

A Study of the Styrene Ion-Molecule Reaction by Ion Cyclotron Resonance¹

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Abstract: Using ion cyclotron resonance techniques, we have established that structurally different C_8H_8 radical cations are produced by electron impact with styrene and cyclooctatetraene (COT). We have also been able, in this way, to study the ion-molecule reactions occurring in styrene and COT. The styrene radical cation was observed to react with neutral styrene to produce a complex at m/e 208 ($C_{16}H_{16}^{\cdot+}$) which subsequently loses the elements of benzene to form $C_{10}H_{10}^{\cdot+}$ (m/e 130). This is the first example of an observable complex in the bimolecular reactions of olefinic radical cations with neutral olefins. By means of deuterium labeling, ion cyclotron double resonance, and conventional mass spectrometry of suspected intermediates, we have been able to establish the probable structure of the $C_{16}H_{16}$ ion as 1-phenyltetralin radical cation. Conventional mass spectrometric measurements of the 1-phenyltetralin-4,4- d_2 have established that this compound loses deuteriobenzene almost exclusively *via* a novel 1,4 elimination to produce an ion at m/e 131. No reaction of $C_8H_8^{\cdot+}$ from COT with neutral styrene was found. This investigation shows the utility of ion cyclotron resonance spectrometry as a means of distinguishing isomeric gas-phase ions.

Deuterium labeling has proved to be a valuable tool for the elucidation of mass spectral fragmentation mechanisms and the investigation of the structures of gas-phase ions. Unfortunately, this method gives only information about those ions possessing sufficient energy to decompose and need not reflect the structure of the nondecomposing ions. For example, the examination of the mass spectra of a number of deuterated styrenes showed the fragmentation was consistent with a mechanism in which all hydrogens became equivalent.² This led, quite naturally, to the conclusion that styrene ions isomerize to cyclooctatetraene ions which then decompose to give the observed mass spectra. Such a conclusion cannot, however, be verified by conventional mass spectrometry for the reasons mentioned above. It was our initial intent to use ion cyclotron resonance (icr) to determine whether the styrene radical cation did, indeed, exist as a discrete observable entity. Intuitively, it would seem reasonable that isomeric ions would undergo ion-molecule reactions at different rates and thus it would be possible, in principle, to distinguish between styrene and cyclooctatetraene radical cations if both were present.

Energetics studies could allow the determination of heats of formation of $C_8H_8^{\cdot+}$ from either cyclooctatetraene (COT) or styrene, but results of that type are complicated by the possibility that the ions formed simply differ in internal energy and not in structure. These measurements have been made and it was found that the heat of formation of the $C_8H_8^{\cdot+}$ ion from styrene is 232 kcal/mol and that from COT is 255 kcal/mol.³ This suggests the two ions are different.

However, such data can only be applied with confidence to ions formed at the appearance potential.

The use of ion-molecule reactions, observed by high-pressure mass spectrometry, to distinguish isomeric ions has been applied by Munson in the cases of various $C_4H_9^{\cdot+}$ and $C_4H_8^{\cdot+}$ ions^{4b} and by Sieck and Futrell in the case of various $C_3H_6^{\cdot+}$ ions.^{4c} Recently, the structure of $C_4H_8^{\cdot+}$ produced in the photoionization of cyclobutane has been determined by a study of ion-molecule reactions observed in a high-pressure mass spectrometer.^{4d} Ion cyclotron resonance spectrometry with its multiple resonance capabilities seems ideally suited for this problem. The icr spectrometer and the principles of its operation have previously been described⁵ and applications of icr to some structural problems have recently appeared.⁶

Experimental Section

Ion cyclotron resonance spectra were obtained with a Varian ICR-9 spectrometer. Potentials between the filament and the cell were determined with a digital voltmeter. Both single resonance and double resonance spectra were obtained while operating in the field modulated mode. In addition, the double resonance experiments were done using the pulsed mode. Trapping, source, and analyzer drift voltages were 0.5, 0.2, and 0.2 V, respectively. The pressures were measured by using the current monitor of the ion pump. Changes in pressure, as in the studies of the effect of pressure on ion abundance, were more accurately obtained by ob-

Radiat. Transfer, **2**, 369 (1962); M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964), as cited in J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26**, 72 (1969).

(4) (a) M. S. B. Munson, *J. Amer. Chem. Soc.*, **89**, 1772 (1967); (b) M. S. B. Munson, *J. Phys. Chem.*, **71**, 3966 (1967); (c) L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, **45**, 560 (1966); (d) L. W. Sieck, S. K. Searles, and P. Ausloos, *J. Amer. Chem. Soc.*, **91**, 7627 (1969).

(5) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(6) (a) J. Diekman, J. K. McLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969); (b) G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91**, 3986 (1969); (c) J. L. Beauchamp and R. C. Dunbar, *ibid.*, **92**, 1477 (1970).

(1) Presented, in part, at the 1969 Midwest Regional Meeting of the American Chemical Society, Kansas City, Kan., Oct 1969.

(2) E. I. Quinn and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, **62**, 39 (1959).

(3) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc.*

servicing changes in the total ion current in the cell. This was necessary due to outgassing of the ion pump at high pressures. The mass assignments for the ions at m/e values greater than 130 were made by adding various organic iodides to styrene and COT. For example, the m/e 153 assignment was established by addition of ethyl iodide (molecular ion mass = 156), the m/e 165, 166 by addition of *n*-propyl iodide (m/e 170), the m/e 179 by addition of *sec*-butyl iodide (m/e 184), and m/e 208 by addition of iodobenzene (m/e 204). Conventional mass spectra were measured using a Hitachi RMU-6D double focussing mass spectrometer.

Materials. The styrene and cyclooctatetraene were commercial samples and were used without further purification. Both the styrene and COT were shown by conventional mass spectrometry to contain no contaminants of mass greater than their molecular mass. The samples were distilled on a vacuum line to a tube cooled at liquid nitrogen temperature prior to introduction into the icr spectrometer. The styrene- α - d was purchased from Mallinkrodt Nuclear and was shown to be 95% d_1 by mass spectrometry. *trans*-Styrene- β - d was prepared by the method of Yoshino and coworkers⁷ and was shown to be 90% *trans* by nuclear magnetic resonance and 94% d_1 by mass spectrometry. 1,2-Diphenylcyclobutanes were prepared by the method of Dodson.⁸ 1-Phenyltetralin was a gift from Dr. F. R. Mayo. 1-Phenyltetralin-4,4- d_2 was prepared by lithium aluminum deuteride-aluminum chloride reduction of 4-phenyltetralone and shown to be more than 95% d_2 by mass spectrometry. The 4-phenyltetralone⁹ was prepared from 4,4-diphenylbutyric acid according to the method of Johnson.¹⁰

Results and Discussion

We sought, at the outset, to find a molecule which would react in the gas phase with ions produced by styrene and COT. Our early choices of what we hoped would be reactive molecules proved to be poor ones. *A priori* there are few guiding principles in making such selections, since there is a dearth of studies of the ion-molecule reactions of complex organic compounds. Attempts to observe reaction products of the $C_8H_8^+$ ions with methyl iodide or acetylene were fruitless. However, a careful examination of the icr spectra of the pure hydrocarbons revealed the presence of products of ion-molecule reactions at m/e values greater than 104. Furthermore, the icr spectra above m/e 104 for the two compounds were different.

The most significant difference we found was that readily observable peaks appeared at m/e 208 and 130 in the styrene icr spectrum but these peaks were absent from the spectrum of COT. The 208/104 ratio increased from 0.0006 at 1×10^{-6} Torr to 0.022 at 1×10^{-5} Torr indicating that this ion is a product of an ion-molecule reaction. These data are summarized in Table I.

In order to interpret the data in Table I it was necessary to know the source of each of the observed ions. So, suitable double resonance experiments were performed. The results are listed in Table II. The effects of pressure and electron energy are also of value in assigning the origin of product ions. These effects are illustrated in Figures 1-3 and in Table I.

Consideration of the studies listed above indicated that the following exothermic¹¹ reactions were occurring

(7) T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, **86**, 4670 (1964).

(8) R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **32**, 28 (1967).

(9) S. Wawzonek and J. Kozikowski, *J. Amer. Chem. Soc.*, **76**, 1641 (1964).

(10) G. D. Johnson, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 900.

(11) A negative double resonance response indicated an exothermic atom-transfer reaction. For a discussion of the thermodynamic implications of double resonance, see J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

Table I. Ion Cyclotron Resonance Spectra of Styrene and Cyclooctatetraene^a

m/e	Ion	% relative abundance			
		Styrene		Cyclooctatetraene	
		5×10^{-7} Torr	1×10^{-5} Torr	5×10^{-7} Torr	1×10^{-5} Torr
39	C_3H_3	0.1	0.1	0.2	0.1
52	C_4H_4	0.1	0.1	0.3	0.1
65	C_5H_5	0.1	0.1	0.1	0.05
77	C_6H_6	3.8	1.3	3.9	6.1
78	C_6H_6	33	8.0	38	16
89	C_7H_7	0.5	0.4	0.9	0.06
91	C_7H_7	0.3	0.5	0.3	0.1
102	C_8H_8	2.3	2.3	7.6	0.2
103	C_8H_7	31	27	52	38
104	C_8H_8	100	100	100	100
105	$^{13}CC_7H_8$	8.5	8.3	8.5	8.5
115	C_8H_7	<i>b</i>	0.6		0.3
117	C_9H_9				0.2
128	$C_{10}H_{10}$		0.2		0.05
129	$C_{10}H_9$	<0.05	1.8	<0.1	0.4
130	$C_{10}H_{10}$	<0.05	0.5		
152	$C_{12}H_{12}$		0.2		0.3
153	$C_{12}H_{11}$		0.4		0.6
165	$C_{13}H_{13}$		1.8		3.0
166	$C_{13}H_{12}$		2.1		2.0
178	$C_{14}H_{14}$		0.3		0.3
179	$C_{14}H_{13}$		0.7		0.5
208	$C_{16}H_{16}$		2.2		

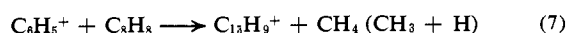
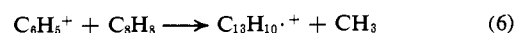
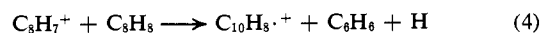
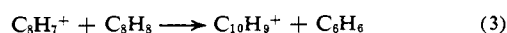
^a Measured at 20 eV. ^b Not detected.

Table II. Origin of Product Ions Determined by Double Resonance

Ion	COT source	Sign ^a	Ion	Styrene source	Sign
115	<i>b</i>		115	<i>b</i>	
117	<i>b</i>				
128	<i>c</i>		128	$C_8H_7^+$	-
129	$C_8H_7^+$	-	129	$C_8H_7^+$	-
			130	$C_8H_8^+$	-
153	$C_6H_5^+$	-	153	$C_6H_5^+$	-
153	$C_8H_8^+$	+	153	$C_8H_8^+$	+
165	$C_6H_5^+$	-	165	$C_6H_5^+$	-
165	$C_8H_8^+$	+	165	$C_8H_8^+$	+
166	$C_6H_5^+$	-	166	$C_6H_5^+$	-
166	$C_8H_8^+$	+	166	$C_8H_8^+$	+
179	$C_6H_5^+$	-	179	$C_6H_5^+$	-
			180	$C_8H_8^+$	+
			208	$C_8H_8^+$	-

^a Positive sign indicates increase of product ion abundance on irradiation at source frequency. ^b Too much interference due to frequency overlap with observing oscillator. ^c Too weak to determine.

in pure styrene at 20 eV and 1×10^{-5} Torr (eq 1-8).



The relative abundances of $C_{16}H_{16}^+$, $C_{10}H_{10}^+$, and $C_{10}H_9^+$ increased linearly with pressure, consistent with the reactions postulated above (Figure 1). The nonzero intercept should not be considered significant

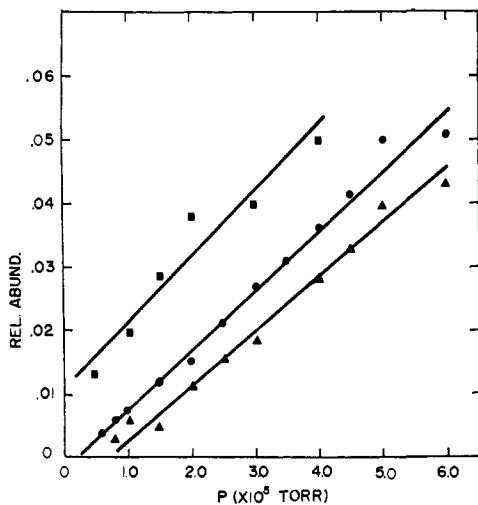
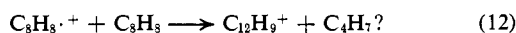
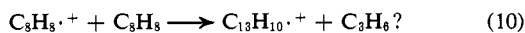


Figure 1. Relative abundance of selected ions for styrene as a function of pressure: 208/104 ($\times 0.2$), \bullet ; 130/104, \blacktriangle ; 129/103, \blacksquare .

since the absolute pressure was not known with great accuracy. The rapid increase in the relative abundance of $C_{16}H_{16}^{\cdot+}$ and $C_{10}H_{10}^{\cdot+}$ as the electron energy was decreased (Figures 2 and 3) may be due to the exothermicity of reactions 1 and 2 or to the existence of two or more isomeric $C_8H_8^{\cdot+}$ radical cations, the reactive isomer being present in greater concentration at low electron volts, or a combination of the above two possibilities. For example, it is known that the cross sections of ion-molecule reactions which presumably occur *via* an intermediate complex increase as the vibrational energy of the reactant ion decreases.¹² This interpretation is consistent with the "phase-space" theory of ion-molecule reactions.¹³

The ion-molecule products at m/e values 179, 166, 165, and 153 produced in reactions 5-8 have as their precursor the $C_6H_5^+$ cation, produced by loss of C_2H_3 from the molecular ions. The relative abundance of these product ions decreased with electron energy. At *ca.* 16 eV these products were no longer observed, which corresponds closely to the appearance potential of $C_6H_5^+$. Double resonance also indicated that the product ions at 179, 166, 165, and 153 can be produced by endothermic processes (reactions 9-12) involving $C_8H_8^{\cdot+}$ as the primary ion (an increase in the abundance of these ions was observed when $C_8H_8^{\cdot+}$ was irradiated¹¹). This conclusion may be questionable in light of the evidence that ion-molecule reactions observed in the mass spectrometer must be exothermic processes.¹⁴



The reactions occurring in COT under identical conditions are completely analogous except for the production of ions at m/e 208 and 130.

(12) (a) A. Weingartshofer and E. M. Clarke, *Phys. Rev. Lett.*, **12**, 591 (1964); (b) W. A. Chupka, M. E. Russell, and K. Refaey, *J. Chem. Phys.*, **48**, 1518 (1968); (c) W. A. Chupka and M. E. Russell, *ibid.*, **48**, 1527 (1968); (d) M. L. Gross and J. Norbeck, submitted for publication.

(13) J. C. Light, *J. Chem. Phys.*, **40**, 3221 (1964); J. C. Light and J. Lin, *ibid.*, **43**, 3209 (1965).

(14) See, for example, F. W. Lampe and F. H. Field, *J. Amer. Chem. Soc.*, **81**, 3242 (1959).

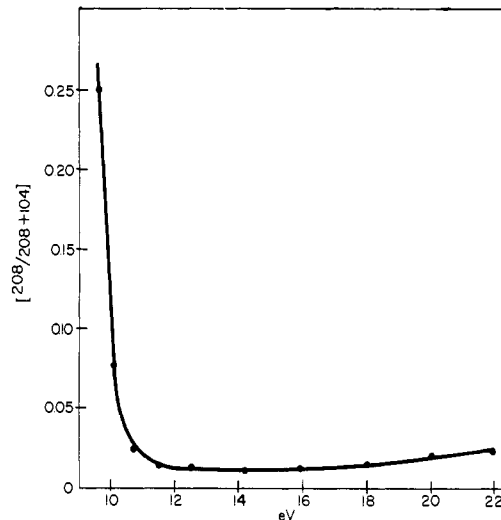


Figure 2. Relative abundance of m/e 208 ($C_{16}H_{16}^{\cdot+}$) for styrene as a function of electron energy; $P = 2 \times 10^{-5}$ Torr.

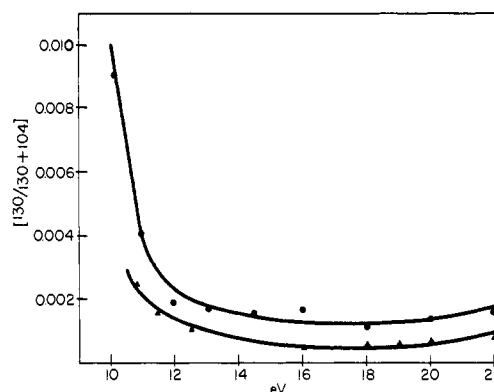


Figure 3. Relative abundance of m/e 130 ($C_{10}H_{10}^{\cdot+}$) as a function of electron energy: styrene at 1×10^{-5} Torr, \bullet ; 1:1 styrene-COT at 2×10^{-5} Torr, \blacktriangle .

The dramatic decrease in the relative abundance of m/e 78 in both the styrene and COT studies at the higher pressure is primarily due to an exothermic charge-exchange reaction (reaction 13). This reaction is 18 and 29 kcal/mol exothermic for styrene and COT, respec-



tively, assuming the C_6H_6 species are cyclic or 24 and 35 kcal/mol exothermic if the C_6H_6 species are acyclic (butadienylacetylene).³ A double resonance experiment was consistent with this suggestion. Irradiation of the $C_6H_8^+$ radical cation produced an increase in the abundance of $C_8H_8^+$ in both the styrene and COT systems.¹¹

While it was clear, at this point, that different ion-molecule reactions involving $C_8H_8^{\cdot+}$ were taking place, it was not clear whether the difference was due to ions of different structure or to the difference in the neutral molecules. It seemed obvious that experiments with mixtures should be undertaken. It also occurred to us that the icr spectrum of a mixture of styrene- α - d and COT might be quite informative.

When we examined styrene and an approximately equimolar mixture of COT and styrene we obtained the results diagrammed in Figure 3. The comparative data for pure styrene are included as well. Significantly, the

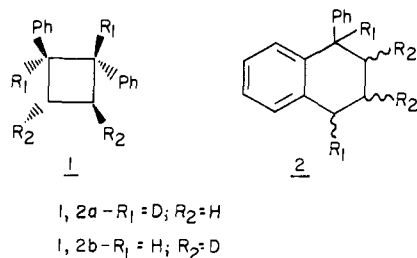
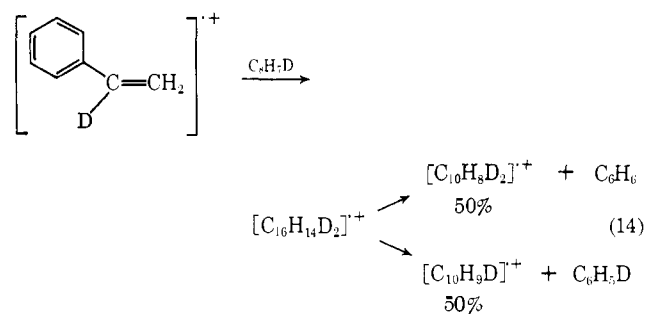


Figure 4. Possible structures of the "dimeric" ion.

ratio of the m/e 130 to the m/e 104 peak at all voltages is approximately the same for pure styrene or styrene in admixture with COT when statistical corrections are made (since in the latter case about half of the m/e 104 ion arises from COT). Likewise the 208:104 ratio decreased by 47% when styrene at 2×10^{-5} Torr was diluted with an equimolar amount of COT. More interestingly, when either an equimolar mixture of styrene- α - d and COT was examined, or when styrene- α - d alone was examined, peaks of equal intensity were found at m/e 131 and 132¹⁵ whereas if COT formed the same ion as styrene we would expect peaks at m/e 130, 131, and 132 in the ratio 1:2:1. These results unambiguously show that COT merely acts as an inert diluent so far as the styrene ion-molecule reaction is concerned and must, therefore, form a different molecular ion than styrene.

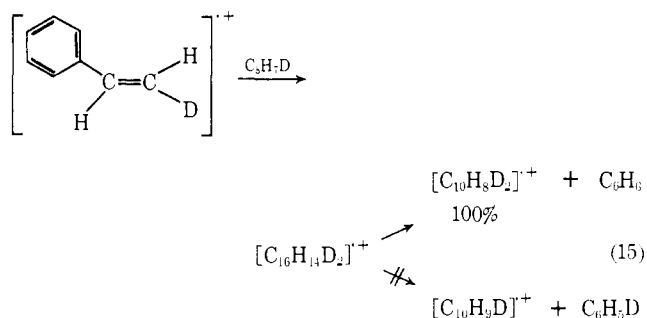
It should be noted that these results do not exclude the possibility of a mixture of isomeric structures for the C_8H_8 radical cation produced from styrene. In fact, the decrease in the abundance of $C_{16}H_{16}^{\cdot+}$ and $C_{10}H_{10}^{\cdot+}$ as the ionizing energy is increased may indicate such a mixture. The results do show that at least a portion of the C_8H_8 radical cations produced from styrene possess a different structure than that from COT. Also, there is essentially no isomerization of $C_8H_8^{\cdot+}$ from COT to the styrene molecular ion.

We had now established that the primary m/e 104 ions from styrene and cyclooctatetraene do possess different structures. One question still remained: what were the details of the ion-molecule reaction we were observing? Our examination of the icr spectrum of styrene- α - d suggested the intriguing possibility that deuterium labeling could help unravel the mystery. The loss of equal amounts of C_6H_5D and C_6H_6 from the 210 ion required a rather specific geometric relationship for this elimination (reaction 14).



(15) These measurements were made at 10.5 eV to eliminate possible interference from the m/e 128 and 129 ions. At this electron energy no m/e 103 or 129 was detectable in the icr spectrum of pure styrene at 2×10^{-5} Torr.

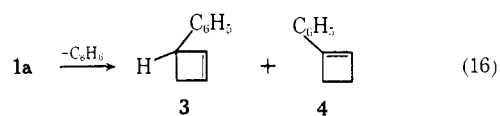
If this were the case, we reasoned, the spectrum of *trans*-styrene- β - d should be equally informative. When we examined that material we found *only* C_8H_8 was lost from the m/e 210 ion (reaction 15).



An equimolar mixture of styrene and *trans*-styrene- β - d showed icr peaks at m/e 130, 131, and 132 in the ratio 1:2:1. This shows (as expected) there is no significant isotope effect on the loss of C_6H_6 from the collision complex.

With the deuterium labeling and double resonance data in hand, we were now able to speculate reasonably on possible structures of the "dimeric" m/e 208 ion. Reference to Mayo's elegant study of the thermal dimerization of styrene shows that 1,2-diphenylcyclobutane (of unspecified stereochemistry) and 1-phenyltetralin are primary products.¹⁶ It seemed not unreasonable to us that the ion-molecule reaction under consideration might be closely analogous to the previously studied thermal reaction. Thus, we considered whether either of the 1,2-diphenylcyclobutanes or 1-phenyltetralin might undergo eliminations with sufficient geometric specificity to accommodate the icr deuterium labeling results. It seemed to us that two compounds could most reasonably fit this requirement. Their structures are indicated in Figure 4.

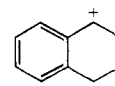
Consideration of each of these, in turn, makes clear how the eliminations of C_6H_6 or C_6H_5D might occur in accord with our data. If the geometric requirements were of overriding importance and only *cis* 1,2 elimination were allowed for compound 1, then **1a** would eliminate C_6H_6 and C_6H_5D while **1b** would lose *only* C_6H_6 . This, of course, would require the somewhat unlikely circumstance that a benzylic and nonbenzylic proton could be eliminated with equal facility. Alter-



nately, a 1,4 elimination from **2a** would yield equal amounts of C_6H_6 and C_6H_5D while the same reaction of **2b** would give only C_6H_6 .¹⁷ This sort of elimination is not without precedent and has been shown to be an important process in the mass spectral decomposition

(16) F. R. Mayo, *J. Amer. Chem. Soc.*, **90**, 1289 (1968)

(17) Although we have written a bicyclic structure for the ion product in eq 17, obviously we do not know the geometry of this ion. A structure consistent with the results might possess a localized charge and radical site, e.g.



1-PHENYLTETRALIN AT 70 ELECTRON VOLTS

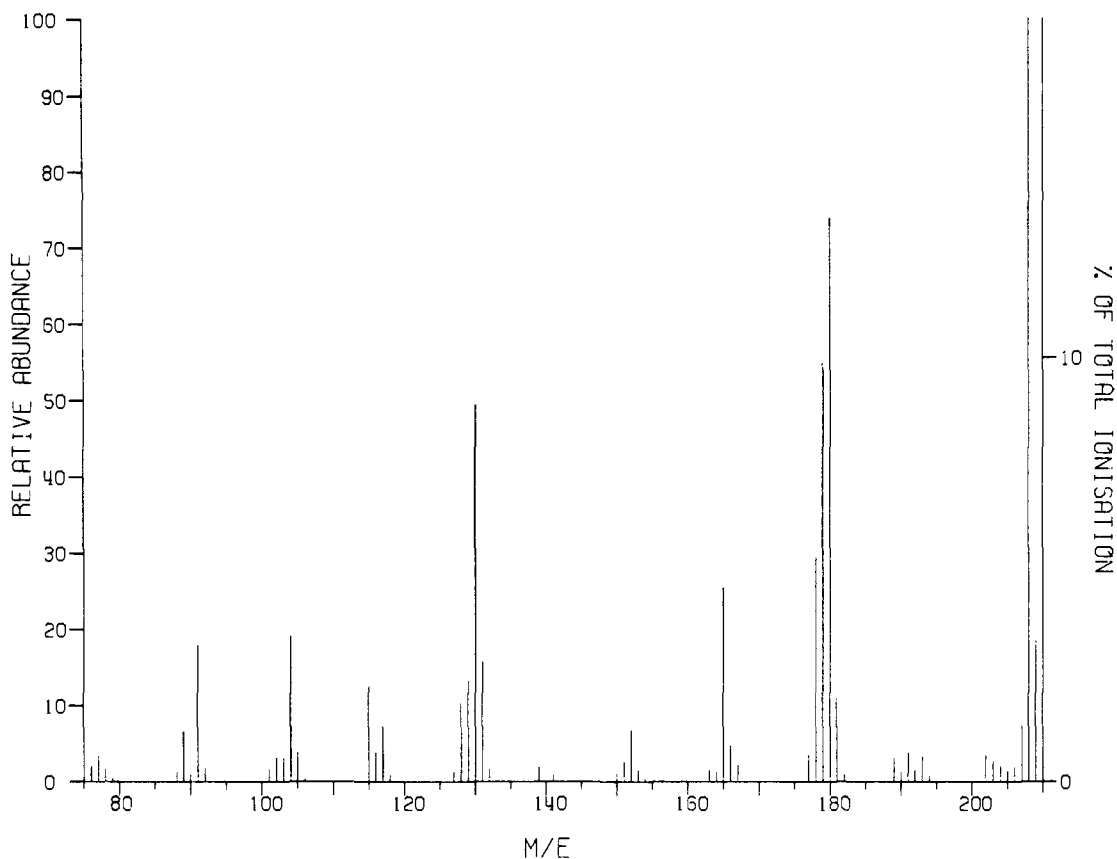
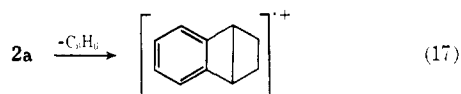
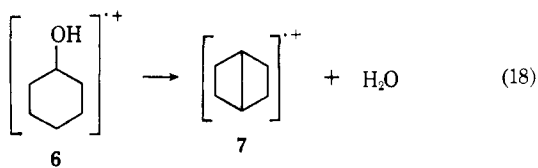


Figure 5. The 70-eV mass spectrum of 1-phenyltetralin.



of cyclohexanol.¹⁸ While we have discussed the elimination in terms of neutral compounds, we have im-



PLICITLY assumed the radical cations would fragment in a similar fashion. Even though it seemed improbable that loss of C_6H_6 and C_6H_5D from 1a would take place with equal facility, nevertheless we felt we could not exclude it simply on that basis. In order for either 1 or 2 to be plausible candidates for the structure of the "dimer" we thought that the fragmentation of the molecular ions derived from these compounds in the conventional mass spectrometer should proceed to give the same product ions we observed in the icr spectrum of styrene. This technique of comparing the unimolecular decomposition products of an ion produced by electron impact with those of an ion of the same composition produced by an ion-molecule reaction was first applied by Field, Franklin, and Lampe¹⁹ to the reaction of

(18) C. G. MacDonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Lett.*, 807 (1963); H. Budziklewicz, Z. Pelah, and C. Djerassi, *Monatsh. Chem.*, 85, 158 (1964).

$C_2H_4 \cdot^+$ with C_2H_4 . Other workers have used the technique to determine the structure of collision complexes formed in the ion-molecule reactions of tetrafluoroethene²⁰ and propene.²¹ Accordingly, we obtained samples of *trans*-1,2-diphenylcyclobutane and 1-phenyltetralin and examined their mass spectra. We also examined the mass spectrum of *cis*-1,2-diphenylcyclobutane. Table III summarizes the relevant features of

Table III. Comparison of Relative Ion Abundances^a

	118	130	180	208
<i>trans</i> -1,2-Diphenylcyclobutane	29		15	100
<i>cis</i> -1,2-Diphenylcyclobutane	9		100	100
1-Phenyltetralin		190	75	100
"Dimer" ^b (<i>m/e</i> 208)		23		100

^a Measured at 19 eV. ^b Measured by icr at 1×10^{-6} Torr.

these spectra and Figure 5 contains the complete spectrum of 1-phenyltetralin. Since the spectra of the 1,2-diphenylcyclobutanes have been presented elsewhere, they will not be reported here.²²

It is readily apparent that the spectra of neither of the cyclobutanes significantly resembles the icr data for the

(19) F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Amer. Chem. Soc.*, 79, 2419 (1957).

(20) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, 86, 4563 (1964).

(21) F. P. Abramson and J. H. Futrell, *J. Phys. Chem.*, 72, 182 (1968).

(22) M. L. Gross and C. L. Wilkins, *Tetrahedron Lett.*, 3875 (1969).

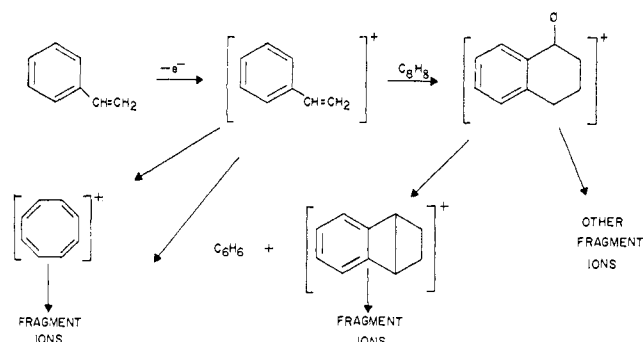


Figure 6. Summary of the major mass spectral fragmentation, isomerization, and ion-molecule reactions of pure styrene.

“dimer.” Most importantly, essentially no peak at m/e 130 (corresponding to loss of C_6H_6 from the molecular ion) is found. On the other hand, this is one of the most abundant ions in the spectrum of 1-phenyltetralin, and the appropriate metastable for the fragmentation $208 \rightarrow 130$ was found ($m^* 81.3$). It is conclusive, from this and the previously discussed labeling evidence, that the structure of the m/e 208 product is not that of the 1,2-diphenylcyclobutanes but is probably that of 1-phenyltetralin.²³ The differences in peak intensities are expected, since ions formed in the two spectrometers probably possess quite different internal energies. Herod and Harrison²⁶ have recently pointed out that a quantitative comparison of the abundances of the decomposition products should not be possible due to differing amounts of internal excitation. In our study, a quantitative comparison is unnecessary since the 1,2-diphenylcyclobutanes do not fragment to lose C_6H_6 .

As a final verification of the interpretation suggested by these results, we prepared 1-phenyltetralin-4,4- d_2 and examined its mass spectral fragmentation. If the 1,4 elimination of eq 17 occurs, C_6H_5D should be lost from this labeled compound. The spectrum unambiguously shows this to be the case, with a minimum of 95% of all C_6H_6 loss proceeding via this pathway. This conclusion was the result of both high (70 eV) and low (12 eV) ionizing potential mass spectra, where an almost quantitative shift of the m/e 130 to 131 was found, and appropriate metastable studies, which revealed that the metastable ion corresponding to $210 \rightarrow 131$ ($m^* 81.7$) was more abundant by a factor of 32 than the metastable ion for $210 \rightarrow 132$ ($m^* 83.0$). This appears to us to firmly establish the structure of the 1-phenyltetralin radical cation for the m/e 208 ion observed in the styrene ion-molecule reaction.

It is of interest to compare the results of this study to the results obtained for ethene and substituted ethenes. The ion-molecule reactions of ethene¹⁹ and tetrafluoroethene²⁰ are thought to produce cyclobutane and per-

(23) Other possibilities for the structure of the m/e 208 ion are acyclic ones (diphenylbutenes). None of the diphenylbutenes are consistent with the labeling results unless the loss of C_6H_6 occurs by an α elimination. Secondly, the 70-eV mass spectrum of 1,3-diphenylbutene-1 has been reported,²⁴ and the favored fragmentation is to produce m/e 115 (base peak), not m/e 130 (19% of base peak). We have also examined the 20-eV spectrum of this compound²⁵ and found the fragmentation yields the m/e 193 ion, one which is not observed in our studies.

(24) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Ed., “Atlas of Mass Spectral Data,” Vol. 2, Interscience, New York, N. Y., 1969, p 1482.

(25) D. C. Best and C. A. Kingsbury, *J. Org. Chem.*, **33**, 3252 (1968).

(26) A. A. Herod and A. G. Harrison, *J. Phys. Chem.*, **73**, 3189 (1969).

fluorocyclobutane radical cations respectively as the “dimer.” More recent results using a photoionization source indicate that the intermediate complex in the ethene case possesses the 2-butene structure.²⁷ The ion-molecule reactions in propene produce an acyclic complex (3-hexene).²¹ In these cases, the intermediate complexes are not detectable, but are considered to be chemically bonded complexes. This has, in fact, been unambiguously proven by crossed beam experiments for the reactions of $C_2H_4^{\cdot+}$ with C_2H_4 at low ion kinetic energies.²⁸

The intermediate complex in the styrene study is detectable and, therefore, is a chemically bonded or tight complex. It must possess a lifetime greater than 1 msec since the complex can be observed in the icr spectrometer. The fact that it is detectable is probably due to the greater number of vibrational degrees of freedom in $C_{16}H_{16}^{\cdot+}$ relative to $C_4H_8^{\cdot+}$ formed in the ethene case, for example. This, to our knowledge, is the first actual observation of an intermediate complex formed in condensation reactions of olefinic radical cations in the gas phase.

Another feature of interest regarding the styrene ion-molecule reaction is the total lack of rearrangement and isotopic exchange in the intermediate complex as shown by the labeling experiments. This fact is a dramatic contrast to the ethene system where total randomization of the label is observed in studies of C_2H_4 and C_2D_4 .²⁹ A similar observation has been made by Henis³⁰ in studies of the ion-molecule reactions of olefins. His studies of the reactions in butenes, pentenes, and hexenes show that little rearrangement takes place after formation of the complex. Our observations in the styrene system are in complete accord with his statement that ion-molecule reactions do *not* always proceed through randomized intermediates, and therefore, specific structures can be proposed for the intermediates.^{30a}

Summary

In conclusion, the considerations presented above now allow us to draw a somewhat detailed picture of the relationships between the styrene and cyclooctatetraene radical cations and the details of the styrene ion-molecule reaction. Figure 6 outlines our conclusions. When styrene is ionized in the icr spectrometer it initially forms a styrene molecular ion which then can isomerize to COT (if sufficient energy is available) or can react with neutral styrene molecules to form the 1-phenyltetralin radical cation. Subsequently, this ion may lose the elements of benzene as a primary fragmentation process as well as fragmenting in various other ways. Examination of the appropriate deuterium-labeled 1-phenyltetralin has provided further confirmation of this picture.

The extent of the styrene ion isomerization to COT seems to increase at higher ionizing potentials (see Figures 2 and 3). The drastic increase in the m/e 130 abundance at low electron volt values may indicate more styrene radical cation has become available for the

(27) R. Gordon, Jr., and P. Auloos, *J. Chem. Phys.*, **47**, 1799 (1970).

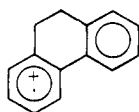
(28) Z. Herman, A. Lee, and R. Wolfgang, *ibid.*, **51**, 452 (1969).

(29) See, for example, M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

(30) (a) J. M. S. Henis, *J. Chem. Phys.*, **52**, 282 (1970); (b) J. M. S. Henis, *ibid.*, 292 (1970).

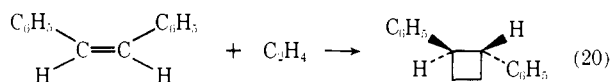
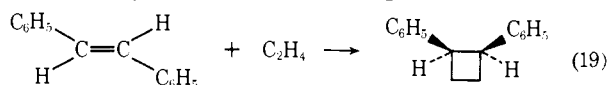
ion-molecule reaction. This interpretation is supported by the observation of a corresponding increase in the m/e 208 abundance. Another fact worthy of note is that when we studied the loss of deuterioacetylene or acetylene from the styrene- α - d radical cation by measuring the metastable abundances for these processes, instead of the 1:3 ratio expected, if prior isomerization to COT occurred, we found the ratio was 1:3.7 indicating an alternate mode of loss of these fragments was important. Hence the mass spectrum of styrene represents a composite of the decompositions of the styrene radical ion and the COT radical ion.³¹

Even though we have shown the 1,2-diphenylcyclobutanes not to be important products of the ion-molecule reaction, there are interesting differences in their mass spectra which require comment. Perhaps the most dramatic is the stereochemical effect on the relative abundance of the m/e 180 ion. We have suggested two possible explanations for this.²² The first is that the ion is a dihydrophenanthrene radical cation (**8**), a suggestion which is not without precedent.³²



8

A more exciting possibility is that the ion is, in actuality, a stilbene ion which arises as a result of the concerted elimination of ethylene from the molecular ion. If we consider the reverse process (*i.e.*, the thermal cycloaddition of ethylene to stilbene) we find an interesting prediction. Only if the addition gives the following stereochemical results would it be thermally allowed (eq 19 and 20). This corresponds to a [2 + 2] antarafacial cycloaddition. Consequently, if we make



(31) All metastable ion abundances in this study were measured by an electrostatic sector scan.

(32) R. A. W. Johnstone and M. J. Millard, *Z. Naturforsch. A.*, **21**, 604 (1966).

the not unreasonable assumption³³ that the gas-phase decomposition of the radical ion will be closely analogous to that of the neutral species, we would predict that the *cis*-diphenylcyclobutane ion would yield *trans*-stilbene radical cation and the *trans*-cyclobutane ion would yield *cis*-stilbene radical cation on fragmentation. Perhaps this could account for the observed differences in their spectra. We hope to be able to check this possibility in the near future.

Irrespective of the particular conclusions we have reached concerning the styrene ion-molecule reaction, we think the enormous potential of icr as a method for obtaining detailed structural and mechanistic information has been well demonstrated by the present study. This suggests the possibility of a wide range of further investigations of the structures of ions which have been asserted to be present as products of electron impact induced fragmentation. We are presently engaged in further such work intended to give us a far more general understanding of organic ion-molecule reactions than we now have. Our results further suggest that the examination of other ion-molecule reactions of styrene might be fruitful.³⁴

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(33) G. B. Gill, *Quart. Rev., Chem. Soc.*, **22**, 338 (1968).

(34) NOTE ADDED IN PROOF. Recently it has been reported that cyclohexene also undergoes a self ion-molecule "dimerization" in the gas phase: R. Lesclaux, S. Searles, L. W. Sieck, and P. Ausloos, *J. Chem. Phys.*, **53**, 3336 (1970).