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Photoionization Studies of Internally Reactive Small Clusters: van der Waals Complexes of 1,3-Butadiene with Sulfur Dioxide

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Abstract: Efficiency functions for ions from the title complexes were measured using a photoionization mass spectrometer in which a molecular beam of target complexes, formed by a skimmed and recollimated free jet expansion of 1,3-butadiene + SO_2, was made to intersect a tunable VUV beam from Brookhaven's 750-MeV electron storage ring. The dissociation energies at 0 K of 1,3-$C_4H_6 \cdot SO_2$ and $(1,3\text{-}C_4H_6 \cdot SO_2)^+$ were measured to be 3.24 ± 0.48 and 3.00 ± 0.68 kcal mol^{-1}, respectively. For 3-sulfolene, the condensation product, the ionization potential was measured to be 10.073 ± 0.006 eV, while the appearance potential of its fragment $C_4H_6^+$ is 10.076 ± 0.029 eV, the same within the experimental uncertainty. However, the sulfolene parent ion is unstable with respect to disintegration into butadiene ion and sulfur dioxide by 0.38 ± 0.03 eV. The ion $C_4H_6SO^+$ is produced in very low yield from the heterodimer but in much higher yields from heterotrimers, showing that it is born excited and is stabilized by the presence of a third "solvent" molecule. Its onset from the heterodimer is 15.90 ± 0.10 eV, about 2.3 eV higher than the threshold, and 1.0 eV into the continuum for butadiene ion plus SO. Possible mechanisms for this surprising reaction are discussed.

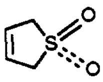
Introduction

The study of reactions induced between the constituents of van der Waals complexes offers an extraordinarily promising approach to understanding chemical processes. With jet expansion–molecular beam techniques a wide variety of possible reactants can be brought together as complexes of known structure under well-defined conditions for experiments. We anticipate that such studies will eventually provide details comparable to what can be obtained via reactive scattering in crossed molecular beams, but be applicable to a wider variety of reactant systems, and be more pertinent than crossed beam work to understanding processes in condensed phases.

Examples of recent progress in this direction include observations of dissociative rearrangement induced by one-photon[1-4] and two-photon[5,6] processes with ionization, and by one-photon[7] and two-photon[8] processes to produce neutral products; ionization of one moiety by a high-lying excited state of the other;[9,10] intradimer photodissociation of one moiety to exploit structure constraints on fragment collisions with the other;[11] real-time measurements of the evolution into products of such intradimer photoinduced colliding reactants;[12] and intracluster reactions induced by electron impact.[13]

This work was undertaken to learn about the potential hypersurfaces of van der Waals dimers, via features such as the dissociation energies, stable geometries, electronic structures, and distributions of product states, momenta, and rotational orientations after reaction has occurred. As a first step toward this goal we use single-photon photoionization mass spectrometry to characterize complexes of reactive pairs of molecules. Recent electron impact investigations[13] have demonstrated the wealth of information that can be obtained, and we explore the added capability provided by tunability of the ionizing photons.

Our efforts focus on mixed clusters comprised of a hydrocarbon plus a simple di- or triatomic inorganic molecule, where the ionization potential (IP) of the organic is substantially lower than that of the inorganic. Experience has shown that this type of system gives fewer products and less complicated processes than one observes with clusters comprised of two organics of similar IP, and the results are therefore easier to understand. Structures and force constants have previously been determined for a few potentially reactive van der Waals heterodimers of this type via microwave spectroscopy in molecular beams ($C_2H_2 \cdot H_2O$,[14] $C_2H_2 \cdot HCl$,[15] $C_2H_4 \cdot HF$,[16] $C_2H_4 \cdot HCl$[17]), but the dissociation energy has been reliably measured for only one of these; viz. $C_2H_4 \cdot HCl$.[18a] The low-temperature reaction rates, however, of all of these systems are very small. A prototype of a more reactive pair of molecules that would be convenient to study in a molecular beam is 1,3-butadiene plus sulfur dioxide, which reacts in gas pressure vessels at room temperature on a time scale of days to form **1**



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(2,5-dihydrothiophene 1,1-dioxide, "3-sulfolene"). [The crossed

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molecular beam technique is not well-suited to the exploration of condensation reactions because there is only one body in the final state.] The work described in this paper demonstrates what can be learned from the photoionization efficiency spectra of ions produced from the title complexes and from their condensation product, **1**.

The target complexes are synthesized in free jet expansions, which means they always occur in mixtures of clusters of a variety of sizes and compositions. Therefore, for measurements to be unambiguously assigned to one particular complex, it is necessary to analyze the products of the expansion. Laser techniques can distinguish one complex from another in favorable cases. Unfortunately, this elegant method is not yet available for the title species. Instead, single-photon ionization is used to identify neutral complexes of 1,3-C_4H_6 + SO_2 and measure their densities among the jet expansion products. From this information photoionization efficiency (PIE) curves for the production of given ions from specified neutral complexes can be resolved from the composite curves actually measured.

Experimental Section

The apparatus utilized for this study is a photoionization mass spectrometer, equipped with a molecular beam source that consists of a skimmed and further collimated free jet expansion, that interfaces with the normal incidence monochromator of the U-11 beam line at the 750-MeV electron storage ring of the National Synchrotron Light Source at Brookhaven National Laboratory. Gratings of 1200 and 3600 lines mm^{-1} were employed. Whenever the wavelength scans were entirely above 1100 Å, a 0.2-cm thick lithium fluoride window was inserted to eliminate second and higher order radiation. Otherwise, corrections for second- and third-order radiation were made as described in ref 18a. Additional details about this apparatus are presented in previous publications.[9,18b,c]

Commercial sulfolene was purified by storage for several weeks in an actively pumped chamber, followed by repeated vacuum sublimation at 50 °C to a surface maintained at 0 °C.

The target species were synthesized by jet expansion of mixed gases. Low signal strengths in parts of this study made it mandatory to achieve beam densities as large as possible. For this reason only binary mixtures of butadiene and sulfur dioxide were employed. Nonreproducible results were obtained with gas mixtures of butadiene and sulfur dioxide produced by on-line flow methods, so premixed gases were prepared and stored in stainless steel cylinders for 1 to 8 h before use; typical useful lifetime of a cylinder was 2 to 4 h. Ratios of 1:4 and 1:9 butadiene–SO_2 were used. A few crystals of 4-*tert*-butylchatechol were included to inhibit polymerization. The extent of reaction was small enough that the data were not seriously affected, although visible amounts of sulfolene were found inside the cylinders after several runs.

Ancillary experiments were carried out to prepare and study the 1,3-butadiene homodimer, (1,3-$C_4H_6)_2$. The homodimers, and larger clusters, were prepared by room-temperature nozzle expansions of 1:4 butadiene–argon mixtures. For this mixture the pressure needed to optimize the production of the dimer was so low[18d] that butadiene–argon mixed dimers were never abundant enough to be important.

Sulfolene could not be studied in the interaction chamber as a nozzle beam because its vapor pressure is too low. Increasing the temperature to raise the vapor pressure caused decomposition. Therefore, the investigation of this molecule was carried out with its room-temperature vapor, which was effused through an orifice 0.02 cm in diameter positioned 0.4 cm below the photon beam inside the ion extraction lens.

Table I presents the yields of the photoionization and dissociative photoionization at 584 Å (21.2 eV) of the dimers $C_4H_6{\cdot}SO_2$ and (1,3-$C_4H_6)_2$ prepared as described above, and of 1,3-butadiene itself. The fragment ion yield pattern of the heterodimer was resolved from the gross photoionization yields of the mixed-gas jet expansions by subtraction of the contributions from monomers and homodimers using data obtained under conditions in which there was essentially no complex formation (e.g., neat butadiene expanded at less than 100 Torr of nozzle pressure), plus the yield pattern of the homodimer obtained in the ancillary experiment with argon. For both complexes the ion of largest yield by far is that of the butadiene parent, in sharp contrast to the result for the uncomplexed butadiene, where the yield of parent ion is only 10%. Yields of ions smaller than $C_4H_6^+$ produced from the heterodimer could not be measured because the production of these ions is dominated by the fragmentation of butadiene and its homodimer. The sum of their yields, however, cannot exceed 4%. The product seen at m/e = 72 is believed to be $C_3H_4O_2^+$ rather than $C_3H_4S^+$ because no trace of an ion involving ^{34}S could be found.

Table I. Yields[a,b] of the Most Probable Products from the Photoionization at 584 Å (21.2 eV) of 1,3-Butadiene·Sulfur Dioxide, (1,3-Butadiene)$_2$, and 1,3-Butadiene

m/e	ion[c]	$C_4H_6{\cdot}SO_2$	$(C_4H_6)_2$	C_4H_6
26	$C_2H_2^+$			1
27	$C_2H_3^+$			14
28	$C_2H_4^+$			15
38	$C_3H_2^+$			1
39	$C_3H_3^+$			32
50	$C_4H_2^+$			1
51	$C_4H_3^+$		2	4
52	$C_4H_4^+$		1	3
53	$C_4H_5^+$		6	19
54	$C_4H_6^+$	91	79	10
55	$C_4H_7^+$		7	
66	$C_5H_6^+$		0.7	
67	$C_5H_7^+$		0.9	
72	$C_3H_4O_2^+$ or $C_3H_4S^+$	≤0.7[d]		
79	$C_6H_7^+$		1.1	
80	$C_6H_8^+$		0.6	
93	$C_7H_9^+$		0.3	
102	$C_4H_6SO^+$	0.0[e]		
108	$(C_4H_6)_2$		0.1_3	
118	$(C_4H_6{\cdot}SO_2)^+$	9		

[a] Yields are given as percent of total ion intensity detected. [b] Yields are corrected for the relative efficiency of the quadrupole mass spectrometer that was used. [c] Intensities include the contribution of the ^{13}C-containing species. [d] The intensity at m/e = 72 has not been corrected for possible contributions from trimers. [e] The yield of $C_4H_6SO^+$ reaches a maximum of about 0.2% near 700 Å, but at 584 Å is too small to measure in the presence of the dominating trimer contribution (see Figure 12).

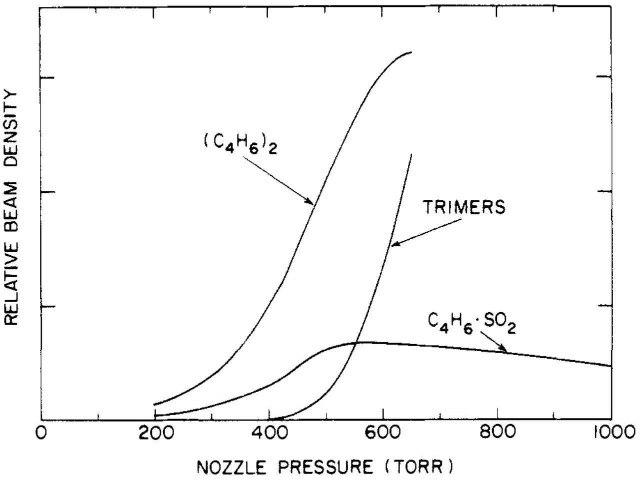

Figure 1. Relative beam densities of 1,3-butadiene·SO_2, (1,3-butadiene)$_2$, and the sum of the butadiene-containing trimers, measured according to ref 18d,e.

The composition of the beam as a function of nozzle pressure was extracted, using methods already described,[18d,e] plus data from Table I and the relative size of the monomer ion yield, to obtain the results[19] shown in Figure 1. At a nozzle pressure of 500 Torr about 1% of the 1,3-butadiene is converted into $C_4H_6{\cdot}SO_2$, and about 7% into $(C_4H_6)_2$. The ratio of $C_4H_6{\cdot}SO_2$ to $(C_4H_6)_2$ is roughly independent of pressure between 200 and 500 Torr. For most of the work, pressures of 500–800 Torr were employed, a range that is amenable to resolution of product ion spectra into contributions from dimers and trimers.

Where feasible the composite spectra at two different nozzle pressures were resolved into spectra for heterodimers and for larger clusters,

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(19) In addition to the analysis methods presented in ref 18d–f, we note that, in general, if the intensity of cluster ions $(A{\cdot}B)^+$ can be systematically measured within a few kcal mol^{-1} above threshold, but below the appearance potentials for production from larger clusters, such measurements can be made the basis of a useful technique to map the nozzle-pressure dependence of the relative beam density of neutral A·B. Our experience with $(C_4H_6{\cdot}SO_2)^+$ (described in the text) affords a good example. The method should also be useful for larger clusters.

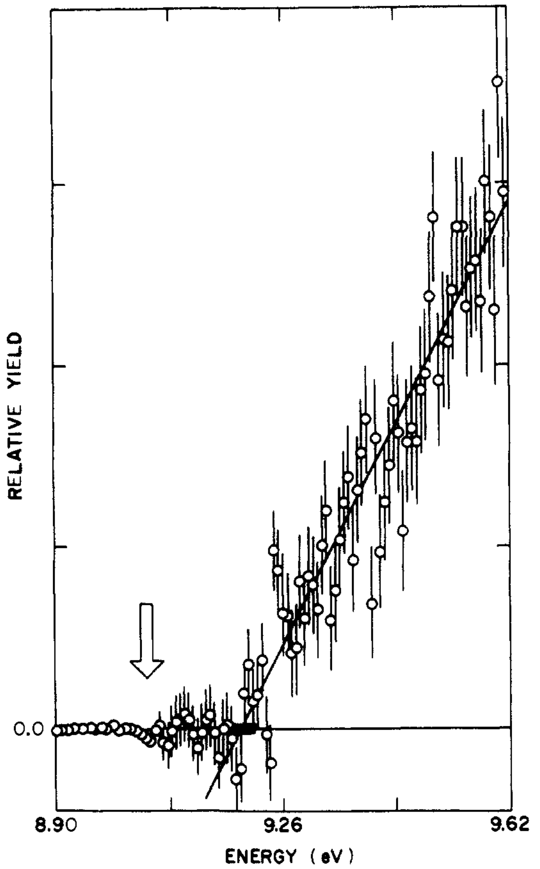

Figure 2. Efficiency function (points) in the onset region for the production of $C_4H_6^+$ by photoionization of the heterodimer 1,3-butadiene$\cdot SO_2$. The arrow marks the ionization potential of monomeric 1,3-butadiene. The most probable straight-line fit and the 68% confidence interval of the intercept, from a χ^2 analysis, are indicated. In this and all the other figures, the error bars show one standard deviation of uncertainty, calculated from the statistics of counting, and the resolution is 2.3 Å (fwhm) unless otherwise specified.

making use of the measured beam composition shown in Figure 1. To the authors' knowledge, such a resolution has not been reported previously. Three different methods were developed.

I. Solution of Simultaneous Equations. At each wavelength the observed yield Y of a given dissociative photoionization product ion at two different pressures P_i ($i = 1, 2$) may be expressed as $Y(P_i) = C_d(P_i) + C_t(P_i) = E_d\rho_d(P_i) + E_t\rho_t(P_i)$, where $C_d(P_i)$ and $C_t(P_i)$ are the contributions from the heterodimers and composite trimers, $\rho_d(P_i)$ and $\rho_t(P_i)$ being the relative beam densities of the heterodimers and composite trimers, while E_d and E_t are their relative photoionization efficiencies to produce the ion. Solution of these simultaneous equations gives $C_d(P_1) = [Y(P_1) - \eta Y(P_2)]/[1 - \eta/\xi]$ and $C_t(P_1) = [Y(P_1) - \xi Y(P_2)]/[1 - \xi/\eta]$, where we define $\xi = \rho_d(P_1)/\rho_d(P_2)$ and $\eta = \rho_t(P_1)/\rho_t(P_2)$. The uncertainties of $C_d(P_i)$ and $C_t(P_i)$ due to the statistics of counting were evaluated from the corresponding uncertainties in the $Y(P_i)$ using the usual rules.

II. Calibration to the Heterodimer Beam Density at Low Nozzle Pressure. At nozzle pressures of less than 400 Torr the efficiency function of ions produced from heterodimers, e.g., $(C_4H_6{\cdot}SO_2)^+$, will be essentially free from contributions from dissociative ionization of the larger clusters. However, if the production cross sections are small, as is the case above, it is difficult to obtain a good spectrum working at such low nozzle pressures. We therefore determined the $(C_4H_6{\cdot}SO_2)^+$ PIE as a function of nozzle pressure down to 300 Torr at 700 Å only, and the complete spectrum at 500 and 800 Torr. Normalization of the heterodimer beam density curve (Figure 1) to the pressure-dependent signal than allowed us to determine the $(C_4H_6{\cdot}SO_2)^+$ contribution at 500 Torr and 700 Å (62%). Assuming the spectrum at 800 Torr gives a reasonable approximation of the contribution from larger clusters, it was adjusted to correspond to the known contribution of 38% at 700 Å and subtracted to obtain the efficiency function from heterodimers alone.

III. Normalization of High Nozzle Pressure Signal to Pressure Dependence of Ions Produced from Trimers. At sufficiently high pressure the fractional contribution of the signal from dimers is small enough to be neglected, and the normalized trimer function (the T function of ref 18d) is then a good estimate of the contribution from trimers at lower nozzle pressure where the correction is small.

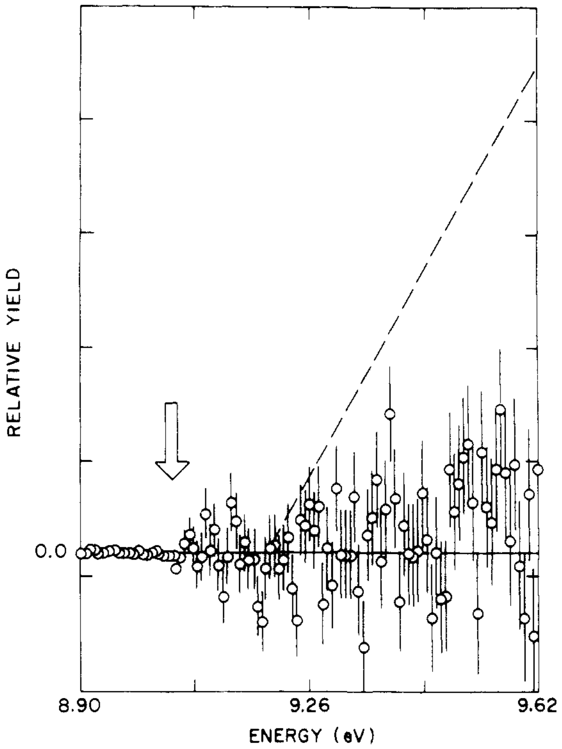

Figure 3. Search for the production of $C_4H_6^+$ by photoionization of the homodimer (1,3-butadiene)$_2$. The arrow marks the ionization potential of monomeric 1,3-butadiene. The yield expected if the cross sections were the same as for the production of $C_4H_6^+$ from 1,3-butadiene$\cdot SO_2$ is depicted by a dashed line.

Results

Figure 2 shows the photoionization efficiency function in the onset region for the production of $C_4H_6^+$ in the process

$$1,3\text{-}C_4H_6{\cdot}SO_2 + h\nu \rightarrow C_4H_6^+ + SO_2 + e \qquad (1)$$

measured at 600 Torr by the spectrum-stripping method.[18c] The appearance potential for reaction 1 is 9.193 ± 0.018 eV at the beam temperature, calculated[18c] to be 46 ± 15 K. After correction to 0 K this becomes 9.210 ± 0.021 eV. Combining this with IP(1,3-C_4H_6) = 9.070 eV,[20] we calculate the dissociation energy to be D_0(1,3-$C_4H_6{\cdot}SO_2$) = 3.24 ± 0.48 kcal mol^{-1}.

Figure 1 demonstrates that at nozzle pressures of 500 to 800 Torr the relative beam density of trimers increases sharply and becomes dominant. The appearance potential for reaction 1 was the same at both pressures, and the same as the result at 600 Torr, so no correction for the production of $C_4H_6^+$ from trimers is necessary. A possible correction due to the production of $C_4H_6^+$ from butadiene homodimers must also be considered. Accordingly, an effort was made to observe the appearance potential for the process

$$(1,3\text{-}C_4H_6)_2 + h\nu \rightarrow C_4H_6^+ + C_4H_6 + e \qquad (2)$$

also via spectrum-stripping. Homodimers were synthesized in a free jet expansion of 1:4 1,3-butadiene–argon at 500 Torr. No $C_4H_6^+$ ions from the homodimers were observed at photon energies expected for the appearance potential (Figure 3) despite our observations[18d] that (1,3-butadiene)$_2$ was abundant in the target beam and that, at the high photon energy of 21 eV, $C_4H_6^+$ is the most prominent product (Table I). Therefore, no correction to the appearance potential for reaction 1 from reaction 2 is necessary. Also, note that the threshold for the production of $C_4H_6^+$

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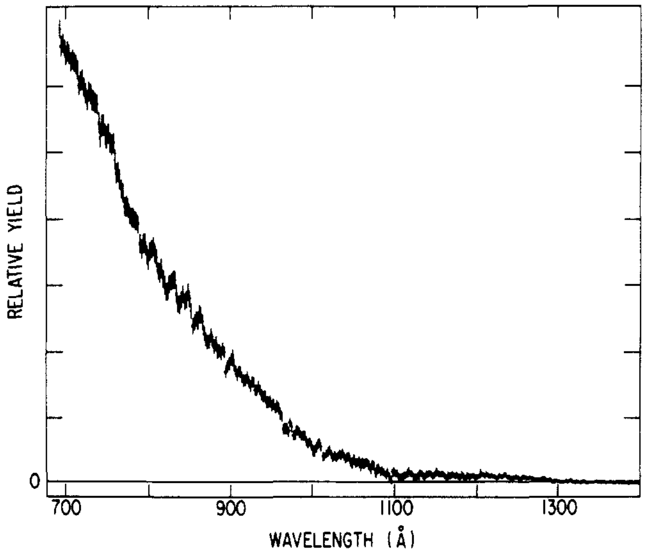

Figure 4. Efficiency function for the production of $C_4H_6^+$ by photoionization of the mixed dimers 1,3-butadiene·SO_2 + (1,3-butadiene)$_2$.

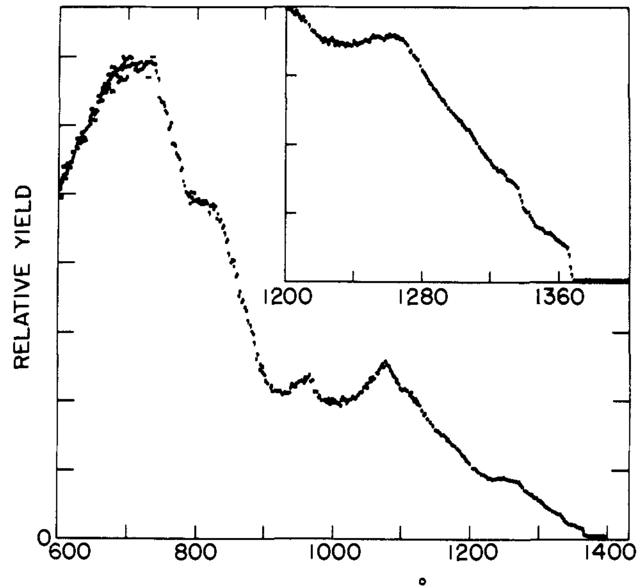

Figure 5. Efficiency function for the production of $C_4H_6^+$ by photoionization of 1,3-butadiene. The inset details the region near threshold.

from $(C_4H_6)_2SO_2$ would be far below the ionization potential of C_4H_6 itself if ground-state sulfolene is formed in the reaction. No evidence for such a special low threshold (at roughly 8.75 eV, 1417 Å) was seen. (However, we did not search with maximum sensitivity, i.e., with the target beam optimized for $(C_4H_6)_2SO_2$.)

Figure 4 gives the sum of the efficiency functions of reactions 1 and 2 over a broad range of wavelengths, obtained by subtraction of the monomer spectrum and corrected for the contribution of trimers by method III above. The efficiency spectrum for the ionization of 1,3-butadiene itself is shown for comparison in Figure 5, which confirms and extends the earlier spectrum reported by Parr and Elder.[21]

The threshold region of the photoionization efficiency function for the ionization of the heterodimer,

$$1,3\text{-}C_4H_6{\cdot}SO_2 + h\nu \rightarrow (C_4H_6{\cdot}SO_2)^+ + e \qquad (3)$$

measured at a nozzle pressure of 500 Torr, is displayed in Figure 6. The onset occurs at 9.062 ± 0.020 eV (1368 ± 3 Å) with no evidence of a still lower onset. This result, corrected to 9.080 ± 0.021 eV at 0 K, together with the appearance potential for reaction 1 yields a dissociation energy for the heterodimer ion of $D_0([C_4H_6{\cdot}SO_2]^+) = 3.00 \pm 0.68$ kcal mol^{-1}. A measurement at a nozzle pressure of 800 Torr (open circles) gave exactly the same appearance potential for $(C_4H_6{\cdot}SO_2)^+$. The slightly lower magnitudes of the ion intensities at 800 than at 500 Torr correlates quite well with the beam density of neutral heterodimers[18e] in Figure 1 and not with the sharply rising beam density of trimers over the same pressure range (cf. Figure 1). Therefore, no correction to the ionization potential due to dissociative ionization of trimers is required.[19]

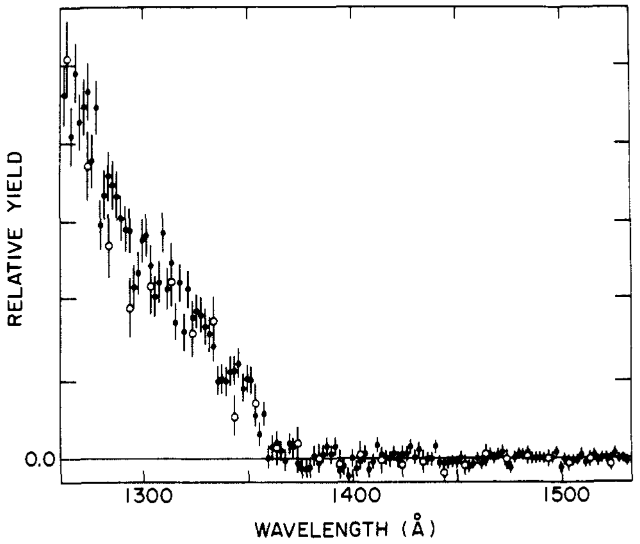

Figure 6. Efficiency function in the onset region for the production of $(C_4H_6{\cdot}SO_2)^+$ by photoionization of the heterodimer 1,3-butadiene·SO_2. Data are at nozzle pressures of 500 Torr (closed points) and 800 Torr (open circles).

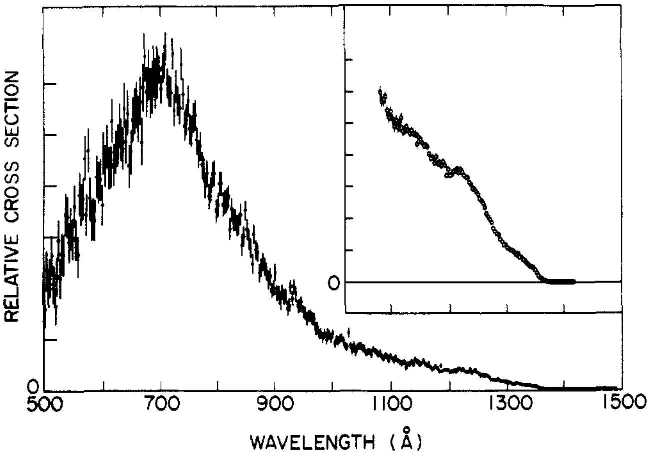

Figure 7. Efficiency function for the production of $(C_4H_6{\cdot}SO_2)^+$ by photoionization of the heterodimer 1,3-butadiene·SO_2. Inset: detail of the threshold region measured at a nozzle pressure of 400 Torr, and utilizing a lithium fluoride window.

At shorter wavelengths the broad-range photoionization efficiency function for the production of $(C_4H_6{\cdot}SO_2)^+$ is much larger for trimers than it is for the neutral heterodimer. However, resolution into spectra due to heterodimers and trimers was effected as described above. The resulting spectrum for ionization of heterodimer 1,3-$C_4H_6{\cdot}SO_2$ alone is shown in Figure 7, while Figure 8 depicts the corresponding efficiency spectrum for the production of $(C_4H_6{\cdot}SO_2)^+$ from trimers (and possibly larger clusters). Near-threshold autoionization, indicated by the structure shown in the inset in Figure 7, allows the threshold to be observed, even though the Franck–Condon factors are most likely adverse.

The photoionization efficiency function for the production of the 3-sulfolene parent ion $C_4H_6SO_2^+$ is plotted in Figure 9a. Figure 9b shows the detail near threshold, giving an IP of 10.073 ± 0.006 eV, consistent with photoelectron spectra.[22,23] The onset

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[21] Parr, A. C.; Elder, F. A. *J. Chem. Phys.* **1968**, *49*, 2659–2665.

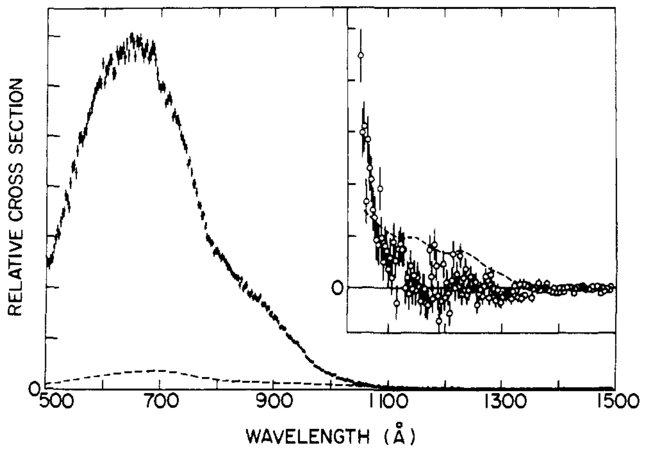

Figure 8. Points: efficiency function for the production of $(C_4H_6{\cdot}SO_2)^+$ by photoionization of heterotrimers (possibly plus larger clusters). Dashed line: efficiency function for the production of $(C_4H_6{\cdot}SO_2)^+$ by photoionization of heterodimers, plotted on the same scale. Inset: detail of the region above 1050 Å.

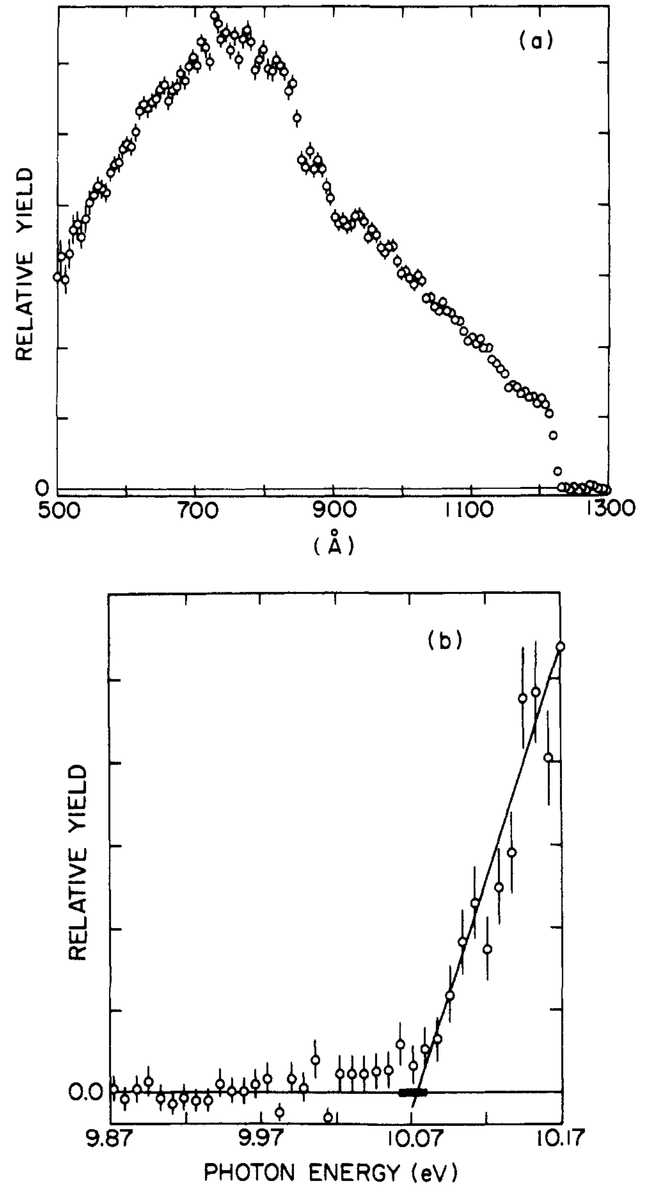

Figure 9. (a) Efficiency function for the production of $C_4H_6SO_2^+$ from sulfolene. (b) Detailed yield measurement in the threshold region for the production of $C_4H_6SO_2^+$ from sulfolene at a resolution of 1 Å (0.008 eV). A LiF window was used to eliminate higher order radiation in this measurement. The 68% confidence region for the threshold is indicated.

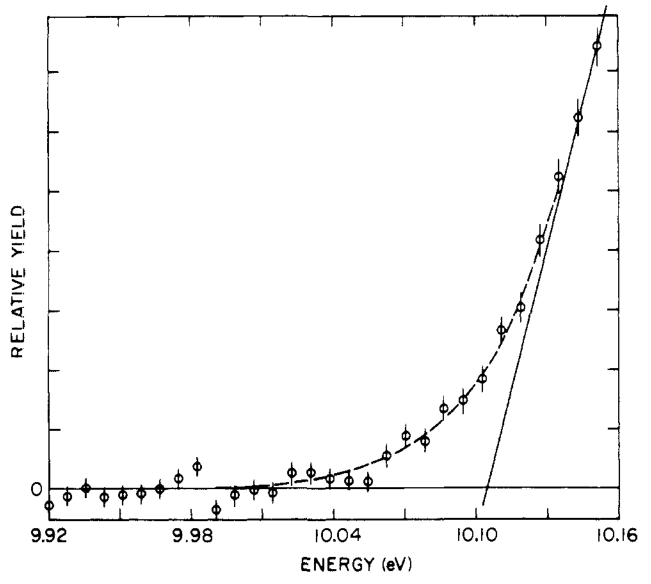

Figure 10. Threshold region for the production of $C_4H_6^+$ from sulfolene. This measurement was made on the vapor at room temperature, necessitating the correction shown by the dashed line. The correction was measured in an ancillary experiment.

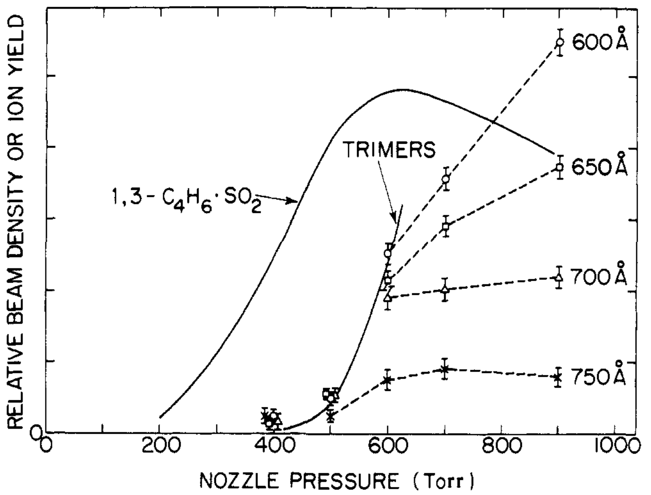

Figure 11. Comparison of the yield of $C_4H_6SO^+$ (points and dashed lines) with beam composition (solid lines), as a function of wavelength and nozzle pressure. This shows that above 500 Torr most of the product comes from trimers (and possibly larger clusters), but that at 400 Torr most comes from the heterodimers.

for the production of $C_4H_6^+$ is the same, 10.076 ± 0.029 eV (Figure 10). Since these spectra had to be measured using room-temperature vapor, the benefit of jet expansion cooling was not available. The thermal excitation of the 3-sulfolene is clearly evident for $C_4H_6^+$ in Figure 10 and contrasts with the sharpness of the threshold function for 3-sulfolene parent ion, for which hot bands due to thermal excitation are absent. We conclude from this comparison that very few states, likely only one, of the 3-sulfolene ion can be detected. In fact, the yield of $C_4H_6SO_2^+$ is only 1 to 2% as large as the yield of $C_4H_6^+$, which supports this conclusion. The contrast between Figures 2, 4, 6, and 7 and Figures 9 and 10 demonstrates that the complex $C_4H_6{\cdot}SO_2$ is a different species altogether than 3-sulfolene. The ion $C_4H_6SO^+$ could not be detected in the photoionization of 3-sulfolene, even when zero-order photon beams were used.

We previously reported[1] the formation of $C_4H_6SO^+$ by dissociative photoionization of clusters of 1,3-butadiene + SO_2, at a

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(22) Solouki, B.; Bock, H.; Appel, R. *Chem. Ber.* **1975**, *108*, 897–913.
(23) Aitken, R. A.; Gosney, I.; Farries, H.; Palmer, M. H.; Simpson, I.; Cadogan, J. I. G.; Tinley, E. J. *Tetrahedron* **1984**, *40*, 2487–2503.

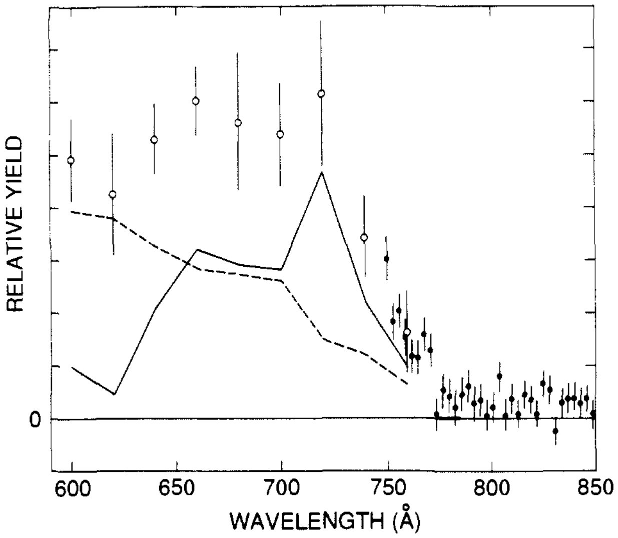

Figure 12. Yield of $C_4H_6SO^+$ from the molecular beam at 500 Torr. Open and closed points represent separate experiments. The wavelength at onset is indicated by a horizontal bar on the abscissa. Between 600 and 760 Å the data are resolved into contributions from heterodimers (solid line) and trimers (dashed line).

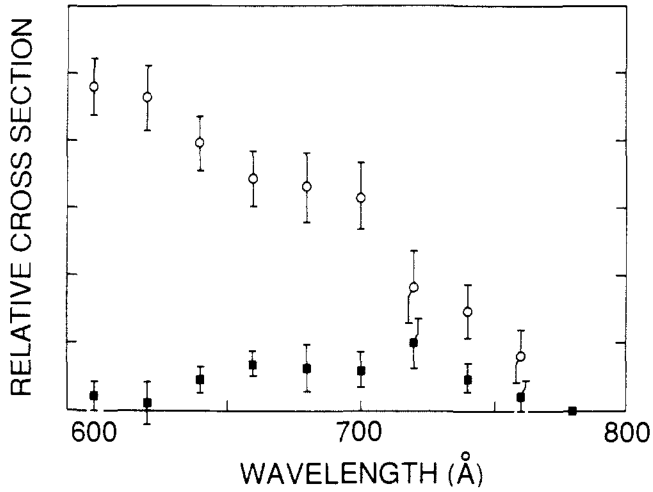

Figure 13. Relative cross sections for the production of $C_4H_6SO^+$ from heterodimers (closed points) and trimers (open points).

nozzle pressure of 800 Torr, and have now made additional observations in an attempt to understand the mechanism of its production. The dependence of its yield on nozzle pressure and wavelength is coplotted, in Figure 11, with the relative beam densities of $C_4H_6{\cdot}SO_2$ and of trimers. From this comparison it is clear that $C_4H_6SO^+$ is formed from both heterodimers and trimers, with the cross section to produce it from trimers greatly exceeding that from the dimers. The photoionization efficiency spectrum at 500 Torr is presented in Figure 12. The background was carefully measured and subtracted, but a residual counting rate below the onset is still apparent, which is mostly, but not entirely, due to second-order radiation (vide infra). The onset for the production of $C_4H_6SO^+$ under these conditions was found to be 15.90 ± 0.10 eV (780 ± 5 Å), a value that contrasts sharply with the value 15.36 ± 0.10 eV (807 ± 5 Å) reported in ref 1 for the spectrum measured at 800 Torr. We made use of the known beam composition and the spectra measured at 500 and 800 Torr to calculate the relative cross sections for the production of $C_4H_6SO^+$ from $C_4H_6{\cdot}SO_2$ and from trimers, with the results shown in Figure 13. This information was used to estimate the resolution of the 500-Torr spectrum of Figure 12 into contributions from heterodimers and trimers, shown as solid and dashed lines, respectively. We see that the onsets at 15.90 and 15.36 eV should be identified with the dissociative ionization of $C_4H_6{\cdot}SO_2$ and trimers, respectively. Note that in the 500-Torr data the trimer onset is weak, and therefore masked by the strong contribution from second-order radiation.

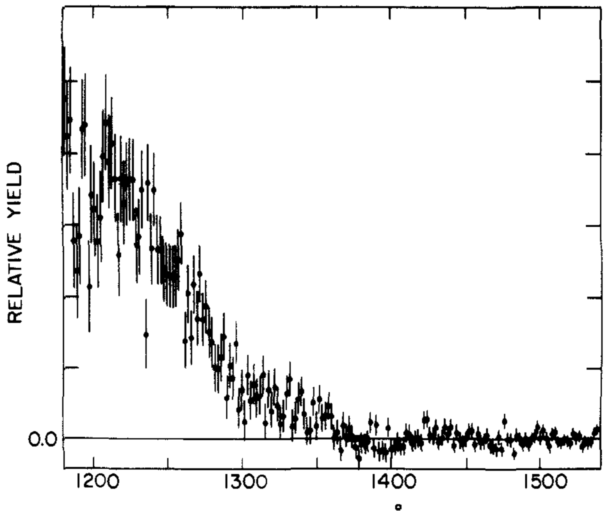

Figure 14. Threshold region for the production of $C_4H_6(SO_2)_2^+$ at a nozzle pressure of 750 Torr.

The threshold for the production of $C_4H_6(SO_2)_2^+$ at a nozzle pressure of 750 Torr is 9.00 ± 0.05 eV (1377 ± 7 Å) (Figure 14). The onset is surprisingly well-marked for such a complex system, suggesting that here, also, autoionization plays a role. The sequence 9.07, 9.08 ± 0.02, 9.00 ± 0.05 eV for the IP's of 1,3-butadiene, $C_4H_6{\cdot}SO_2$, $C_4H_6(SO_2)_2$, respectively, suggests a trend to lower values with increasing cluster size, in common with what is observed for homoclusters.[24]

Discussion

Energy Diagram. The threshold and onset data are combined with known thermochemical and spectroscopic information[20,25-30] in an energy diagram (Figure 15).

The exothermicity at 298 K of the reaction of *s-trans*-1,3-butadiene with SO_2 to produce 3-sulfolene is 0.71 ± 0.03 eV (16.4 ± 0.7 kcal mol^{-1}), or 0.62 eV (14.3 kcal mol^{-1}) at 0 K based on reasonable estimates for the normal mode distribution of 3-sulfolene.

The low dissociation energy of $(C_4H_6{\cdot}SO_2)^+$, 3.00 kcal mol^{-1}, is difficult to understand, but is in line with many other heterodimer parent ions.[18c] A qualitative molecular orbital argument is that homodimer ions enjoy extensive electron delocalization, while heterodimer ions do not. This explains why the dissociation energies of heterodimer ions are smaller than they are for homodimer ions,[18c] but the observed energies are so small that a more complete explanation is needed. For example, a simple electrostatic plus van der Waals calculation (vide infra) predicts 7 kcal mol^{-1} for $(C_4H_6{\cdot}SO_2)^+$.

The sulfolene ion is less stable than the heterodimer ion by 0.52 eV (11.9 kcal mol^{-1}). It is also unstable with respect to dissociation into $C_4H_6^+ + SO_2$ by 8.8 kcal mol^{-1}, so it is quite surprising that the 3-sulfolene parent ion can be observed at all. Its very weak

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[28] Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1666-1671.

[29] Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

[30] Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 436-438. The IP of 2,5-dihydrothiophene 1-oxide was estimated to be 8.6 eV from the photoelectron spectra of several sulfoxides reported in this paper.

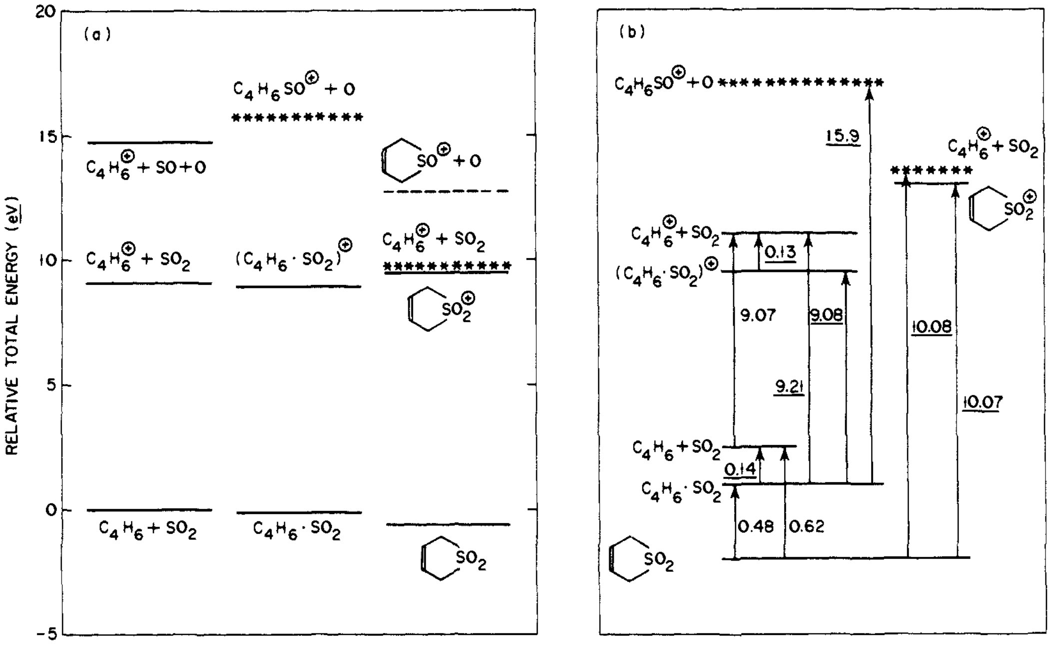

Figure 15. Energy diagram (a) and transition energy schematic (b) of the 1,3-butadiene + SO_2 system. Measurements made in this work are underlined.

intensity relative to the $C_4H_6^+$ ion produced by dissociative ionization is therefore quite understandable.

The estimated threshold of about 13.6 eV[31] for producing $C_4H_6SO^+$ from the heterodimer is much lower than the observed onset at 15.90 ± 0.10 eV.

Structure of the Heterodimer. To understand the role of the weak complex in the dynamics of the addition reaction it is necessary to know its structure. This structure has not yet been determined, so we seek guidance from calculations.

The weak van der Waals heterodimer can involve either the s-trans or the s-cis configuration of 1,3-butadiene. The s-trans is the more stable by 2.5 kcal mol^{-1} (ref 28), so that even at room temperature it is by far the major component (98.5%). It has long been known that in the condensed phase there is a barrier between the two isomers,[32] i.e., that when the s-cis structure is produced by thermolysis in solution at 100 °C it persists long enough to add to a trapping reagent. This barrier, about[33] 6 to 7 kcal mol^{-1}, is larger for the isolated transition state than it is in a liquid where solvation confers additional reaction pathways. The relative abundances of the two structures are hence very little affected by the rapid (microseconds) cooling due to jet expansion, and therefore the butadiene moiety in the observed van der Waals heterodimer is almost entirely s-trans. The question arises whether the endothermicity plus barrier of the s-trans to s-cis transformation allows existence of corresponding isomers of the complex. Although the fraction of heterodimer is about the same in the beam as the fraction of the s-cis isomer in butadiene, viz. 1% at 500 Torr nozzle pressure, it is not reasonable that the SO_2 would selectively complex only with the s-cis butadiene leaving the s-trans form relatively untouched. Calculations (vide infra) predict that the s-trans complex with SO_2 is ~2.1 kcal mol^{-1} more stable than the s-cis complex.

The minimum energy configurations corresponding to Lennard-Jones nonbonding and electrostatic terms were calculated with the program CHARMM.[34] For each conformer a single structure that is not very sensitive to changes in the input parameters was predicted; see Figure 16. In each case the sulfur atom is located halfway between the two middle carbon atoms. For the s-trans structure, **7**, one of the oxygen atoms approaches hydrogen atoms bound to the first and third carbons while the other oxygen atom points away from the butadiene. The angle between the sulfur dioxide and butadiene planes is very floppy, but with parallel planes strongly, and perpendicular planes slightly, disfavored. For the s-cis structure, **8**, one of the oxygen atoms approaches the hydrogen atoms bound to the second and third carbons while the other points away, forming a structure of C_s symmetry. Here, also, the two planes are very nonrigid. The calculated dissociation energies for **7** and **8** are 3.0 and 3.4 kcal mol^{-1}, respectively, fortuitously close to the 3.2 ± 0.5 kcal mol^{-1} actually measured.

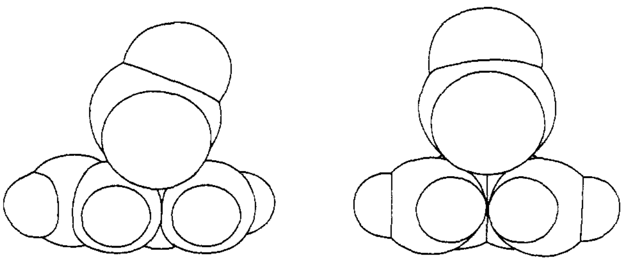
7 8

Figure 16. Calculated structures for the van der Waals heterodimers 1,3-butadiene·sulfur dioxide: for the s-trans conformer, **7**; for the s-cis conformer, **8**.

Instability of the Sulfolene Ion. Since the ionization potential of the s-cis 1,3-butadiene ion is no less than that of the s-trans isomer,[35] its heat of formation is at least 2.5 kcal mol^{-1} greater than s-trans, and might be as much as 5.5 kcal mol^{-1} greater.[35] Therefore, the observed 3-sulfolene ion is unstable with respect to dissociation into the s-cis butadiene ion and SO_2 by 3.4 to 6.5

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[31] To estimate the threshold for the production of $C_4H_6SO^+$ from 1,3-$C_4H_6 \cdot SO_2$ we first estimated the heat of formation of 2,5-dihydrothiophene-1-oxide using Benson's tables.[29] Then, to estimate the energy of the complex $C_4H_6 \cdot SO$ this value was increased by 0.48 eV, which is the difference between the heats of formation of 3-sulfolene and 1,3-$C_4H_6 \cdot SO_2$.

[32] Hatch, L. F.; Peter, D. *Chem. Commun.* **1968**, 1499.

[33] We assume that this barrier corresponds to the increase in energy due to the loss of alternate double-bond character when the butadiene molecule becomes nonplanar, which can be estimated as the difference in heat of formation of *s-trans*-1,3-pentadiene and 1,4-pentadiene, about 6.6 kcal mol^{-1}.

[34] Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187–217. Published by Polygen Corp., 200 Fifth Ave., Waltham, MA. The dissociation energy includes contributions from a Lennard-Jones potential energy function and an electrostatic energy, using partial charges on the atoms. The structure is found by iteratively minimizing the energy. We used the input parameters supplied by the program.

[35] Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1968**, *49*, 2454–2455.

kcal mol^{-1} (0.15 to 0.28 eV), and, most significant, when enough energy is supplied to produce 3-sulfolene ions, $C_4H_6^+$ appears in abundance (Figure 15). The data are thus consistent with the expectation that the $C_4H_6^+$ is born in the s-cis configuration. In this respect an experiment to measure the distribution of final-state translational energies of $C_4H_6^+$ produced in the dissociative photoionization of 3-sulfolene would be very enlightening.

Production of $C_4H_6SO^+$. The production of $C_4H_6SO^+$ in the photoionization of 1,3-$C_4H_6{\cdot}SO_2$ is quite unexpected. The dissociation energies of the heterodimer and heterodimer ion, 3.2 and 3.0 kcal mol^{-1}, respectively, are very much smaller than the energy needed to break the SO bond, about 131 kcal mol^{-1} for SO_2 and 85 kcal mol^{-1} for SO_2^+. Indeed, RRKM and QET calculations show that this product simply should not be detectable at the sensitivity of our experiment.[1] It is therefore produced nonstatistically. This conclusion is supported by two facts.

(1) The efficiency function strongly reflects the properties of one moiety. The observed onset for the production of $C_4H_6SO^+$, at 15.90 ± 0.10 eV, is essentially the same as that for SO^+ from SO_2, 15.965 eV.[36,37] The simplest explanation is that SO_2 is the chromophore while butadiene is only a spectator[38] that subsequently captures the recoiling SO^+. For the isolated SO_2 molecule the onset of SO^+ starts just below the adiabatic IP of the $\tilde{C}\,^2B_2(000)$ state of SO_2^+, at 15.992 eV.[42] Coincidence measurements[36,43] show that the state $\tilde{C}\,^2B_2$ and the states $\tilde{D}\,^2A_1$ and $\tilde{E}\,^2B_1$ which lie just above it[42] all predissociate extensively and nonstatistically[43] to form SO^+.

(2) The onset is 2.3 eV higher than the thermodynamic threshold of about 13.6 eV.[31] For the ion to survive decomposition long enough to reach the detector, too much of this extra energy must appear as translation to be explainable by the statistical model.

It is useful to know that $C_4H_6SO^+$ is formed from the heterodimer in a fast process because this is compatible with a structure such that the sulfur atom lies between the butadiene and at least one of the oxygen atoms; cf. structure 7 (Figure 16).

By a strict spectator mechanism the product $C_4H_6SO^+$ ion is born excited by the binding energy of 1,3-butadiene to the SO^+ plus any SO^+ recoil energy. Such a highly excited ion is unlikely to survive long enough to be detected, suggesting that the spectator mechanism should be slightly modified. Measurements of the distribution of final state translational energies would be very helpful here.

The production of $C_4H_6SO^+$ from trimers (and perhaps larger clusters) proceeds with much larger cross sections than from heterodimers (Figure 13). This means that the ion is usually born too excited to survive, but it can be stabilized by the ejection of a third "solvent" molecule. The observed onset of $C_4H_6SO^+$ at 15.36 eV is well below the threshold for the production of SO^+ from SO_2, suggesting that the reaction is too complicated to be described by a simple spectator mechanism.

We have also seen third-molecule stabilization effects in the production of $C_6H_6Cl^+$ from mixed clusters of benzene and HCl, where the $C_6H_6Cl^+$ is produced entirely by dissociative photoionization of trimers and larger clusters, and cannot be detected at all from the heterodimers.[18f] Indeed, further work[44] is revealing this third-molecule stabilization to be very general for obtaining products from the photoionization-induced dissociative rearrangement of mixed clusters.

Summary

Molecular beams of mixed van der Waals complexes of the molecules 1,3-butadiene and sulfur dioxide were studied using single-photon photoionization in the range 8 to 25 eV, to examine the potential hypersurface involved in the addition reaction. The complexes were synthesized in free jet expansions of the mixed gases, and the resulting target beams were analyzed as a function of nozzle pressure using tunable photon beams. Fragmentation patterns for 1,3-$C_4H_6{\cdot}SO_2$, (1,3-$C_4H_6)_2$, and 1,3-butadiene itself were obtained and compared at a photon energy of 21 eV. The photoionization efficiency spectra for the production of $C_4H_6^+$, $C_4H_6{\cdot}SO_2^+$, and $C_4H_6SO^+$ at different nozzle pressures were resolved into spectra originating from $C_4H_6{\cdot}SO_2$ (+(1,3-$C_4H_6)_2$) and from mixed trimers. Above their onset energies, cross sections for the production of $(C_4H_6{\cdot}SO_2)^+$ and $C_4H_6SO^+$ from trimers are much larger than those for their production from $C_4H_6{\cdot}SO_2$. Several thresholds and onsets were measured: (from $C_4H_6{\cdot}SO_2$: $C_4H_6^+$, 9.210 ± 0.021 eV; $(C_4H_6{\cdot}SO_2)^+$, 9.080 ± 0.021 eV; $C_4H_6SO^+$, 15.90 ± 0.10 eV; and from $C_4H_6(SO_2)_2$: $C_4H_6(SO_2)_2^+$, 9.00 ± 0.05 eV). These data were used to obtain dissociation energies for the heterodimer and heterodimer ion: D_0(1,3-$C_4H_6{\cdot}SO_2$) = 3.24 ± 0.48 kcal mol^{-1}, and $D_0([C_4H_6{\cdot}SO_2]^+)$ = 3.00 ± 0.68 kcal mol^{-1}. The onset energy for the production of $C_4H_6SO^+$ from either heterodimer or trimers is much larger than threshold, and much of the energy difference appears as excitation causing most of these ions to be born too excited to survive unless they are stabilized by a third "solvent" molecule. The photoionization of the reaction product 3-sulfolene was also studied for comparison. The efficiency spectra for the production of $C_4H_6SO_2^+$ and $C_4H_6^+$ from 3-sulfolene were measured, and the cross sections for the latter were found to be 50–100 times larger than for the former. The thresholds for the production of $C_4H_6^+$ and $C_4H_6SO_2^+$ are 10.076 ± 0.029 and 10.073 ± 0.006 eV, respectively. The 3-sulfolene parent ion is therefore unstable with respect to dissociation into 1,3-$C_4H_6^+$ and SO_2 by 8,8 kcal mol^{-1}. The ion $C_4H_6SO^+$ is not produced from 3-sulfolene at any photon energy up to 30 eV.

We conclude that photoionization spectroscopy of complexes of reactants using tunable photons provides useful but limited information about the reaction hypersurface. Further advances will be possible with experiments that add a capability to measure dynamic quantities, such as lifetimes and the distribution of final-state translational energies.

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(38) However, our data cannot exclude the possibility that there are contributions in which the chromophore is butadiene. The photoelectron spectrum of 1,3-butadiene includes a prominent peak between 15 and 16 eV due to population of the ^2A_g and ^2B_u states of[39,40] $C_4H_6^+$. This excited $C_4H_6^+$ could ionize the SO_2 to its dissociating states. Charge-exchange processes in collisions between benzene and polyatomic ions are known to proceed with retention of electronic energy and without strong propensity rules.[41]

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