A plot of the right-hand side of (A4) vs. I at constant t will be linear only when $N_n^{(t)}$ is chosen to correspond to the population of nondissociating ions. (With some reworking, this equation also allows analysis of data for $N(t)$ vs. t at constant I.)

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Photodissociation Spectroscopy and Structural Rearrangements in Ions of Cyclooctatetraene, Styrene, and Related Molecules

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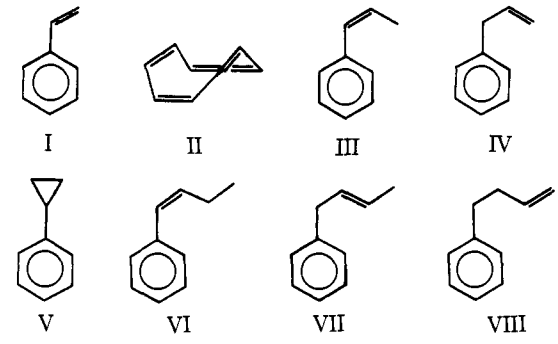
Abstract: Photodissociation spectra of the gas-phase parent ions derived from cyclooctatetraene, styrene, and several hydrocarbons related to styrene have been obtained, along with photoelectron spectra of the neutrals. There is no observable interconversion of styrene and cyclooctatetraene ions. Comparison with the photoelectron spectra and consideration of the likely spectral changes in going from benzene ions to styrene ions suggests that the ions obtained from styrene retain the original structure and account in a satisfactory way for the observed spectrum, while the spectrum obtained for cyclooctatetraene ions is not in accord with expectation and indicates a likely rearrangement or severe distortion of the neutral structure. The spectra of 1-phenylpropene and 3-phenylpropene ions were similar, suggesting migration of the double bond into conjugation, but a similar migration was found to be at most incomplete for 1-phenyl-2-butene and completely absent in 4-phenyl-1-butene. The spectrum of cyclopropylbenzene ion suggests retention of the neutral structure. Positions of a number of the peaks are discussed in terms of interactions of the benzene and ethylene π systems.

Standard methods of mass spectrometry have compiled a large volume of information on the structures and rearrangement processes of fragmenting gas-phase ions.[2] The recent emergence of several techniques having the capacity for characterizing thermalized, nondecomposing ions has given impetus to the reexamination of such questions for many ions of labile geometry. The two new approaches which provide unequivocal information about the nondecomposing ions are photodissociation spectroscopy[3-14] and selective ion-molecular reactions,[15-17] while the collisional activation approach, while nominally a technique characterizing decomposing ions, has also been claimed to provide information about structures of nondecomposing ions.[18] The present study employed the photodissociation-spectroscopic approach in a close examination of rearrangement processes in stable $C_8H_8^+$ ions[17,19-21] and some related species (I–VIII). The two types of rearrangement of interest were the ring-expansion/ring contraction isomerization of styrene (I) and cyclooctatetraene (COT) (II) and the migration of double bonds into conjugation. The species examined also expand substantially the body of information about spectroscopic properties of highly conjugated and aromatic cations.



Experimental Section

The experimental arrangement was the same as that used for previous photodissociation studies.[3-14] A standard square ICR cell was used to trap the ions with a trapping voltage of 2–3 V and near zero drift potentials. An ionization electron energy of about 10 eV was used for most of the compounds. Sample pressures were varied from 10^{-8} to 10^{-7} Torr to keep the trapping times of the ions comparable and the ions were typically trapped for the order of 20 s.

A 2.5 kW Xenon arc lamp and a 2.5 kW Xe–Hg arc lamp have both been used as the light sources. The wavelength selection was provided by using both a monochromator and interference filters. The Baird-Atomic interference filters have a bandwidth of 100 Å, spaced 200 Å apart from 4000 to 7000 Å, and a bandwidth of 150 Å at 7500 and 8000 Å. The Schoeffel monochromator with two 4-mm slits gives a nominal band-pass (FWHM) of 132 Å. An Eppley thermopile was used to measure the relative light intensities and the photodissociation rates at different wavelengths were normalized to the same photon intensity.

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Table I. Photoelectron Peaks[a]

	PES, eV		Excitation
	Adiabatic	Vertical	energy, eV
Styrene (I)	8.43	8.58	
	~9.1	9.35	0.92
	~10.4	10.56	2.13
	11.2	(σ onset)	
COT (II)	8.03	8.43	
	9.4	9.85–10.15	1.82–2.12
		11.15	3.12
		11.65	3.62
		12.4	4.4
1-Phenylpropene (III)	8.15	8.28	
	9.1	9.18	1.03
		9.7–9.9	1.55–1.75
		10.35	2.20
	11.1	(σ onset)	
Allylbenzene (IV)	8.70	8.9–9.15	
		9.38	0.68
		9.80	1.10
	11.0	(σ onset)	
Cyclopropylbenzene (V)	8.35	~8.6	
		9.23	0.88
	10.0	10.58	2.23
	11.7	(σ onset)	
1-Phenyl-2-butene (VII)	8.48	8.85	
		9.35	0.87
	10.9	(σ onset)	
4-Phenyl-1-butene (VIII)	8.6	8.83	
		9.38	0.8
		9.83	1.2
	10.8	(σ onset)	

[a] All the values given were measured from our own spectra; for I, II, and IV the literature spectra are in good agreement, the small differences reflecting some judgement in assignment of peak onsets and maxima.

Time-resolved photodissociation experiments[10,22] were performed for the cations and for toluene cations under identical experimental conditions, so that the absolute cross sections of the photodissociation spectra could be obtained by comparing the cation photodissociation rates from the time-resolved experiments to that of toluene cation, which has a known absolute photodissociation cross section of 5.2×10^{-18} cm^2 at 4000 Å.[13]

As will be discussed later, the parent ions of styrene and COT were regenerated from the photodissociation product ions $C_6H_6^+$; therefore the $C_6H_6^+$ ions were ejected from the cell continuously by efficient cyclotron ejection during experiments on styrene and COT.

The high-resolution photoelectron spectra of all but compound VI were obtained on a Varian photoelectron spectrometer. The samples of allylbenzene, β-methylstyrene, 1-phenyl-2-butene, and 4-phenyl-1-butene were obtained from ICN-K&K Laboratories, Inc., and 1-phenyl-1-butene was from Chemical Sample Co. We are indebted to Dr. G. A. Olah for providing us with the samples of cyclopropylbenzene and cyclooctatetraene and to Dr. I. Krieger for the sample of styrene.

Results and Discussion

The Photoelectron Spectra. Photoelectron spectra of all the benzene derivatives in question are quite similar: the lowest IP between 8 and 9 eV is sharp, corresponding to π-electron removal; several additional sharp peaks normally appear below 11 eV, corresponding to lower-lying π orbitals, and then near 11 eV there is a steep onset to a very broad, structured plateau region which represents overlapping σ (and perhaps π) orbital ionizations. At energies above this σ onset the spectrum becomes largely useless for comparison with optical spectra. In Table I the vertical IP's (and adiabatic IP's where they can be resolved) are listed up to the σ onset for the compounds studied.

Table II. Photodissociation Peak Energies (in eV)

Ions	Visible[a]	UV[a]
Styrene (I)	2.14	3.75, 4.05
COT (II)	2.50	3.25, 3.54, 4.74
III	2.14	3.50
IV	2.14	3.50
V	2.30	4.00
VI	2.14	3.50
VII	2.14, 3.00	3.36
VIII	2.14, 2.80	

[a] The estimated uncertainties for the peak energies are ±0.05 eV.

As has been discussed in detail,[8] it is appropriate to compare hole-promotion-type optical or photodissociation peaks with the peaks in the PES spectrum corresponding to π orbitals, taking the adiabatic first ionization potential as the zero of energy in the PES spectrum. The hole-promotion energies calculated from the PES spectra are given in Table I for direct comparison with the photodissociation peaks.

Photodissociation Pathways. Aside from styrene ions, COT ions, and 1-phenyl-1-butene ions, all the ions studied photodissociate through hydrogen atom loss:

$$C_9H_{10}^{+\cdot} \xrightarrow{h\nu} C_9H_9^+ + H\cdot \quad (1)$$

$$C_{10}H_{12}^{+\cdot} \xrightarrow{h\nu} C_{10}H_{11}^+ + H\cdot \quad (2)$$

The 1-phenyl-1-butene ions photodissociate through the loss of a methyl group,

$$C_{10}H_{12}^{+\cdot} \xrightarrow{h\nu} C_9H_9^+ + \cdot CH_3 \quad (3)$$

Generally, some additional reactions appeared during irradiation by light; these are undoubtedly ion–molecule reactions of photofragment ions and were not very extensively investigated. Different reactions were often observed with different isomers and may reflect the structural differences of the neutral molecules.

Styrene and COT molecular ions follow the same photochemical sequence:

$$C_8H_8^{+\cdot} \xrightarrow{h\nu} C_6H_6^{+\cdot} + C_2H_2 \quad (4)$$

$$\uparrow \quad \downarrow$$

$$C_8H_8$$

in which the parent ions were regenerated from the photodissociation product ions ($C_6H_6^{+\cdot}$) via a charge-transfer reaction. This is an interesting case of catalytic photochemical conversion of C_8H_8 into C_2H_2 and C_6H_6. The ion–molecule reactions of these two systems have been carefully examined.[17]

Among the possible dissociation channels, the observed dissociation to $C_6H_6^{+\cdot}$ and C_2H_2 is the least endothermic one for styrene and COT ions,[20] so it appears that the photodissociation pathways were determined thermochemically, as has been found true in other systems.[10] Thermochemical data were unavailable for the other compounds, and no conclusions are possible about the factors influencing their dissociation channels.

The Photodissociation Spectra. The photodissociation spectra of the molecular ions are shown in Figures 1, 2, and 3. The peak energies are listed in Table II for convenient comparison.

Styrene ions. Using the Hg–Xe arc lamp as the light source and interference filters for wavelength selection, photodissociation of styrene ions in the visible region was observed only at 5800 Å (this wavelength being favored because of the strong

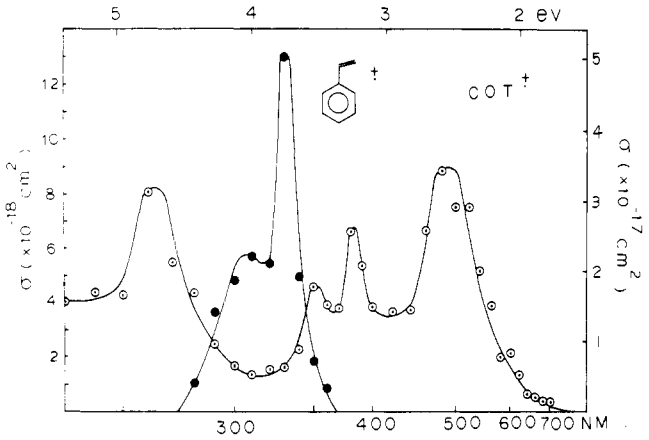


Figure 1. The photodissociation spectra of the styrene cation and the cyclooctatetraene cation. The styrene cation spectrum corresponds to the right-hand scale and the COT cation to the left-hand scale.

Hg line at 5790 Å). The heats of formation of styrene and benzene ions are accurately known from photoionization measurements and these values yield an endothermicity of 55.2 kcal/mol (5180 Å) for the observed photodissociation pathway; 5800 Å is somewhat below the thermochemical threshold and a preliminary result using a more intense dye laser source has shown that the photodissociation of the parent ions can be observed at least up to 6300 Å. It seems probable, accordingly, that styrene ion photodissociation in this wavelength region is a sequential two-photon process of the sort postulated by Freiser and Beauchamp for benzene cation.[12,23,24] A quadratic dependence of photodissociation rate on light intensity would then be expected and is approximately, although not exactly, observed. This accounts for the failure to observe dissociation with the arc source except at 5800 Å.

Apparently, therefore, styrene cation has a photodissociation peak spanning 5800 Å, although neither the cross section nor the shape was determined. Such a conclusion is in accord with the expectation from the photoelectron spectrum (see below) that the lowest $\pi \rightarrow \pi$ transition[34] should lie near 5820 Å, and also with the observation of optical absorption in the 5900–6300-Å region in the spectrum of styrene ion in glassy matrix.[25]

Above the thermochemical threshold at 5180 Å, there are no corresponding uncertainties in the photodissociation spectrum, which shows a highly asymmetric, and probably split, feature around 3200 Å, which we take to be a barely resolved pair of peaks at 3.75 and 4.05 eV.

The absorption spectrum of styrene radical cations formed in a γ-ray-irradiated glassy matrix has been reported.[25] This spectrum is compared directly with the photodissociation spectrum of styrene ions in Figure 4. The solid-state UV peak is close in position to the gas-phase peak but is red shifted by about 0.1 eV. (A similar red shift in glassy matrix has been observed previously in the methyl–naphthalene cation system.[12]) The solid-state visible peak at 6300 Å with an obvious shoulder around 5900 Å presumably corresponds to the photodissociation peak near 5800 Å. It has been suggested that the 4600-Å shoulder in the solid state spectrum may be due to other species present in the glassy matrix.[27] No such peak was observed in the photodissociation spectrum, lending support to the suggestion that this peak is not due to styrene cation. In other work a short-lived species with an absorption maximum near 3400 Å was detected in an electron pulse radiolysis experiment on styrene.[27] This species was assigned as styrene radical cation formed by charge transfer. This absorption is highly asymmetric and, in agreement with the glassy-matrix spectrum, is shifted by about 0.1 eV to lower energy as compared with the gas-phase peak. The long-wavelength peak near 5800 Å was not observed in this experiment due to the insensitivity of the spectrometer in this region.

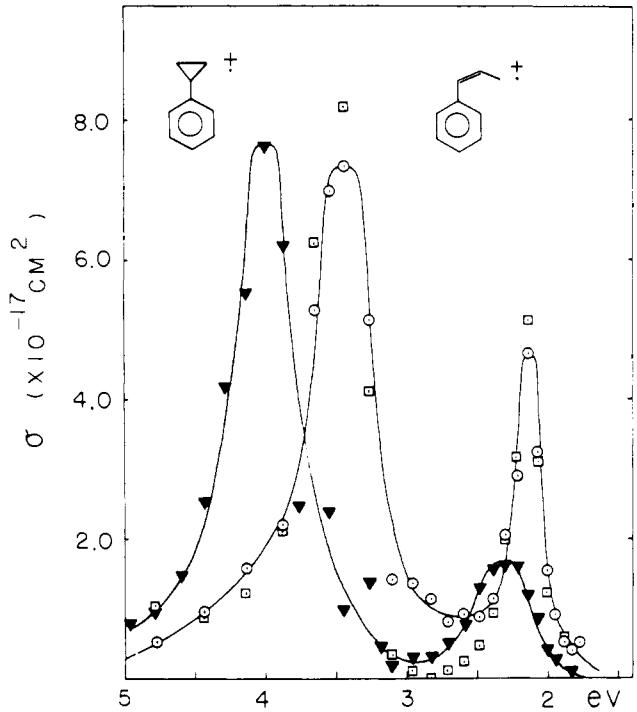


Figure 2. The photodissociation spectra of the cyclopropylbenzene cation (▼), 1-phenyl-1-propene cation (⊡), and allylbenzene cation (⊙). The absolute photodissociation cross section scale of allylbenzene cation is not shown in the figure.

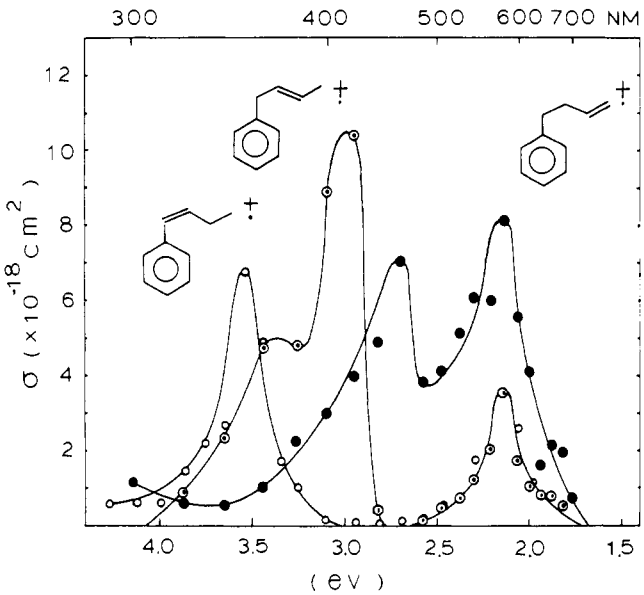


Figure 3. The photodissociation spectra of 1-phenyl-1-butene cations (○), 1-phenyl-2-butene cations (⊙), and 4-phenyl-1-butene cations (●). Note that the cross section scale of 1-phenyl-1-butene cation is ten times the scale of the figure and that only several points were drawn for the 5800-Å peak to avoid overlapping.

Although a detailed excited-state calculation is apparently not yet available for the styrene radical ion system, some understanding of the spectrum can be gained from orbital correlation and comparison with the neutral photoelectron spectrum. The ionization bands in the low-binding energy region of the PES spectra of I and IV have been identified and assigned by Rabalais and Cotton[26] and can be interpreted in

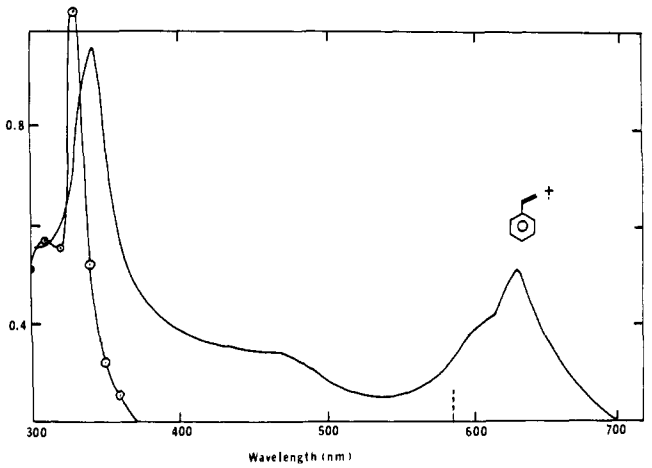


Figure 4. The gas-phase photodissociation spectrum (⊙) of styrene cations is compared directly with the solid-state absorption spectrum of styrene cations. The dotted line indicates that photodissociation of styrene cations was observed around 5800 Å.

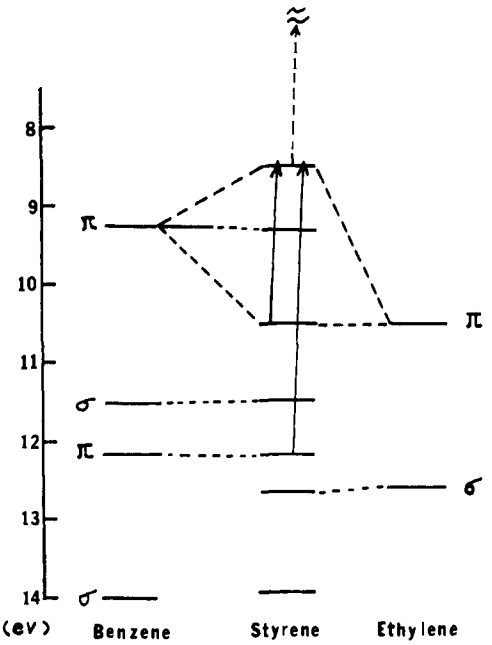


Figure 5. Orbital energy diagram of styrene, benzene, and ethylene. The solid arrows represent the possible $\pi \rightarrow \pi$ transitions; the dotted arrow represents the $\pi \rightarrow \pi^*$ transition.

terms of an interaction diagram for the benzene and ethylene constituent units as shown in Figure 5, with IP's as taken from the PES spectra.[26,28]

Styrene ion has several possible π-system optical transitions in the visible-UV region, of which three are denoted in the figure. The two transitions indicated by solid arrows are $\pi \rightarrow \pi$ transitions, predicted to lie at 5820 and 3280 Å (2.13 and 3.78 eV), and probably are both allowed. These are in excellent correspondence with the strong 3.75-eV peak and the peak in the 2.14-eV region in the photodissociation spectrum.

The other possible optical transition (indicated by a dotted arrow in Figure 5) involves excitation to an empty orbital and is thus not comparable with PES. For insight into this transition, it is useful to recall the benzene radical cation.[23] In the visible region, benzene cation undergoes photodissociation by a two-photon mechanism; the peak position was not determined in Freiser and Beauchamp's study but can be roughly estimated by comparison with the benzene photoelectron spectrum to be near 3 eV (as suggested by Figure 5). The correlation of Figure 5 indicates that this visible π-π transition is blue shifted in styrene cation to correlate with the 3.75-eV peak.

The other peak of benzene cation at 4.9 eV is the $\pi \rightarrow \pi^*$ transition which corresponds to the ^1L_b transition in benzene neutral. (Although it has been suggested that this UV peak might correspond to a $\pi \rightarrow \sigma$ transition,[23] we consider this unlikely and accept the more conventional interpretation of this optical peak as a $\pi \rightarrow \pi^*$ transition.) There has been considerable attention to the question of why this transition is so intense in benzene radical ions, and both vibronic and configuration interactions are apparently significant.[29] Two lines of reasoning lead to the expectation that this transition should be red shifted in going from benzene to styrene ions. First, the ^1L_b transition shifts to the red by about 0.45 eV in going from benzene to styrene neutrals, and since the cation transition in question is closely comparable to the neutral ^1L_b, a red shift of this order of magnitude might be expected in the cation. Second, it can be seen from Figure 5 that the perturbation of the benzene ring π and π^* orbitals by the ethylene unit should qualitatively raise the highest occupied π orbital (as it is seen to do in the photoelectron spectrum),[26] giving a red shift of more than 0.8 eV to the π-π^* transition. Based on these considerations, we expect to find the styrene cation $\pi \rightarrow \pi^*$ transition peak in the 4.0-4.5-eV region and believe that the observed peak at 4.1 eV can be confidently so assigned on this basis.

Cyclooctatetraene Ions. Four peaks are observed for the COT ions, and the spectrum is clearly different from the rest of the compounds studied in this work. Assuming a cyclic structure for $C_6H_6^{+\cdot}$, the threshold of reaction 4 for COT ions is 1.4 eV (8900 Å). Therefore the ion photodissociations in the visible and UV region are well above the threshold and were treated as one-photon photodissociations.

The photoelectron spectrum of COT has been studied, and the first three bands in PES were assigned as arising from the four π orbitals of COT.[30,31] The lowest optical transition should be the x-y allowed $\pi \rightarrow \pi$ transition $A_1 \rightarrow E$, corresponding to hole excitation from the 8.42-eV (vertical) orbital to the 9.78-eV orbital. Judging from the PES spectrum, this transition should have its 0-0 position near 1.4 eV (8800 Å) and might be expected to peak at perhaps 1.8-2.1 eV (7000-5900 Å). The observed peak onsetting at 1.75-2 eV and peaking near 2.55 eV is in very poor agreement with this expectation and raises very serious doubts as to whether the structure of the $C_8H_8^+$ ion from COT actually retains the COT structure. In view of this uncertainty, it is pointless to analyze the photodissociation spectrum in terms of a COT geometry, and our use of the spectrum will be based on the obvious fact that the ion, whatever its geometry, does not spectroscopically resemble the styrene cation.

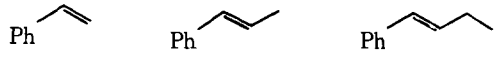
The absorption spectrum of COT^+ ions has also been examined in glassy environment.[32] This spectrum extends only to ~3600 Å and can therefore be compared with only part of the gas-phase spectrum. The broad and structureless visible peak near 5000 Å in the matrix spectrum agrees in both shape and peak position with the visible photodissociation peak; however, the next prominent gas-phase peak near 3850 Å was not observed in the matrix spectrum.

$C_9H_{10}^{+\cdot}$ and $C_{10}H_{12}^{+\cdot}$ Ions. A number of substituted benzenes related to styrene were investigated from the point of view of looking at side-chain rearrangement processes upon electron impact; also, the selection of this particular set of ions allows one to look into several interesting questions about the electronic structure of the ions, as will be discussed later. Photodissociation spectra of these ions are shown in Figures 2 and 3, and the peak positions are tabulated in Table II.

All three $C_9H_{10}^{+\cdot}$ ions (III, IV, and V) show one UV (or blue) peak and one visible peak, both peaks being symmetrical. The three $C_{10}H_{12}^{+\cdot}$ ions (VI, VII, and VIII) show a symmet-

rical visible peak, but the UV peaks of VII and VIII appeared to be rather asymmetric; in fact, there is an apparent shoulder on the short wavelength side of the UV peak of 1-phenyl-2-butene ions (VII). It is noteworthy that all but the cyclopropylbenzene cations show a visible peak near 5800 Å (2.14 eV).

A useful comparison may be made between ions I, III, and VI which share the styrene π system but with varying degrees of perturbation from the alkyl substitution on the β carbon position. The photodissociation spectra of I, III, and VI are



I III VI

directly compared in Figure 6. Remembering that styrene cations have a peak around 5800 Å (although absolute cross section and the curve shape were not determined), it is apparent that the general features of the photodissociation spectra of the three ions are quite similar. It appears, however, that the alkyl substitution shifts the 3.75 eV peak of styrene slightly toward longer energy (by about 0.25 eV). The spectra of III and VI have identical peak positions and very similar cross sections for the peaks, indicating that different alkyl groups have similar effects on the electronic transitions involved. It seems clear that the spectral pattern of III and VI can be taken as characteristic of the styrene radical cation chromophore.

The 2.14-eV photodissociation peak of III is accurately reflected in the PES peak at 2.20 eV. Unfortunately the UV region of III is obscured by the σ plateau in the PES spectrum.

Rearrangement of Ions. From the present photodissociation study, it is clear that the styrene and COT molecular ions formed near threshold do not rearrange to a common structure to any significant extent. This is consistent with the results of Wilkins and Gross[17] from ion–molecule reaction patterns that also deal with the structure of the nondecomposing ions. Their results indicate that at least a portion of the $C_8H_8^+$ ions produced from styrene possesses a different structure than that of COT ions and there is essentially no isomerization of COT ions to the styrene structure.[17] The present evidence is stronger, however, first because it rules out rearrangement on a time scale of seconds and second because it rules out both COT $\rightarrow$ styrene (<10%) and styrene $\rightarrow$ COT (<10%) rearrangement.

The photodissociation onset for $COT^{+\cdot}$ ions was observed at about 1.75 eV. The possibility of forming any acyclic $C_6H_6^{+\cdot}$ ions as product is ruled out except for the 4.7-eV peak, since the formation of acyclic $C_6H_6^+$ has a thermochemical threshold of 4.3 eV or higher. In order to form benzene ions as the dissociation product, the $COT^{+\cdot}$ ions may rearrange after the absorption of the photon, possibly with a mechanism analogous to the photoinduced rearrangement observed in the neutral COT system.[33]

The photodissociation spectra of allylbenzene (IV) and β-methylstyrene (III) ions are very similar, showing the visible peak near 5800 Å and a near-UV peak around 3600 Å. The UV-to-visible peak intensity ratios for these two ions are identical, and the absolute cross sections were estimated to be identical within experimental uncertainty. This strongly suggests that the ions derived from these two precursors have identical structures. As noted above, the photodissociation and PES spectra of III are in excellent agreement; on the other hand, the 2.14-eV peak observed in the photodissociation spectrum of IV has no counterpart in the PES spectrum,[26] which argues strongly for a rearranged structure for the ion. It would, in any case, be difficult to believe that IV, with a break in the π system, would have π orbitals and optical transitions precisely matching those of the fully conjugated III ions. This suggests that allylbenzene ions rearrange to the β-

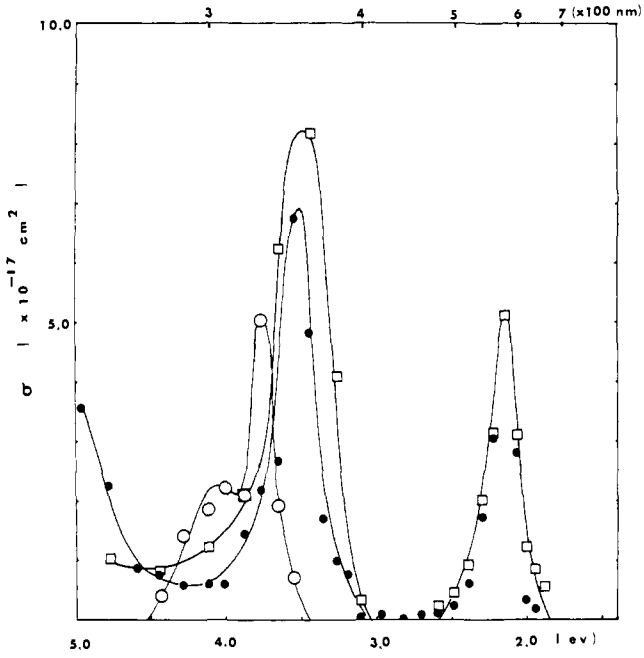


Figure 6. The photodissociation spectra of styrene cation (○), β-methylstyrene cation (□), and 1-phenyl-1-butene cation (●).

methylstyrene structure, presumably via a 1–3 hydrogen shift, as commonly observed in mass spectrometry.[2]

Cyclopropylbenzene ions show a spectrum that is clearly different from that of the other two isomers. Both the UV and the visible peaks for this ion are shifted toward higher energy, the UV peak shifted more than 0.5 eV. It is apparent that although the allylbenzene ions isomerize to β-methylstyrene structure, the cyclopropylbenzene ions do not rearrange. The PES peak at 2.23 eV above the ground state ion corresponds very well to the visible photodissociation peak for this ion, suggesting that it retains its structural identity.

Three $C_{10}H_{12}^{+\cdot}$ ions were examined to determine whether the same type of isomerization observed in allylbenzene and β-methylstyrene ion systems would occur for this set of isomers. Any rearrangement to a common stable structure upon electron impact should be recognized easily by comparing their photodissociation spectra. It is clear from Figure 3 that these three ions have rather different spectra, and it is therefore unlikely that significant rearrangement occurs upon ionization. It is however reasonable to suspect that a small fraction of ion VII might have rearranged to ion structure VI as suggested by the shoulder near 3.3 eV in the spectrum of VII overlapping the 3.5-eV peak of VI. In contrast to the apparently complete rearrangement of IV to III upon ionization, the additional methyl substituent in VII inhibits (at least partially) its rearrangement to VI. In VIII, the interposition of an additional methyl group between benzene and ethylene completely blocks movement of the double bond into conjugation, as shown by the complete lack of similarity of the spectra of VI and VIII.

Other than differentiating the isomeric species, some insight into the nature of the UV transition can be gained by understanding the origin of the difference in the spectra of VI, VII, and VIII ions. The observation that a red shift of the UV peak results by shifting the double bond away from the ring π system is consistent with the earlier suggestion that the 3.75-eV styrene peak is due to a π(ring) $\rightarrow$ π(ring) transition. It is likely that the UV peaks of these isomeric ions correspond to the same type of transition. The energy of this transition can be affected by the interaction between the ring π orbitals and the side-chain π system.[26] As the double bond is shifted away from the ring, the extent of interaction and therefore the splitting

of the ring π orbitals is reduced with a resulting decrease in the energy difference for this $\pi \rightarrow \pi$ transition, in agreement with the experimental observation. This picture does not, however, account for the 2.2-eV peak in the spectrum of VIII; we can offer no resolution of this question beyond suggesting that this peak may belong to an unidentified structure resulting from partial rearrangement of VIII.

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(34) Note on terminology: in discussing π excited states of the radical cations, a useful distinction may be drawn between states obtained by promoting an electron within the set of occupied orbitals, which will be termed π excited states, and states obtained by promoting an electron from an occupied orbital into an empty orbital, which will be termed π^* states. A distinction is thus made between $\pi \rightarrow \pi$ transitions (which may be compared with neutral photoelectron spectra) and $\pi \rightarrow \pi^*$ transitions (which may be compared with neutral optical absorption spectra).

Spin–Lattice Relaxation in Triphenylphosphine, Triphenylarsine, and Triphenylstibine

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Abstract: The spin–lattice relaxation times (T_1) have been determined for all carbons in triphenylphosphine, triphenylarsine, and triphenylstibine. The ortho, meta, and para carbons all relax exclusively by the dipole–dipole mechanism. The α carbons in triphenylphosphine and triphenylarsine relax predominantly by the dipole–dipole mechanism below about 40 °C while the spin–rotation mechanism is most important above this temperature. The α carbon in triphenylstibine shows nonexponential decay since carbon bound to ^{121}Sb relaxes by the scalar coupling mechanism at all temperatures while carbon bound to ^{123}Sb relaxes by the dipole–dipole mechanism at low temperatures and spin–rotation at higher temperatures. The ^{121}Sb–^{13}C coupling constant is calculated to be 450 Hz.

Relaxation times for carbon-13 in molecules containing a metal or metalloid have not been widely reported. A number of ^{13}C NMR studies of molecules containing phosphorus, usually in a ring, have been reported by Gray,[1] while Lambert[2] has recently reported on six-membered rings containing O, S, Se, and Te at the 1 position. No studies have been reported on triphenyl derivatives of the group 5 elements, P, As, and Sb. It is known that relaxation times provide information on structure, conformation, motions, and interactions.[3] This work has been carried out to determine the various relaxation mechanisms for triphenylphosphine, triphenylarsine, and triphenylstibine. In order to sort out the various mechanisms, the relaxation time has been studied as a function of temperature.

Experimental Section

Spin–lattice relaxation times were determined on a JEOL FX-60 spectrometer. The compounds were all examined as ~1 M solutions in $CDCl_3$ which provides the deuterium lock. The inversion–recovery technique $(180°-t-90°-T)_n$ was used to obtain relaxation data. The time, t, between the 180° pulse for spin inversion and the 90° observation pulse was varied over a broad range so as to bracket the relaxation times of all carbons. The waiting time between pulses, T, was always greater than five times the longest T_1. The 180° pulse width, 28 μs, as well as the 90° pulse width, 14 μs, was determined in the usual way.[2] All spectra were obtained using 8K data points over a sweep width of 1000 Hz. Chemical shifts are reported relative to Me_4Si as an internal standard.

The T_1 software for the FX-60 automatically digitizes the intensities, plots the intensities, and produces the T_1 value. In addition, for

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