 ion is provided by the results of high-energy collisional activation with helium target gas (Table I). Major



Figure 1. Product relative kinetic energy distribution for metastable dissociation of $(OCS:C_2H_2)^+$ yielding OCS^+ and C_2H_2 . The apparent structure is not reproducible and is an artifact of statistical noise in the experimental data. The average energy release is $\langle E_T \rangle = 0.06 \text{ eV}$.

product ions formed are OCS⁺, $C_2H_2S^+$, C_2HS^+ , and $C_2H_n^+$ (n = 0-2). The production of OCS⁺ and $C_2H_2^+$ species suggests that these are intact moieties in the parent ion. Although the appearance of C₂H₂S⁺ could be considered indicative of rearrangement, the results of metastable dissociation of the m/z 86 ion provide further evidence that the ion is well-described as $(OCS:C_2H_2)^+$. Note that the $C_2H_2S^+$ ion is also a product of an exothermic bimolecular reaction between OCS⁺ and C₂H₂ and thus is not inconsistent with the parent ion being $(OCS:C_2H_2)^+$. Production of $C_2H_2S^+$ can be taken as evidence of chemical bonding in the $(OCS:C_2H_2)^+$ cluster ion, as opposed to simply electrostatic bonding. In the latter case, we might expect to see only OCS⁺ and $C_2H_2^+$ and their fragments.

Metastable Dissociation. When an $(OCS:C_2H_2)^+$ adduct ion escapes from the ion source without being collisionally stabilized, it can undergo unimolecular dissociation during the flight through the mass spectrometer. When these metastable ions dissociate, any internal energy that is converted to translational energy during the dissociation causes broadening in the laboratory kinetic energy of the products. Energy analysis of the product ions by the electrostatic analyzer yields a peak shape that reflects their laboratory energy distribution. The laboratory energy distribution can then be converted to a relative kinetic energy distribution, which reflects the kinetic energy released in the dissociation.18,19,29,30

The product ions formed by metastable dissociation of $(OCS:C_2H_2)^+$ in the second field-free region are OCS⁺ and $C_2H_2S^+$. The branching ratio for these two ions varies with the pressure in the ion source. The $C_2H_2S^+$ ion is the major product formed, comprising about 90% of the total integrated product ion intensity at the lowest ion source pressures at which the product ions can be detected. As the source pressure is increased, the fraction of $C_2H_2S^+$ also increases, indicating that the critical energy for formation of this product is lower than that for formation of OCS⁺. Although a very weak signal corresponding to $C_2H_2^+$ can also be detected, it comprises less than 0.5% of the integrated product intensity and may arise from collisional activation of the adduct with background gas. Formation of C₂H₂⁺ and OCS requires 0.23 eV more energy than formation of OCS+ and C_2H_2 ,^{32,33} so the failure to observe $C_2H_2^+$ as a significant fraction of the products from metastable dissociation is to be expected.

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Figure 2. Product relative kinetic energy distribution for metastable dissociation of $(OCS:C_2H_2)^+$ yielding $C_2H_2S^+$ and CO. The average energy release is $\langle E_T \rangle = 0.43$ eV.

The peak observed for the OCS⁺ product formed by metastable dissociation is narrow and near Gaussian in shape. The kinetic energy release distribution (KERD) peaks near zero and decays smoothly with increasing energy (Figure 1). The average release calculated at the lowest source pressure (i.e., under ion formation conditions of little or no collisional stabilization) is 0.06 eV. As the source pressure is increased and stabilizing collisions become more frequent, the average release calculated for the OCS⁺ product decreases slightly. The peak observed for the C₂H₂S⁺ product formed by metastable dissociation is broad and flat-topped. Analysis of the peak shape yields a KERD that is triangular in shape, with the maximum probability strongly offset from zero (Figure 2). The average kinetic energy release, $\langle E_T \rangle$, is 0.43 eV at the lowest source pressures.

Photodissociation. For the photodissociation experiments, the ion source was held at higher pressures than were used for the studies of metastable dissociation. The higher source pressures facilitate collisional stabilization of the cluster ions. At the pressures used, most of the cluster ions experience many stabilizing collisions prior to exiting the cell, and their internal energy is close to thermal. However, some fraction of the ions that have short residence times in the source can exit without being completely thermalized. If these nonthermal ions have internal energies above the dissociation limit or above energetic barriers to reactions, they may undergo unimolecular metastable dissociation. Product ion signals arising from metastable dissociation or from collisionally activated dissociation are subtracted from photoproduct signals by mechanically chopping the laser beam and employing up/down counting of the product ion signal.

Photodissociation experiments were carried out in the energy range 2.10-3.5 eV (590-365 nm). The product ions formed upon excitation with visible light in the range 590-458 nm are OCS+ and $C_2H_2^+$. The branching ratio for these ions remains essentially constant at about 85% OCS⁺ and 15% $C_2H_2^+$ throughout this region.³⁴ Excitation with UV light (3.5 eV) yields, in addition to the OCS⁺ and $C_2H_2^+$ products, a third species corresponding to $C_2H_2S^+$. Accurate peak-shape analysis for the $C_2H_2S^+$ photoproduct was precluded by the accumulation of statistical noise resulting from up/down counting of the abundant $C_2H_2S^+$ product arising from dissociation of metastable (OCS: C_2H_2)⁺. From the integrated area of the peak, we estimate the upper limit of the branching fraction of this channel to be about 25%. The remaining two ionic products, OCS⁺ and $C_2H_2^+$, are still observed in a 6:1 ratio, corresponding to a branching ratio of about 65% and 10% respectively.

1. Cross Sections. Our experimental configuration does not permit direct measurements of absolute cross sections for photodissociation. However, it is possible to obtain reliable estimates



Figure 3. Total cross sections for photodissociation of $(OCS:C_2H_2)^+$: \Box , this work; \times , from ref 15. In both cases absolute cross sections were obtained by normalizing to $(N_2)_2^+ + h\nu \rightarrow N_2^+ + N_2$.

of the cross sections by measuring the product ion yields and comparing them to yields for photodissociation of a reference system with a known cross section.³⁴ Ideally, the reference system should have a photodissociation cross section and critical energy for dissociation that are of about the same magnitude as those of $(OCS:C_2H_2)^+$, the photodissociation kinematics should be comparable, and the reference ion should coexist in the ion source with $(OCS:C_2H_2)^+$. All but the last of these conditions can be readily satisfied by using $(N_2)_2^+$ as the reference.

Preliminary observations of the peak shapes of the photoproducts formed by excitation of $(OCS:C_2H_2)^+$ with polarized light indicated that the photoproducts were scattered anisotropically, with the intensity peaking along the direction of the electric vector of the photon. A similar angular distribution is observed for photodissociation of $(N_2)_2^{+.17}$ In the apparatus used for these experiments, ion loss due to instrumental discrimination is greatest for product ions formed with large components of velocity perpendicular to the direction of the ion beam, whereas ions that recoil parallel and antiparallel to the direction of the ion beam are collected with high efficiency. Therefore, to maximize the collection of the product ions and thus to avoid the difficulty of accounting for differential ion loss, all cross-section measurements were made with the electric vector of the incident light oriented parallel to the direction of the ion beam.

The product ion yields were derived from the ratio of the integrated peak areas for the product ions and the reactant ion and were corrected for mass discrimination caused by the increase in the energy resolving power $(E/\Delta E)$ of the electrostatic analyzer for product ions with low laboratory energy (i.e., with low mass). The yields were corrected for any changes in laser power that occurred between measuring the $(N_2)_2^+$ yield and the $(OCS:C_2H_2)^+$ yield (such changes in power were typically negligible). Care was taken to ensure that the intensity of the main beam of reactant ions remained constant throughout the measurement. The largest source of error in these measurements arises from uncertainties in the area of overlap of the ion beam and the laser beam. However, the beams are crossed at the focal point of the magnet in the second field-free region, where the ion beam comes to a spatial focus with the cross-sectional ion beam dimensions defined primarily by the geometry of the ion source exit slit. Thus, the cross-sectional area of the ion beam available for photoexcitation should be the same for $(N_2)_2^+$ and $(OCS:C_2H_2)^+$ so long as the source slit width is constant. It was found that obtaining the maximum product ion intensity for the $(N_2)_2^+$ and $(OCS:C_2H_2)^+$ systems generally did not require any adjustment of the laser beam position. This suggests that the beam overlap areas do not vary to a significant extent between the two systems.

The ratios of the product ion yields for photodissociation of $(N_2)_2^+$ and $(OCS:C_2H_2)^+$ were scaled to the absolute photodissociation cross section of $(N_2)_2^{+,35}$ We observe a steadily in-

⁽³⁴⁾ Branching ratios and cross sections are corrected for discrimination due to the higher energy resolution of the ESA for lower mass product ions. Jarrold, M. F.; Illies, A. J.; Bowers, M. T. J. Chem. Phys. 1984, 81, 222.



Figure 4. Product relative kinetic energy distribution for the OCS⁺/C₂H₂ photoproducts from photodissociation of (OCS:C₂H₂)⁺ at 514 nm. The apparent structure at low energies is not reproducible and probably results from statistical noise caused by subtraction of the metastable signal. The average energy release is $\langle E_T \rangle = 0.73$ eV.

creasing cross section, rising from about 8×10^{-20} cm² at 590 nm to 4×10^{-18} cm² with UV excitation (Figure 3). Also shown in Figure 3 for comparison are the measurements of Orlando et al.¹⁵ For the photon energies common to the two data sets, the cross sections measured are in fair agreement and probably are equal within the combined error of the two methods. The maximum observed by Orlando et al. between 450 and 340 nm falls in a wavelength region where there are no lines available with the argon ion laser used for the present experiments. We did not detect any increase in cross section at wavelengths larger than 529 nm.

2. Kinetic Energy Release Distributions. It has been shown in a previous publication that when the laser polarization vector is oriented at 54.7° relative to the ion beam direction (the so-called "magic angle"), the observed peak shape mimics the shape that would be detected for an isotropic angular distribution.¹⁷ Therefore, the photoproduct peak shape observed for a polarization angle of 54.7° can be analyzed to deduce the kinetic energy release distribution for photoexcitation.

In Figure 4 is shown the kinetic energy release distribution obtained from analysis of the peak shape observed for excitation at 514 nm, with a laser polarization angle of 54.7°. The distribution is roughly triangular and peaks at a relatively large energy. This shape is characteristic of a dissociation process dominated by repulsive forces. The average relative kinetic energy of the OCS⁺ and C₂H₂ photoproducts from excitation at 514 nm is 0.73 eV, which is about 30% of the photon energy (2.41 eV), and the maximum kinetic energy is 1.2 eV. The apparent structure at low energies is not reproducible and is probably an artifact of the statistical noise from up/down counting of the metastable signal. The same overall triangular shape of the kinetic energy release distribution is observed at all excitation wavelengths. As the photon energy increases, the distribution broadens and shifts to higher energy.

The kinetic energy release distributions observed for the $C_2H_2^+/OCS$ product channel are similar to the distributions seen for the OCS⁺/ C_2H_2 channel. As an example, we show in Figure 5 the distribution obtained at 514 nm for the $C_2H_2^+/OCS$ products. The same, roughly triangular distribution is observed, indicating that the dissociation dynamics in this channel are also dominated by repulsive forces. The average relative kinetic energy for the $C_2H_2^+/OCS$ products from photodissociation at 514 nm is 0.70 eV, or 29% of the photon energy, and the maximum kinetic energy is 1.3 eV. The distribution shifts to higher energy and broadens when higher photon energies are used, but the overall shape remains similar.

The average kinetic energies deduced from the distributions for the two photodissociation channels at different excitation



Figure 5. Product relative kinetic energy distribution for the $C_2H_2^+/OCS$ products from photodissociation of $(OCS:C_2H_2)^+$ at 514 nm. The average energy release is $\langle E_T \rangle = 0.70$ eV.

TABLE II: Average Kinetic Energy Releases for Photodissociation of $(OCS:C_2H_2)^+$

Wa	avelength,		Emax, ^b
	nm	$\langle E_{\rm T} \rangle$, ^{<i>a</i>} eV	eV
	A. Photopro	ducts: $OCS^+ + C_2H_2$	
52	9	0.686 ± 0.001	1.2
51	4	0.729 ± 0.010	1.2
50	2	0.749	1.25
49	7	0.751 🛳 0.001	1.3
48	8	0.791 🛳 0.020	1.3
47	6	0.800 🛳 0.007	1.4
47	3	0.804	1.4
45	8	0.857 🛳 0.003	1.5
334	4, 351, 364	1.28	2.3
	B. Photopro	ducts: $C_2H_2^+ + OCS$	
52	9 ·	0.684	1.2
51-	4	0.696	1.3
48	8	0.792	1.5
45	8	0.894	1.6

^aAverage kinetic energy released. Error bars indicate reproducibility for multiple measurements. ^bMaximum kinetic energy released.

energies are compiled in Table II, along with the maximum relative kinetic energy observed. Comparison of the maximum energy partitioned to translation with the photon energy provides an approximate upper limit to the cluster bond dissociation energy of about 1.2 eV (relative to the OCS⁺/ C_2H_2 products). For the OCS^+/C_2H_2 product channel, the average energy partitioned to product translation in the photodissociation process increases from about 29% of the photon energy at 529 nm to 37% for UV photons. The energy partitioned to translation of the $C_2H_2^+/OCS$ photoproducts also increases slightly, from 29% of the photon energy at 529 to 33% at 458 nm. For both photodissociation channels, the average kinetic energy released increases linearly with the energy available to the photoactivated cluster (Figure 6). In the present study, we define the available energy as the sum of the photon energy and the thermal energy of the cluster ion. For the purposes of clarity, the difference in the ionization potential of OCS and C_2H_2 ($\Delta IP = 0.23 \text{ eV}$)^{32,33} has been subtracted from the available energy for the higher energy dissociation channel leading to $C_2H_2^+$ and OCS. Least-squares analysis of this data yields for the OCS⁺/ C_2H_2 product channel the following relationship:

$$\langle E_{\rm T} \rangle = (0.52 \pm 0.02)(E_{\rm av}) - (0.60 \pm 0.04)$$
 (4)

and for the $C_2H_2^+/OCS$ channel, we obtain

$$\langle E_{\rm T} \rangle = (0.61 \pm 0.05)(E_{\rm av}) - (0.68 \pm 0.11)$$
 (5)

where $\langle E_T \rangle$ is the average kinetic energy release and $\langle E_{av} \rangle$ is the available energy as defined above. The error bars correspond to 1 standard deviation for the parameters of the least-squares linear fit to the data points.

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Figure 6. Plot of the photoproduct average relative kinetic energy against the total available energy (as defined in the text). The lines are linear least-squares fits to the data.

3. Angular Distributions. Absorption of a photon arises from the interaction between the electric vector of the photon and the transition dipole of the cluster ion. The absorption occurs preferentially when the electric vector and the transition dipole are aligned, yielding an anisotropic distribution of excited species. With time, the anisotropy of such a distribution can be blurred by molecular rotations. Dissociation of the excited species yields an angular distribution of products that reflects the original orientation of the species as well as any rotational averaging. Thus, the angular distribution of the product ions can provide information about the lifetime of the excited cluster as well as on the nature of the electronic transition.

In our experiments, the cluster ions (and consequently, their transition dipoles) are isotropically oriented in the ion beam. However, the output beam of the argon ion laser is plane-polarized. With use of a polarization rotator, the orientation of the laser polarization can be varied. (For laser output lines in the UV region, the polarization rotator cannot be used and the rotation is instead effected with the arrangement of mirrors.) If the dissociation products recoil along the direction of the transition dipole moment, then a broader peak will be observed when the electric vector is oriented along the ion beam direction than when it is oriented perpendicular to the ion beam direction. The peak shape observed for any given orientation of the photon electric vector relative to the ion beam direction arises from a convolution of the recoil angular distribution and the kinetic energy release distribution. The functional form for the angular recoil probability for products of photodissociation is given by

$$P(\theta) = (4\pi)^{-1} [1 + \beta P_2(\cos \theta)]$$
(6)

where θ is the angle of product recoil with respect to the electric vector of the photon and $P_2(\cos \theta)$ is the second-degree Legendre polynomial in $\cos \theta$.^{36,37} The asymmetry parameter β contains information on the excited-state lifetime and the electronic transition and can take values between +2 and -1.

We derive values for the asymmetry parameter by comparing the peak shapes measured for electric vector orientations of 0° and 90° relative to the direction of the ion beam with the corresponding peak shapes obtained from a computer simulation.¹⁷ The simulation uses a kinetic energy release distribution determined from the peak shape measured for electric vector orientation of 54.7° relative to the ion beam and an angular product recoil distribution from eq 6. For the present experiments, we assume an average value of β and adjust the value iteratively to optimize the agreement between the calculated peak shapes and the ex-



Figure 7. Peak shapes for OCS⁺ from photodissociation of $(OCS:C_2H_2)^+$ at 488 nm, with laser polarization angles of 0° and 90° relative to the ion beam direction. The points are the experimental data and the lines are simulated peak shapes assuming the asymmetry parameter $\beta = 1.45$.

TABLE III: Values of the Asymmetry Parameter β for the OCS⁺/C₂H₂ Photoproducts

 wavelength, nm	β	
514	1.39	
488	1.45	
458	1.63	
334, 351, 364	$(1.52)^{a}$	

^a Lower limit (see text).

perimental ones. The simulations do not account explicitly for discrimination.

An example of this kind of analysis is shown in Figure 7 for the OCS⁺ product formed at 488-nm excitation wavelength. Good agreement was obtained for an average β value equal to 1.45. These analyses were carried out for four different wavelengths, and the results are summarized in Table III. As the photon energy increases, the value of β that gives the best fit also increases, until the highest energy where a decrease is observed. This apparent decrease is probably an artifact of the neglect in the computer simulation of instrumental discrimination, which becomes more important for larger kinetic energy releases. When the photoproducts are formed with large components of velocity perpendicular to the ion beam direction (as would be the case for the 90° polarization angle), some of the ions are lost due to beam divergence and collisions with slits. The effect on the shape of the product ion peak for a 90° polarization angle is to flatten and broaden it, which in the peak shape analysis leads to an artificially low value for β . For the OCS⁺ photoproduct, the peak shape arising from UV excitation with a 54.7° polarization angle was slightly dished, which is clear evidence of instrumental discrimination. Thus, the value of the asymmetry parameter at the highest excitation energy should be considered only as a lower limit.

Instrumental discrimination against $C_2H_2^+$ product ions recoiling perpendicular to the ion beam was more severe than for the OCS⁺ product ions, because of the lower mass and hence higher velocity of the $C_2H_2^+$ ion. For this product channel, we observed peak shapes for 0° polarization angles that were similar in appearance to those seen for OCS⁺ but with somewhat sharper and narrower "horns" and less intensity between them. However, the $C_2H_2^+$ peak shapes for excitation with 90° polarization angles differed substantially from the peak shapes for OCS⁺, appearing typically with flattened tops, and at the highest photon energy studied (2.71 eV) were actually dished. This is strong evidence for discrimination and prevents accurate analysis of the asymmetry parameter for the angular distribution of products for the $C_2H_2^+/OCS$ dissociation channel. Qualitatively, the angular distributions of the $C_2H_2^+$ product are similar to those observed for the OCS⁺/C_2H_2 dissociation channel.

Theoretical Calculations. Ab initio calculations were carried out for the reactants and products involved in the ground-state

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TABLE IV: Structural Parameters, Total Energies, and Zero-Point Vibrational Energies from ab Initio Calculations for Reactions 1 and 2

				energy, ^b hartrees			
molecular species	····	struct param HF/6-31+G(d)	s ^e MP2/6-31+G(d)	MP2/6-31+G(d)// HF/6-31+G(d)	MP2/6-31+G(d)// MP2/6-31+G(d)	zpe ^c	
CO	<i>r</i> (CO)	1.1133	1.1504	-113.033 428 3	-113.036 546 2	3.095	
OCS	r(CO) r(CS)	1.1319 1.5700	1.1812 1.5623	-510.708 549 6	-510.713 320 2	4.048	
OCS ⁺	r(CO) r(CS)	1.1036 1.6707	1.1 259 1.6800	-510.304 835 1	-510.306 731 3	3.839	
C ₂ H ₂	r(CC) r(CH)	1.1881 1.0576	1.2188 1.0673	-77.080 922 5	-77.082 884 8	16.425	
$C_2H_2^+$	r(CC) r(CH)	1.2291 1.0715	1.2583 1.0818	-76.678 431 6	-76.674 009 2	15.803	
CH ₂ =C=S ⁺	r(CS) r(CC) r(CH) ∠HCC	1.5134 1.3513 1.0774 119.73	1.4921 1.3496 1.0887 119.94	-474.431 537 6	-474.432 252 3	16.217	
у нс≕сн	r(CS) r(CC) r(CH) ∠HCC	1.7473 1.2825 1.0717 153.25	1.7621 1.3116 1.0841 152.82	-474.418 491 3	-474.4199312	17.889	
HC ≕ CSH⁺	r(CS) r(CC) r(CH) r(HS) ∠HSC ∠SCC	1.6205 1.2257 1.0662 1.3359 98.43 174.98	1.6381 1.2109 1.0766 1.3521 96.40 175.66	-474.379 405 1	-474.380 442 2	14.966	

^a Bond lengths in angstroms, angles in degrees. ^b 1 hartree = 627.5 kcal/mol. "//" means "at the geometry calculated by". ^cZero-point vibrational energy in kcal/mol, calculated from scaled frequencies, treating vibrations of scaled frequency less than 500 cm⁻¹ as classical rotations.

TABLE V: Calculated Energies of the Reaction of $OCS^+ + C_2H_2$ at 0 K

	ΔE ,	" kcal/mol
reaction	MP2/6-31+G(d)//6-31+G(d)	MP2/6-31+G(d)//MP2/6-31+G(d)
$OCS^+ + C_2H_2 \rightarrow CH_2 = C = S^+ + CO$	-50.655	-50.639
$\operatorname{ocs}^{+} + \operatorname{c_2H_2} \longrightarrow \operatorname{H_c = cH}^{S^{+}} + \operatorname{co}$	-40.797	-41.235
$OCS^+ + C_2H_2 \rightarrow HC = CSH^+ + CO$	-19.192	-19.378
$OCS^+ + C_2H_2 \rightarrow C_2H_2^+ + OCS$	2.584	1.023
$OCS^+ + C_2H_2^- \rightarrow (OCS:C_2H_2)^+$	-20.169	Ь

^aReaction energy including zpe correction. ^bThe cluster ion geometry was not optimized at this level.

ion-molecule reactions 1 and 2. The three isomeric forms of $C_2H_2S^+$ considered were thioketene, thiirene, and ethynethiol molecular ions. Full geometry optimizations were performed using the 6-31+G(d) basis set at the Hartree-Fock level (HF/6-31+-G(d)), and single-point correlation energies were computed for these geometries by using second-order Møller-Plesset perturbation theory. The structural parameters and energies calculated at this level are collected in Table IV.

To determine whether inclusion of electron correlation would affect significantly the calculated structures, an additional round of geometry optimizations were carried out at the MP2/6-31+-G(d) level. These results are included in Table IV. The effects of electron correlation at this level on these monomer species are small, generally resulting in slightly increased bond lengths. This effect is greatest for the C-O bonds in neutral CO and OCS, and these species also experience the largest decreases in energy. Also included in Table IV are the zero-point vibrational energies, which are computed from the scaled frequencies calculated for the HF/6-31+G(d) geometries. From these results, we can compute the energies for reactions 1 and 2, and these results are given in Table V.

Preliminary geometry optimizations were carried out for the $(OCS:C_2H_2)^+$ cluster using the 3-21G(*) basis set. At this level of theory, several alternative and widely differing initial geometries collapsed upon optimization to the same final structure, and no other stationary point was found. Further optimization of the 3-21G(*) stationary point geometry was performed at the HF/ 6-31+G(d) level. The resulting optimized stationary point is a local minimum, as shown by the frequency calculations executed

at the same level. The structure of this species is a sulfur-carbon bonded cluster in which the acetylene moiety has essentially rehybridized to sp^2 bonding at the carbons. The C-S bond length of 1.838 Å is comparable to a normal carbon-sulfur single bond. The OCS moiety remains nearly linear and is bent out of the plane of the acetylene, with a C-C-S-C dihedral angle of 102°. The structural parameters and energy calculated for this cluster are given in Table VI. From the results of these calculations, we cannot absolutely rule out the existence of alternative isomeric forms of the cluster ion. However, this cluster ion structure is consistent with all of the experimental results, as we will demonstrate in the Discussion.

Discussion

The ground-state bimolecular ion-molecule reaction of OCS⁺ and C_2H_2 that yields $C_2H_2S^+$ and CO proceeds at thermal energy with a rate constant less than the collision rate constant,¹⁴ and no other major exothermic reaction channels are observed. The observation of a metastable (long-lived) (OCS: C_2H_2)^{+*} adduct and the fact that unimolecular dissociation of this adduct also yields $C_2H_2S^+$ and CO suggests that the bimolecular reaction proceeds by initial formation of a complex that can then either back-dissociate to the reactants or proceed to products (eq 3). The statistical kinetic energy release distribution observed for the dissociation channel yielding OCS⁺ and C_2H_2 indicates that there is not an energetic barrier separating the reactant species and the complex. This result supports the designation of the adduct species as a complex of OCS⁺ and C_2H_2 , in which the original bond connectivity is retained.

TABLE VI: Structural Parameters, Energy, and Zero-Point Vibrational Energy for (OCS:C2H2)+a



bond lengths, Å		bond angles, deg		dihedral angles, deg		energy, ^b hartrees	zpe, ckcal/mo
r(CO) r(C ¹ S) r(C ² S) r(CC) r(C ² H ¹) r(C ³ H ²)	1.1025 1.6788 1.8385 1.3143 1.0728 1.0697	20C'S 2C'SC ² 2SC ² H 2SC ² C ³ 2H'C ² C ³ 2C ² C ³ H ²	178.17 97.32 113.82 119.30 126.57 140.53	∠C ¹ SC ² C ³ ∠H ² CCS	102.28 3.46	-587.418 229 3	20.471

^a6-31+G(d). ^bSingle-point energy MP2/6-31+G(d)//6-31+G(d). ^cZero-point vibrational energy from scaled 6-31+G(d) frequencies, treating frequencies less than 500 cm⁻¹ as $1/_2RT$.

The large kinetic energy release observed for the metastable dissociation process leading to $C_2H_2S^+$ and CO indicates that the overall reaction in eq 1 is exothermic by at least 22 kcal/mol. This result effectively rules out that the $C_2H_2S^+$ product has an ethynethiol structure because the reaction yielding this species is only 19 kcal/mol exothermic. The nonstatistical distribution of the kinetic energy release (see Figure 2) indicates that the complex occupies a potential well that is separated from the products by a transition state intermediate in energy between the zero-point energy of the separated reactants and the zero-point energy of the complex. Moreover, once the system passes through this transition state, the products separate rapidly, such that the energy released by the reaction does not randomize among the translational and internal modes of the products. In such a system, it is the nascent structure of the $C_2H_2S^+$ within the complex when it passes the transition state that controls the further dynamics of the reaction. That is, if the nascent $C_2H_2S^+$ undergoes further structural rearrangement in a unimolecular process subsequent to product separation, the energy released by that process will not appear as kinetic energy.

The energies of reaction 1 yielding thiirene molecular ion and thicketene molecular ion differ by nearly 8 kcal/mol, or more than 0.3 eV. However, the kinetic energy release distribution for the metastable dissociation leading to C₂H₂S⁺ and CO is smooth and essentially structureless. For the peak shape analysis method used in this experiment, the nominal energy resolution is 0.05 eV, and the energy resolution of the ESA is even smaller. Thus, we might expect to observe a bimodal distribution if these two isomeric $C_2H_2S^+$ products were formed. The results suggest (but do not mandate) that a single isomer is formed as the nascent $C_2H_2S^+$ product. However, with the data available, we cannot determine which isomer (i.e., thiirene or thioketene) is implicated. We plan to examine this reaction in further detail using theoretical ab initio and phase space calculations and will report our observations in a future paper.

For the photodissociation of $(OCS:C_2H_2)^+$, there is information about the excited state contained in the kinetic energy release distributions and photoproduct angular distributions. From the widely different shapes of the experimental peaks observed for laser polarization angles of 0° and 90° (see Figure 7), it is apparent that the angular distributions of the photoproducts are strongly anisotropic. A quantitative measure of the anisotropy is given by the asymmetry parameter β (eq 6), which for the OCS⁺ product falls in the range 1.4-1.6. The asymmetry parameter can take values in the range $-1 \le \beta \le 2$. Values of β outside the range $-0.25 < \beta < 0.5$ indicate that the lifetime of the excited species is much less than a rotational period.^{38,39} Positive values of β correspond to systems in which the transition dipole is oriented in approximately the same direction as the axis of recoil, which in the present case is along the cluster bond. The observed values of β (1.4-1.6) indicate that dissociation of the photoactivated $(OCS:C_2H_2)^+$ species occurs much faster than rotation of the cluster. Such rapid dissociation is suggestive of a repulsive potential energy surface in the excited state. Although we do not have accurate values of β for the C₂H₂⁺/OCS product channel, it is nevertheless clear that these products are also formed with a strongly anisotropic angular distribution, indicative of excitation to a repulsive excited-state surface. These results are consistent with the suggestion of Orlando et al.,¹⁵ who interpreted the photodissociation cross section spectrum in terms of excitation to repulsive excited-state surfaces.

The first excited electronic state of C_2H_2 lies at 5.23 eV, and that of OCS lies at 4.86 eV above the respective ground state.⁴⁰ For the isolated molecular ions, the first excited state of C₂H₂⁺ is 4.89 eV above the ground state,⁴¹ and the first excited state of OCS⁺ lies 3.88 eV above its ground state.⁴² None of these states in the isolated species is accessible with the photon energies employed in the present experiments. Ab initio calculations indicate that in the cluster the charge is predominantly localized on the OCS moiety, which has the lower ionization potential, but that the charge is somewhat delocalized into C_2H_2 , which has undergone considerable geometric distortion. Thus, it is possible that the states of the isolated species are considerably perturbed. However, the nature of the products observed and the dynamics of the photodissociation process suggest that the excitation is actually based in the cluster bond. The products we observe correspond to the two charge states of the $(OCS:C_2H_2)^+$ precursors, i.e., to OCS^+/C_2H_2 and $C_2H_2^+/OCS$. The branching ratio for these sets of products remains essentially constant throughout the photon energy range of our experiment. It is of interest to consider possible mechanisms that could lead to these observations.

Two alternative mechanisms can be proposed for the formation of the observed sets of photoproducts from the precursor cluster ion $(OCS:C_2H_2)^+$. One scenario is that photoactivation results in excitation to two repulsive excited states, one of which correlates to ground state OCS^+ and C_2H_2 and the other to ground state $C_2H_2^+$ and OCS. This alternative requires that the branching occurs in the photon absorption step. However, it seems unlikely that the branching in absorption to two different repulsive surfaces would be independent of photon energy over the wide range explored in these experiments (2.35-3.5 eV).

A second possibility is that both product channels arise from the same initially accessed excited state, with the branching occurring via surface crossing as the products start to separate subsequent to photon absorption. This could involve, for example, excitation to a charge-transfer state that correlates to the higher energy $C_2H_2^+/OCS$ product channel. The branching might then occur at an intersection of the charge-transfer state with another repulsive surface that correlates to $\overline{OCS^+}$ and C_2H_2 . In this case it is difficult to predict what the effect of the initial excitation energy should be on the branching ratio.

A third possibility that might also be proposed is that there are actually two (or more) unique precursor species, each of which

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gives rise to a different set of products on photoactivation. We consider this alternative explanation improbable for the following reasons: We expect that under the conditions of ion production in our experiments, the $(OCS:C_2H_2)^+$ species are predominantly in the lowest energy geometry. If there are multiple structures of comparable energies, then the thermal energy ensemble of the $(OCS:C_2H_2)^+$ cluster ions might include more than one isomer. However, our search for minimum energy structures with ab initio methods revealed only one stationary point, in spite of considering numerous starting points.

The average relative kinetic energy of the products formed by photodissociation increases linearly with photon energy (Figure 6). Because the dissociation apparently arises from a repulsive potential energy surface, we can model the process as an impulsive half-collision, in which the repulsive forces acting on the photoactivated species are treated as impulsive interactions.³⁷ In this framework, the vibrational excitation of the photoproducts arises from the geometry differences between the products and their counterpart moieties in the activated cluster and from the impulsive interactions of the nascent products. With this model, we fit the present kinetic energy release data to the expression

$$\langle E_{\rm T} \rangle = (\mu_{\rm bc}/\mu_{\rm f})(E_{\rm av} - {\rm DE} - E_{\rm vib}) \tag{7}$$

where μ_{bc} is the reduced mass of the atoms connected by the breaking bond, μ_f is the reduced mass of the dissociation products, E_{av} is the available energy (as defined previously for Figure 6), DE is the cluster bond dissociation energy, and E_{vib} is the vibrational energy of the products.

For OCS⁺/ C_2H_2 product channel, the dependence of the average kinetic energy on E_{av} is given by eq 4. Rearranging into the form of eq 7 yields a value of 9.4 \pm 0.2 amu for μ_{bc} . According to the impulsive model, this value should correspond to the reduced mass of the two atoms involved in the cluster bond. The largest possible value of the μ_{bc} for a bond between any two atoms of the OCS^+ and C_2H_2 products is 8.7 amu for a sulfur-carbon bond. The disagreement between the experimental value and the largest theoretical value of μ_{bc} may be simply a result of experimental error, but it is also possible that the bonding in the $(OCS:C_2H_2)^+$ cluster is not well-described in terms of a simple two-atom bond. We can consider alternative bonding for the cluster ion, treating for example the triple-bonded carbon atoms of acetylene as a rigid pseudoatom with a mass twice that of carbon. For a bond between sulfur and this C₂ pseudoatom, we obtain $\mu_{bc} = 13.7$ amu, which is considerably larger than the experimental result. For a bond between oxygen and the C₂ pseudoatom, $\mu_{bc} = 9.6$ amu, which is an excellent agreement with the experimental result. However, before we conclude that the data are indicative of an oxygen- C_2 bond, we should consider this proposition more carefully. From the ab initio calculations, we find that Mulliken population analysis of the charge distribution in OCS⁺ indicates that the positive charge is localized on the sulfur and carbon atoms. In C_2H_2 , the electron density is greatest in the carbon–carbon π system. Thus, we would predict a priori that the strongest interaction between OCS^+ and C_2H_2 will be between the sulfur atom and the acetylene π cloud. In neutral OCS, the oxygen atom does have excess electron density, but the dipole moment for this species is small (0.3 D). Moreover, in $C_2H_2^+$, the positive charge localizes on the hydrogens rather than the carbons. Thus, the strongest interaction of $C_2H_2^+$ with OCS in electrostatic terms will probably be between oxygen and hydrogen atoms, for a reduced mass μ_{bc} of only 0.94 amu.

We conclude that the most probable bonding interaction in $(OCS:C_2H_2)^+$ is between the sulfur and carbon atoms of OCS⁺ and C_2H_2 , respectively. The discrepancy between the experimental values of μ_{bc} and the theoretical value for a carbon-sulfur bond probably arises from the limitations of the impulsive model for describing a bond that is not purely two-atom centered. Our conclusion is supported by the results of the ab initio calculations carried out for the $(OCS:C_2H_2)^+$ cluster ion. At the level of theory employed for the search for local minima (HF/3-21G(*)) we found that several widely differing starting geometries collapsed to the same final structure upon optimization. For initial geometries in which the oxygen atom of OCS was located adjacent to the carbon atoms of acetylene, the energy was lowered during optimization by moving the oxygen atom farther away. This suggests that the interaction between the oxygen and carbon atoms is nonbonding or repulsive. The same final cluster ion geometry was obtained regardless of whether we used the calculated structural parameters for OCS⁺ and C₂H₂ or for OCS and C₂H₂⁺ in the initial geometry. Thus, at this level of theory, there does not appear to be a cluster ion in which the charge remains localized on acetylene.

From the single-point energy calculated for the cluster ion (MP2/6-31+G(d)//6-31+G(d)) and the zero-point vibrational energy, we can deduce a cluster ion bond dissociation energy of 0.875 eV, or 20.17 kcal/mol. This value is somewhat higher than the bond energy that has been reported for $(OCS)_2^+$ of 0.745 eV, or 17.2 kcal/mol, from molecular beam photoionization experiments.³² It is generally expected that the bond energy in cluster ions (A:B)⁺ will increase as the difference between the ionization potential of A and B decreases,43,44 such that homogeneous clusters A_2^+ will be more strongly bound than heterogeneous clusters (A:B)⁺. This prediction is based on a picture of cluster bonding in which the dominant interaction is due to orbital overlap of the highest occupied molecular orbital of the neutral molecule and the singly occupied orbital of the ion. When these orbitals are close in energy, the overlap is greatest and consequently the interaction is strongest. This simple picture succeeds in predicting the trends observed in the binding energy for many small dimer clusters.45 In the present case, however, it is clear from the substantial distortion in geometry in the acetylene moiety in the $(OCS:C_2H_2)^+$ cluster that the bonding interaction involves more than the highest lying molecular orbitals. What we observe amounts to formation of a σ bond and rehybridization of the acetylene to sp² bonding.

The analysis of the kinetic energy releases by impulsive theory also yields a value for $(DE + E_{vib})$ from the y-axis intercept of the fitted line. For the $(OCS:C_2H_2)^+$ channel, the value of (DE)+ $E_{\rm vib}$) is 1.15 ± 0.06 eV. With use of the calculated cluster ion bond dissociation energy of 0.875 eV, we obtain $E_{vib} = 0.27$ eV. This value corresponds to the amount of intrinsic vibrational excitation resulting from geometry differences between the cluster and the products. From consideration of the calculated structural parameters for the cluster ion (Table VI), it appears that this vibrational energy will be localized largely in the C_2H_2 product. Inspection of the data in Tables IV and VI reveals that the C-O and C-S bond lengths and the O-C-S bond angle in the cluster are essentially equal to those of OCS⁺. Thus, for an impulsive mechanism, the OCS⁺ product should be largely in the vibrational ground state (although molecular rotations may be excited in the dissociation process). In contrast, the C-C bond length and H-C-C bond angles are strongly distorted in the cluster relative to C_2H_2 . Thus, both the C-C stretch and the trans-bending modes will be excited in the C_2H_2 product.

Analysis of the kinetic energy release data for the $C_2H_2^+/OCS$ product channel yields a value for μ_{bc} of 11.0 ± 0.9 amu (where the quoted error pertains to the uncertainty of the slope of the fitted line). It is difficult to ascertain whether the discrepancy between this value of μ_{bc} and the value deduced for the OCS⁺/ C_2H_2 product channel is experimentally significant. The effects of instrumental discrimination are considerably greater for the peak shape of the $C_2H_2^+$ photoproduct than for the OCS⁺ photoproduct. This introduces a larger uncertainty in the average kinetic energy releases obtained for $C_2H_2^+/OCS$ as compared to OCS^+/C_2H_2 . In the analysis of the $C_2H_2^+$ product shapes, we saw that accurate knowledge of the apparatus dimensions was critical.⁴⁶ Thus, the difference between the value of μ_{bc} obtained for the two channels may be a result of systematic error in the

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data analysis. Another possible origin for this lack of precise agreement is the existence of a second isomeric cluster ion that gives rise to the $C_2H_2^+/OCS$ products. However, as stated previously, we consider the presence of structured isomers to be improbable. A third possibility is that the $C_2H_2^+/OCS$ products arise from the same cluster species and the same excited state as the OCS⁺/ C_2H_2 products and that the branching occurs via curve crossing. In this scenario, the dynamics of the dissociation may be modified at the intersection of the two surfaces, where the cluster bond has already begun to stretch. This mechanism might also account for the invariance of the branching ratio with photon energy.

Conclusions

The dynamics of metastable dissociation and photodissociation of the $(OCS:C_2H_2)^+$ cluster ion have been studied. Metastable dissociation yields $C_2H_2S^+$ and CO as the dominant product channel. These products are formed with a large and nonstatistical release of energy to translation, which is indicative of an exothermic reaction proceeding through a tight transition state separating the $(OCS:C_2H_2)^+$ species from the products. Theoretical calculations of the reaction energetics indicate that the $C_2H_2S^+$ product can be either the thiirene molecular ion or the thicketene molecular ion, but that a third $C_2H_2S^+$ isomer, ethynethiol, is not energetically accessible. The experimental results suggest that only one isomer of $C_2H_2S^+$ is formed but do not permit reliable identification of which isomer is implicated.

The photodissociation cross sections measured in the present

experiments are in qualitative agreement with previous results of Orlando et al.¹⁵ Photoexcitation of the $(OCS:C_2H_2)^+$ cluster ion in the visible region of the spectrum accesses one or more repulsive excited states that correlate to ground state OCS⁺ and C_2H_2 and to $C_2H_2^+$ and OCS. The two ionic products of photodissociation, OCS^+ and $C_2H_2^+$, are formed in an essentially constant ratio of about 6:1, respectively, throughout the energy range studied. From consideration of the experimental results, we propose that the $(OCS:C_2H_2)^+$ cluster is a sulfur-carbon bonded species. This is supported by the results of theoretical calculations of the cluster ion structure, which also yield a cluster bond energy of 0.875 eV for $(OCS:C_2H_2)^+$ dissociating to OCS^+ and C_2H_2 .

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Cationic Polymerization within van der Waals Clusters of the Form $(CH_2=R)_n^+$ (R = CH_2 , CF_2 , and $CHCH_3$)

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The cluster ion mass spectra resulting from electron ionization of van der Waals clusters composed of ethene, 1,1-difluoroethene (1,1-DFE), or propene molecules were observed as a function of expansion and ionization conditions. Expansion conditions favoring the formation of large neutral clusters lead to the observation of anomalous ion intensity distributions characterized by strong peaking as a function of cluster size. Comparisons are made between the present results and previous observations in both the gas and condensed phases. We propose that the anomalous cluster ion distributions arise as a consequence of the production of molecular (i.e., covalently bonded) ions produced by a series of intracluster addition (polymerization) reactions. The anomalous intensity distributions may then be accounted for in terms of kinetic bottlenecks in the addition reaction sequences which most likely result from the production of ions of low reactivity, most likely cyclic ions.

Introduction

Clusters are the subjects of an ever increasing number of experimental and theoretical studies.¹⁻⁷ The current interest in clusters stems from their unique position as an aggregated state of matter intermediate between the gas and condensed phases of matter. Since clusters exist as isolated particles in the gas phase, they are susceptible to study by many of the powerful techniques used in the observation of gas-phase reactions, which have led in many cases to fundamental understanding of chemical reactivity at a truly microscopic level.

For the physical chemist, clusters represent a singular opportunity to directly observe the influence of solvation and solvent structure on chemical reactivity. At the same time, clusters represent a medium of greatly reduced simplicity in which to study processes of chemical interest including charge and energy transfer, bond formation and cleavage, etc.

Supersonic expansions are the most widely utilized methods for generating clusters.⁸ Unfortunately, these molecular beam cluster sources do not allow one to selectively produce a given cluster size. Instead a distribution of cluster sizes is produced

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