# Absorption Spectra and Photochemical Rearrangements of Xylene and Methylcycloheptatriene Cations in Solid Argon

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Matrix photoionization experiments have been performed for several p-dialkylbenzenes and alkylcycloheptatrienes. Broad absorptions at 23 500 and 34 700 cm<sup>-1</sup> following UV matrix two-photon ionization of p-xylene are assigned to the parent cation, in agreement with photodissociation spectra of gaseous cation. A broad absorption at 20240 cm<sup>-1</sup> following vacuum-UV matrix photoionization of 7-methylcycloheptatriene is assigned to the parent cation, in agreement with the difference between photoelectron bands. Mercury arc photolysis has been used to activate the extensive rearrangements of the p-xylene and 7-methylcycloheptatriene cations, which finally rearrange to a common conjugated triene cation identified as a substituted methylenecyclohexadiene cation.

## Introduction

Structural rearrangements of molecular cations have been of great interest to mass spectroscopists.<sup>1</sup> Because of the importance of these rearrangements, molecular cations produced by matrix photoionization methods have been irradiated in absorption bands to explore the rearrangement processes. Earlier studies have demonstrated the usefulness of the matrix isolation technique in following the isomerization of benzyl cation to tropylium cation<sup>2</sup> and the rearrangement of cycloheptatriene and toluene radical cations to methylenecyclohexadiene cation.<sup>3</sup> Both studies showed that one structural form of the cation could be photolytically converted to an isomeric form by irradiating in an absorption band of the initial isomer of the cation.

Rearrangements of cycloheptatriene and substituted cycloheptatrienes have been studied extensively.<sup>4-6</sup> Of particular interest here are the hydrogen rearrangements that occur readily when a 7-hydrogen is present and the formation of a substituted norcaradiene from the substituted cycloheptatriene precursor. These same rearrangements have been described for the gaseous toluene and cycloheptatriene cations.<sup>7</sup> The present matrix photoionization study deals with photoisomerizations of methyland ethylcycloheptatriene, xylene, and p-ethyltoluene cations. Because these ions are larger and structurally more complex than those studied earlier, the potential pathways for rearrangement are correspondingly increased. The extensive photolysis data collected here allow for the close monitoring of the isomerization process.

# **Experimental Section**

The cryogenic equipment, matrix argon resonance photoionization, and matrix two-photon ionization techniques have been described in earlier papers.<sup>8-10</sup> Xylene and p-ethyltoluene (Aldrich) samples were degassed by several freeze-thaw cycles and then the vapors were diluted with argon for the discharge experiments or the vapors

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were diluted with an argon-CCl<sub>4</sub> mixture for the twophoton ionization experiments. 7-Methylcycloheptatriene was prepared from the room-temperature reaction of 25 mmol of tropylium tetrafluoroborate and 38 mmol of methyllithium in 50 mL of anhydrous diethyl ether following the method of Conrow.<sup>11</sup> A mixture of methylcyclopheptatriene isomers was prepared by heating a portion of the 7-methylcycloheptatriene at 180 °C overnight. 7-Ethylcycloheptatriene was synthesized from tropylium tetrafluoroborate and ethylmagnesium bromide in anhydrous dimethyl sulfoxide. All of the substituted cycloheptatriene compounds were purified by distillation and their identifications were confirmed by NMR, the original synthesis produced >95% 7-methylcycloheptatriene (1), and the mixture contained predominantly



3-methylcycloheptatriene (4) with weak signals due to the 1- and 2-isomers (2 and 3), based on the NMR analysis of the x,7,7-trimethylcycloheptatriene isomers.<sup>6</sup>

For all experiments, diluted samples (Ar/reagent = 100-500/1 or Ar/CCl<sub>4</sub>/reagent = 100-500/5/1) were condensed at about 3 mmol/h total gas with about 1 mmol/h of argon flowing through a 3-mm orifice quartz tube onto a 20  $\pm$  2 K sapphire plate. In the argon resonance vacuum-UV photoionization experiments, the argon flowing through the quartz tube was excited by a microwave discharge. In the UV two-photon ionization experiments, matrix samples containing  $CCl_4$  as an electron trap were irradiated with the full output of a high-pressure mercury arc lamp for periods of up to 30 min. Spectra were recorded on a Cary 17 spectrophotometer, digitized on a Nicolet 1180 minicomputer, and replotted on a wavenumber scale. For simplicity, band positions and photolysis energies are given in the text as units of  $10^3$  cm<sup>-1</sup>, band positions in the table are given in wavenumber units rounded to the accuracy of the measurement.

# Results

Argon resonance vacuum-UV and mercury arc UV photolysis experiments performed with alkylcycloheptatriene and dialkylbenzene matrix samples with and

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<sup>(2)</sup> Andrews, L.; Keelan, B. W. J. Am. Chem. Soc. 1981, 103, 99.
(3) (a) Andrews, L.; Keelan, B. W. J. Am. Chem. Soc. 1980, 102, 5732.
(b) Kelsall, B. J.; Andrews, L. Ibid. 1983, 105, 1413. (b shows that the sharp 430-nm band in a is due to methylenecycloheptatriene cation and not toluene cation.)

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<sup>(5)</sup> Berson, J. A. Acc. Chem. Res. 1968, 1, 152 and references therein.
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<sup>(7)</sup> Baldwin, M. A.; McLafferty, F. W.; Jerina, D. M. J. Am. Chem.

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<sup>(11)</sup> Conrow, K. J. Am. Chem. Soc. 1961, 23, 110.



**Figure 1.** Absortion spectra for 7-methylcycloheptatriene subjected to vacuum-UV photoionization during condensation with excess argon: (a) spectra after sample preparation for 3 h, (b) after  $16-10 \ (\times 10^3 \ cm^{-1})$  photolysis for 80 min, (c) after 20–10 photolysis for 2.5 h, (d) after 21–10 photolysis for 4.5 h, (e) after 27–22 photolysis for 4 h, and (f) after 21–10 photolysis for 30 more min.

without chlorocarbon electron traps will be described.

Alkylcycloheptatriene Precursors. Three argon resonance vacuum-UV photoionization experiments with 7methylcycloheptatriene, 1a, yielded spectra with absorptions in both the visible and UV regions. These are illustrated in Figure 1 for an experiment where an extensive series of photolyses was performed. In the visible region of the spectrum trace a shows a prominent feature at 20.2 (×10<sup>3</sup> cm<sup>-1</sup>) (A = 0.06, full width at half maximum = fwhm = 400 cm<sup>-1</sup>) following matrix sample preparation. This band is accompanied by a slightly broader absorption at 21.3, a poorly resolved shoulder at 19.7, and a weak, sharp band at 22.7 (A = 0.005). A 60-min 13-10 photolysis had no effect on any of the absorptions. As is shown in trace b, 16-10 photolysis nearly destroyed the 20.2 band, revealed a new 20.1 peak, substantially increased the 19.7 absorption, and sharpened the 21.3 peak by destroying a broad absorption near 21.1. A 2.5-h photolysis with 20-10 radiation, shown in trace c, destroyed the 20.2 and 19.7 bands while leaving the 21.3 absorption. Prolonged irradiation with 21-10 light for 4.5 h reduced the 21.3 band by more than 80%, while it markedly increased the 22.7 band (A = 0.055, fwhm = 140 cm<sup>-1</sup>) and produced a new. sharp, weak band at 23.5, trace d. When the sample was illuminated with 27-22 radiation, the 22.7 and 23.5 bands were nearly destroyed while a very broad, weak band (A = 0.004) appeared in the spectrum between 19.6 and 20.8. trace e. A final photolysis with 21-10 radiation increased the 22.6 (A = 0.1) band slightly and destroyed the broad band, trace f. In the UV spectral region, a broad band at 31.5 (A = 0.06) was detected after sample preparation. None of the photolyses between 16 and 10 had any effect on the absorption, although the 20-10 photolysis produced an intense band at 31.2 (A = 0.25) and two weak bands near 31.8 (A = 0.04) and 32.7 (A = 0.03), trace c. Further 21-10 radiation increased all these absorptions by 40%. In contrast with the sharp 22.7 band, the UV absorptions were unchanged by 27-22 photolysis. The final 21-10 photolysis did not promote any additional growth in the UV bands. In another experiment where the matrix sample was irradiated with UV light after an extended 21-10 illumination, 34-10 radiation did not change the UV bands but 45–10 photolysis reduced the 31.2 absorption by 80% and increased the 32.7 band 3-fold, leaving the 31.8 band unchanged.

To complement the experiments with 1a, an argon resonance photoionization experiment was performed using a mixture of the four methylcycloheptatriene isomers containing primarily 4a. The general features of the spectra were the same as for the 1a precursor, and the photochemistry was identical. The major difference was that the experiment with a mixture of methylcycloheptatriene isomers gave a different relative yield of product absorptions in the 19-22 region as compared with the 7-methylcycloheptatriene experiment. The 21.3 band was sharper and more intense than in the previous experiments; its intensity was about equal to the 20.2 band. With a 15-min photolysis by 17-10 radiation, the 20.2 band was substantially reduced, revealing a 20.1 peak, and increasing the 19.7 band. Following irradiation with 19-10 light, the 20.2 band was completely destroyed, while the 19.7 band was reduced about 50% and the 21.3 absorption was decreased slightly. The 21.3 band was diminished by half with 15 min of 21-10 photolysis as the 22.7 band grew and the weak 23.5 band appeared. All of the absorptions in the visible region disappeared during a brief 34-10 photolysis. Except for a more scattering background, the UV absorptions following sample preparation and photolysis were essentially the same as those produced in the la experiment.

In addition to the methylcycloheptatriene isomers, 7ethylcycloheptatriene, **1b**, was examined. Three argon resonance photoionization experiments performed with this compound gave spectra which closely resembled those obtained with the methylcycloheptatrienes. Figure 2 illustrates selected spectra showing photoinduced changes. The visible region of the spectrum showed a broad absorption peaking at 20.1 with shoulders at 19.7 and 21.3 and a weak 22.6 band, trace a. As with the methylcycloheptatrienes, the intense 20.1 band was decreased by 17–10



**Figure 2.** Absorption spectra for 7-ethylcycloheptatriene following matrix photoionization during condensation at 20 K: (a) spectrum after sample preparation for 3 h, (b) after 17-10 photolysis for 15 min, (c) after 20-10 photolysis for 15 min, (d) after 21-10 photolysis for 10 h, (e) after 24-10 photolysis for 15 min, and (f) after 45-10 photolysis for 30 min.

photolysis as the 19.7 absorption grew; photolysis with 20-10 radiation then destroyed the 20.1 and 19.7 bands while increasing the 21.3 absorption 50% and the 22.6 band 500%, traces b and c. Trace d shows that prolonged irradiation with 21-10 light destroyed the broad absorptions, increased the sharp 22.6 (A = 0.08) band, and produced a sharp, weak band at 23.4 (A = 0.01). Trace e shows that photolysis with 34–10 radiation substantially reduced the two new, sharp bands and produced weak, new bands at 21.6 and 20.5. Final 45-10 photolysis reduced all of the absorptions detected in the visible region. Only a weak, broad absorption was seen in the UV region prior to photolysis; however, after 20-10 photolysis, a weak band was detected at 31.1. This band grew markedly (A = 0.22)with 21-10 irradiation as new bands appeared at 31.9 (A = 0.002) and 32.6 (A = 0.08). All three absorptions were unaffected by the 27-22 photolysis and only the 32.6 (A = 0.14) band grew with 34–10 photolysis. The final illumination with 45-10 radiation decreased the 31.1 (A = 0.05) band, left the 31.9 band unchanged, and increased the 32.6 (A = 0.2) band.

Dialkylbenzene Precursors. p-Xylene samples were



**Figure 3.** Absorption spectra for *p*-xylene samples subjected to vacuum-UV radiation during condensation with excess argon, Ar/p-xylene = 200/1, for 6 h: (a) *p*-xylene-*d*<sub>10</sub>, (b) *p*-xylene-*h*<sub>10</sub>, (c) spectrum from b after 24–10 photolysis for 30 min.

subjected to both argon resonance vacuum-UV photoionization and UV two-photon ionization techniques in 16 experiments. Figure 3 illustrates spectra for typical photoionization experiments where 12 mmol of Ar/p-xylene = 200/1 sample were codeposited with argon from the open discharge tube for 6 h. The product spectrum, trace b, reveals a weak, broad band with maxima near 21.1 and 21.3 and a sharp, strong, new band at 22.7 (A = 0.048) with sharp, weak satellites at 22.0, 23.0, and 23.5. Trace c shows that, except for the 22.0 band, these sharp bands were nearly destroyed by irradiation at 24-10, while the broad 21.1 absorption was reduced by 30%, and the broad 21.3 absorption was reduced only slightly. In the UV region, sharp, strong product bands were observed at 30.3 (A = (0.34), (A = 0.08), and (A = 0.16) and a broad band was observed at 32.7. The 24-10 irradiation had no effect on these absorptions, but 34–10 photolysis reduced the 30.3 and 31.1 bands by 30% and left the 31.8 band unchanged. A final photolysis with 45–10 radiation further reduced the bands sensitive to 34-10 radiation, markedly increased the 31.8 band (to A = 0.54), and produced new features at 32.3 and 33.1. In the visible region, the 22.0 band increased substantially and new bands appeared at 22.6 and 22.8. The absorptions which increased markedly on 45-10 photolysis were the only new bands in a *p*-xylene sample irradiated first at 45-10.

Similar experiments were performed with p-xylene- $d_{10}$ . The general features of the absorptions produced by the argon resonance radiation were the same as with the hydrogen compound; the only differences were a small blue shift of the band positions and a lower yield, as can be seen in Figure 3a. In the visible region, only a sharp 22.8 (A = 0.01) band was seen after a 6-h deposition. A 90-min 21-10 photolysis doubled the intensity of this band and produced a new band at 23.6 (A = 0.003), and a 30-min 27-22 photolysis reduced both by about 50%. These two bands correspond with the two most intense absorptions detected in this region with the hydrogen compound. In the UV region, intense bands were observed at 30.5 (A = 0.003) and a 30-fine the two most intense at 30.5 (A = 0.003).



**Figure 4.** Absorption spectra for 12 mmol of  $Ar/CH_2Cl_2/p$ -xylene = 700/2/1 sample: (a) spectrum after deposition for 3 h, (b) after 45–10 irradiation for 30 s, (c) after 45–10 irradiation for 30 min, (d) after 34–10 irradiation for 30 min. Inset scan shows expansion of 15 640-cm<sup>-1</sup> band.

0.17), 31.2 (A = 0.08), and 31.9 (A = 0.03), sharp, weak bands at 30.9 and 31.5, and a moderately intense, broad band at 32.8. A 30-min 34-10 photolysis reduced all of these absorptions by 70% except for the 31.9 band. An additional photolysis with 45-10 radiation completely destroyed all of the absorptions, which had been reduced with the earlier photolysis, and it made the 31.9 band grow along with two very weak, new bands at 32.4 and 33.3. Because the 31.9 band did not grow as intense as its hydrogen counterpart, it was impossible to identify any corresponding new bands in the visible region.

Two argon resonance photoionization experiments were done with p-xylene- $d_{10}$  samples doped with Cl<sub>2</sub> to serve as an electron trap. The sharp 22.8 (A = 0.03) product band was superimposed on a broad 23.4 (A = 0.03) absorption and the sharp 30.5 band was observed as without added electron traps. Again, 21–10 photolysis doubled the 22.8 band and left the 30.5 and 31.9 bands unchanged. A similar experiment with the hydrogen compound and  $CH_2Cl_2$ as the electron trap gave a 30% greater yield of the sharp 22.7 band than in the experiment in Figure 3b, and this sharp feature was superimposed on the broad 23.4 band (A = 0.03). The UV region was observed like that shown in Figure 3b. Photolysis between 21 and 10 increased the 22.7 band and 23.0 and 23.5 satellites by 50%; a following 24-10 irradiation reduced these bands 30%, and a final 45-10 photolysis doubled the sharp and broad visible product bands, destroyed the 30.3 and 31.1 bands, and increased the 31.8 band, as found in the matrix two-photon ionization experiments to be described next.

Matrix samples of p-xylene were subjected to intense mercury arc radiation with  $CH_2Cl_2$  added as an electron trap. Figure 4 shows the spectrum of 12 mmol of Ar/  $CH_2Cl_2/p$ -xylene = 700/2/1 sample deposited for 3 h; no absorption was observed up to the precursor beginning at 36.8. After 45-10 irradiation for 30 s, broad bands were observed at 23.5 (A = 0.05, fwhm = 2800) and 34.7 (A =0.12, fwhm = 1600) and weak, sharp bands appeared at 31.8 and 22.7, as illustrated in trace b; additional broad product absorptions were observed at 45.0 ± 0.5 and 9.1. The broad bands increased with longer 45-10 irradiation,

the former reaching absorbance values of 0.11 and 0.26, respectively, after 30 min, as shown in trace c. In addition, the sharp, strong band at 22.7 (A = 0.11) with vibronic structure at 23.0 and 23.5 increased 5-fold, the sharp band at 31.8 (A = 0.48) with associated vibronic structure increased 12-fold, and weak, sharp bands at 15.0 (A = 0.002)and 22.0 (A = 0.02) were evident. In contrast, 34-10 irradiation decreased the product bands by different amounts, as is shown in trace d. The four broad bands were reduced 10%, the sharp 22.7 band and vibronic components and the sharp, weak 15.0 band were reduced 70%, and the sharp, weak 22.0 band and strong 31.8 band with vibronic structure were unchanged. A similar experiment was done with p-xylene- $d_{10}$  under still more dilute conditions  $Ar/CCl_4/p$ -xylene = 3000/5/1. Broad bands appeared at 23.5 and 34.7 after 15 s of 45-10 irradiation (A = 0.03 and 0.07), and the bands increased 50% with 5-min irradiation. No absorption was observed in the 9.0 region.

Argon resonance photoionization experiments with pethyltoluene gave results similar to the p-xylene experiments. After a 5-h deposition, the visible spectral region exhibited sharp absorptions at 22.0 (A = 0.01), 22.6 (A =0.1), and 23.4 (A = 0.005) and a slightly broader band at 21.6 (A = 0.005) superimposed on a broad absorption peaking at about 22.0 (A = 0.025, fwhm = 2000 cm<sup>-1</sup>). Irradiation with 24–10 light reduced the 22.0 band by 70%. destroyed the other sharp bands, and left the broad band. The 22.0 and 21.6 bands returned to their original intensities after photolysis with 34–10 radiation and increased by 50% after 45–10 irradiation. In the same experiment, the UV region showed sharp bands at 30.4 (A = 0.13), 31.2(A = 0.07), 31.5 (A = 0.02), and 31.8 (A = 0.04). None of these bands were affected by the 24–10 photolysis, but the 30.4 and 31.2 bands were reduced by more than 80% with 34–10 radiation, and they were completely destroyed by 45-10 photolysis. The latter also increased the 31.5 and 31.8 absorptions 4-fold.

An  $Ar/CH_2Cl_2/p$ -ethyltoluene = 1200/3/1 sample subjected to 45-10 photolysis for 15 s yielded a broad 22.7 band with very weak, sharp 22.0 and 21.6 peaks superimposed. Continued 45-10 photolysis for 1 min doubled the broad band and increased the two sharp bands 4-fold. A 30-min 21-10 irradiation increased the sharp bands by 40% and produced a sharp, weak 22.6 band, without measurably changing the broad band. A subsequent 34-10 irradiation doubled the 22.0 and 21.6 bands, revealed a weaker 22.8 component, and destroyed the 22.6 band produced on visible photolysis. A final 45-10 irradiation doubled the broad band (to A = 0.08), increased the sharp bands 3-fold (22.0 to A = 0.17, 21.6 to A = 0.05), and produced new absorptions at 16.4 (A = 0.24), 16.9, 27.6 (A= 0.02), and 28.8 cm<sup>-1</sup>, which are due to p-methylstyrene cation in solid argon,<sup>12</sup> and sharp, new bands at 31.5 and 31.8 (A = 0.04).

The o-xylene and m-xylene isomers were the object of both matrix photoionization techniques. In argon resonance photoionization experiments using 200/1 samples, o-xylene gave a strong, sharp 31.7 band and a weaker 30.6 absorption; the latter was destroyed by 34-10 photolysis whereas the former was not affected; the former, however, increased with 45-10 photolysis; o-xylene also gave a weak band near 22.7 that was destroyed by 24-10 photolysis. In argon resonance photoionization experiments with mxylene, a strong, sharp 31.2 band and weaker 31.8 and 31.9 bands were observed; Pyrex-filtered photolysis destroyed

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TABLE 1: Origins of Vibronic Band Systems  $(cm^{-1})^{\mu}$  That Increase on Full Mercury Arc Photolysis in Substituted Benzenes Isolated in Solid Argon at 20 K

toluene <sup>b</sup>	<i>p</i> -xylene	$p$ -xylene- $d_{10}$	<i>p</i> -ethyl- toluene	<i>m</i> -xylene	o-xylene
32 210	31 7 6 0	31 880	31 470/ 31 780	31 7 50	31 660
22240	22000			$21\ 997$	
<sup>a</sup> Uncer	tainty, ±2	0 cm <sup>-1</sup> . <sup>b</sup>	Reference	e 13.	

the 31.2 and 31.9 bands and produced a strong, sharp 31.8 band and a weak, sharp 22.0 absorption.

Three two-photon ionization experiments were done with o-xylene using  $Ar/CH_2Cl_2/o$ -xylene ratios of 7000/ 12/1, 3600/9/1, and 400/2/1. Broad bands were observed at 23.4, 35.5, and 44.0 in all three experiments after short 45-10 photolysis. After 1-h photolysis, the 3600/9/1 experiment gave absorbances of 0.10 for each of the broad bands, and the first sharp o-xylene vibronic band at 37.3 was reduced from A = 0.28 to 0.19 An additional sharp doublet at 22.5 and 22.7 (A = 0.04) was superimposed on the broad visible band and a new, sharp band appeared at 31.7 (A = 0.12). A broad near-infrared band was observed at 9.8 in the more concentrated experiments. A similar pair of experiments was performed with *m*-xylene. In a more concentrated 200/1/1 experiment, a weak peak was observed at 22.1 (A = 0.15) and a broad band was found at 9.5 (A = 0.6) after 1 min of 45–10 irradiation; longer irradiation produced a strong, sharp 31.7 band and a weak, sharp 22.0 band. In a less concentrated 2000/10/1experiment, a sharp doublet at 22.5 and 22.7 (A = 0.008) was superimposed on a very broad band (A = 0.15) in this region after 5 min of 45–10 photolysis.

#### Discussion

Identification of Product Absorptions. The product absorptions observed in this study may be divided into five groups based upon the experiment required to produce them and their photochemical behavior.

The first class of products consists of sharp absorptions with a strong origin in the 31.5-31.8 region and a weak band near 22.0, which were produced by 45-10 photolysis in all of the alkylbenzene experiments. These bands, collected in Table I, are assigned to neutral substituted benzyl radicals since their yield is not affected by the presence of electron-trapping species and their absorption positions closely resemble benzyl radical absorptions produced by UV photolysis toluene.<sup>13</sup> The strong 31.8 band origin for p-methylbenzyl radical in solid argon is in agreement with the 31.0 origin for this radical in EPA glass<sup>14</sup> at 77 K when the different environments are considered; similar agreement is found for the o- and mmethylbenzyl radical absorptions in solid argon and EPA glass. The weak 22.0 band probably corresponds to the excitation of an electron in the  $a_2$  orbital to the partially occupied  $b_1$  nonbonding level of benzyl radical while the 31.8 band corresponds to the promotion of an electron in the second highest  $b_1$  level to the nonbonding level. A comparison of the position for the 32.0 band shows that heavier substituents systematically shift the origins to lower energy. For *p*-ethyltoluene two origins were observed, the stronger, high-frequency one corresponding to the loss of  $\alpha$ -hydrogen from the methyl substituent, and the weaker, low-frequency one corresponding to the loss of  $\alpha$ -hydrogen from the ethyl group. In this study and

TABLE II: Photosensitive UV Absorptions  $(cm^{-1})^a$ Produced by Vacuum-UV Photolysis of Dialkylbenzenesduring Condensation in Excess Argon at 20 K

<i>p</i> -xylene	$p$ -xylene- $d_{10}$	<i>p</i> -ethyltoluene	<i>m</i> -xylene
30 330	30 530	30 400	31 220
30 7 20 (320) <sup>b</sup>	30 900 (370)		
B1 060 (730)	31 221 (696)		
31 480 (1120)	31 530 (1000)		

<sup>a</sup> Uncertainty,  $\pm 20$  cm<sup>-1</sup>. <sup>b</sup> Vibrational intervals.

others involving benzyl radicals isolated in solid argon,<sup>13</sup> it appears as though hydrogen is dissociated preferentially from a methyl group even though the C-Me bond is substantially weaker than the C-H bond. Simple molecular orbital calculations predict other UV absorptions for benzyl radicals. In most of the experiments performed for this study, the UV region was obscured by intense parent absorptions; however, a new origin was observed at about 38.5 for *p*-methylbenzyl radical. This likely corresponds to the excitation of an electron in the filled  $a_2$  level to the vacant  $a_2$  level ( ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$  in benzene). The second group of absorptions, produced exclusively

by argon resonance vacuum-UV photolysis in the substituted-benzene experiments, consisted of a strong origin near 30.0 with a weaker 700-cm<sup>-1</sup> spaced vibronic counterpart as listed in Table II. In like behavior with the substituted benzyl radical absorptions, these bands were unaffected by electron traps or by photolysis that photoneutralized charged species, but, in contrast to substituted benzyl radical bands, these bands were destroyed by UV photolysis. The strong 31.2 product in m-xylene experiments is in very good agreement with the 30.7 origin assigned to the substituted cyclohexadienyl radical  $C_8H_{11}$ produced by radiolysis in methanol glass.<sup>15</sup> The observation of a single, sharp product band in the *m*-xylene and p-ethyltoluene experiments and INDO calculations of electron density in alkylbenzene anions<sup>15</sup> suggest that the unique hydrogen is attached to a ring carbon containing an alkyl group and that the alkyl group is not intimately involved with the free radical. The fact that alkyl substituted cyclohexadienyl radicals are more photosensitive than cyclohexadienyl radical itself<sup>16</sup> suggests that the former may eliminate a methyl radical upon dissociation.

The third class of absorptions consists of very broad bands produced by mercury arc photolysis of precursor molecules trapped with  $CH_2Cl_2$  or  $CCl_4$  in solid argon (Figure 4). Since these absorptions were enhanced by the presence of electron-trapping species, they are assigned to molecular cations. The broad near-IR bands are assigned to the intervalence transitions of the complex between a xylene cation and a neutral xylene molecule, i.e., the dimer cation. The present 9.5 band for (m-xylene<sub>2</sub><sup>+</sup> is in agreement with the 9.7 absorption assigned to the dimer cation in glassy matrices.<sup>17</sup> In benzene and toluene experiments, where the analogous absorptions were studied more extensively,<sup>3b,17</sup> the intensity was enhanced by concentration and diffusion conditions favoring dimer formation, which supports the dimer cation assignment.

The very broad absorptions measured at 23.5 and 34.8 for p-xylene and at 23.4 and 35.5 for o-xylene are assigned to the respective monomeric precursor cations. For p-xylene, the positions of both the visible and UV bands agree well with the maxima in the gas-phase photodisso-

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#### Photochemical Rearrangements of Xylene

ciation spectrum<sup>18</sup> at 23.8 and 36.0. Agreement for the visible bands is within experimental error, but the higher energy band is red shifted owing to greater interaction with the matrix as the electron affinity of the excited state approaches the ionization energy of argon; a similar effect has been reported for the higher excited states of naphthalene cation in solid argon.<sup>19</sup> The matrix bandwidths. 2800 and 1600 cm<sup>-1</sup>, respectively, are substantially less than the 4200- and 2600-cm<sup>-1</sup> photodissociation bandwidths. The observation of reduced bandwidths in solid argon as compared to electron-impact-produced ions in the gas phase has been ascribed to excess internal energy for the gaseous ions in similar studies of substituted stryene and naphthalene cations.<sup>12,19</sup> The ground-state benzene cation is formed by the removal of an electron from the degenerate  $e_{1g}$  level. Photoelectron spectra show that degeneracy of the  $e_{1g}$  level is broken by 4000 cm<sup>-1</sup> when the symmetry is reduced to  $D_{2h}$  in p-xylene.<sup>20</sup> From theoretical considerations the b<sub>2g</sub> level is expected to be more stable than the  $b_{3g}$  level (wave function node at methyl-substitution points). Consequently the  ${}^{2}B_{2g}$  ground state is deduced for the *p*-xylene and *p*-diethylbenzene cations. The visible band is assigned to  ${}^{2}B_{2g} \rightarrow {}^{2}B_{1u}$  transition ( ${}^{2}E_{1g} \rightarrow {}^{2}A_{2u}$  for  $C_{6}H_{6}$ ). The very broad photosensitive absorption near 22.7 in the *p*-ethyltoluene photoionization experiments probably corresponds to this transition for this parent cation. The UV transition corresponds to excitation to the lowest  ${}^{2}E_{2}$  state of  $C_{6}H_{6}^{+}$ . Like the degenerate ground state, the  $^2\mathrm{E}_{2u}$  excited state will be split slightly into two states of different energy, a  ${}^{2}B_{1u}$  state of lower energy and a  ${}^{2}A_{u}$  state of higher energy. Transitions from the ground state to both of these states are allowed. Because the *p*-xylene UV absorption shows an unresolved shoulder at about 1000 cm<sup>-1</sup> lower than the maximum, the dominant absorption will be tentatively assigned to the  ${}^2B_{2g} \rightarrow {}^2A_u$  transition and the shoulder will be tentatively assigned to the  ${}^{2}B_{2g}$  $\rightarrow$  <sup>2</sup>B<sub>1u</sub> transition. In the *p*-xylene experiment, another broad UV absorption was detected on the low-energy side of the  ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$  *p*-xylene neutral absorption. Theoretical calculations on  $C_6H_6^+$  predict a weak transition to a second  $E_{2u}$  state 42 000 cm<sup>-1</sup> above the ion ground state.<sup>18</sup> Although the photodissociation study on p-xylene cation did not reveal this state because of spectral limitations, it seems likely that the 45.0 absorption belongs to a second set of  ${}^{2}B_{2g} \rightarrow {}^{2}A_{u}$  and  ${}^{2}B_{2g} \rightarrow {}^{2}B_{1u}$  transitions derived from the second  $E_{2u}$  benzene cation state. These parent cation absorptions are collected in Table III.

The broad 21.0 absorption in argon resonance photoionization experiments with p-xylene, which showed a 30% decrease on 30 min of 24–10 photolysis, is in agreement with the minor 21.0 absorption in methylcyclopheptatriene experiments, which was destroyed by prolonged irradiation at 21–10. Absorption at 21.3 was more resistant to photolysis with both precursors. The 21.1 and 21.3 absorptions will be assigned to the methylcycloheptatriene cations in the following paragraph.

The fourth group of absorptions contained broad bands produced from alkylcyclopehtatriene precursors in argon resonance photoionization experiments (Figures 1 and 2). These absorptions are assigned to substituted cycloheptatriene cations based upon their positions with respect to cycloheptatriene cation<sup>3</sup> and their similar decrease on photolysis. In contrast to the single major absorption produced in the cycloheptatriene experiments, two major

TABLE III: Broad Absorptions (cm<sup>-1</sup>) inAlkylcycloheptatriene and Dialkylbenzene MatrixPhotoionization Experiments Assigned to Radical Cationswith the Parent Formula

<i>p</i> -xylene <sup><i>a</i>, <i>b</i></sup>	<i>p</i> -ethyl- toluene <sup>b</sup>	methylcyclo- heptatriene <sup>c</sup>	ethylcyclo- heptatriene <sup>c</sup>
$\begin{array}{r} 23\ 500\\ 34\ 700\\ 45\ 000\\ 21\ 100 \end{array}$	22700	$\begin{array}{c} 20\ 240\\ 20\ 080\end{array}$	20 110
21 300		${ 21 \ 320 \atop 19 \ 700^d }$	21 300 19 650 <sup>d</sup>

<sup>a</sup> Broad band observed at 9050 cm<sup>-1</sup> is due to parent dimer cation. <sup>b</sup> Uncertainty,  $\pm 200$  cm<sup>-1</sup>. <sup>c</sup> Uncertainty,  $\pm 20$  cm<sup>-1</sup>. <sup>d</sup> These bands are tentatively assigned to 7-alkylnorcaradiene cations.

and two minor absorptions were produced in methylcycloheptatriene experiments. The four absorptions may be attributed to the four isomeric 1a, 2a, 3a, and 4a cations. Specific identification of the isomers cannot be made with certainty; however, the strongest band produced with the 1a precursor, 20.2, probably corresponds to the 1a parent cation. Support for this indentification may be taken from the photoelectron spectrum of 7-methylcycloheptatriene;<sup>21</sup> the difference between the onset of ionization (8.25 eV) and the peak of the third photoelectron band (10.80 eV) predicts a  $\pi_3 \rightarrow \pi_1$  transition at 20.6, in excellent agreement with the photoelectron spectrum.

Red visible photolysis studies showed that, as the parent absorptions were destroyed, the first new absorption appeared at 19.7 in methylcycloheptatriene experiments. Further photolysis decreased the latter new absorption and the major product band, revealing a minor product absorption at 20.1. Continued photolysis decreased the above absorptions and minor absorption at 21.1 and sharpened the major peak at 21.3 (Figure 1). The latter major absorption is probably due to the 4a cation, based upon the greater stability for the alkyl substituent located in the center of the conjugated triene and the greater yield of the 21.3 band when an isomeric mixture heavily enriched in 4a was used as a precursor. If the minor absorptions are due to the 2a and 3a cations, this leaves the first new rearrangement product band at 19.7 to be assigned to a different structure. In a description of concerted rearrangement pathways for cycloheptatriene molecules, Berson and Willcott have proposed that electrocyclic ring closure to norcaradiene requires a lower activation energy  $(\sim 11 \text{ kcal/mol})$  than successive 1.5-hydride shifts ( $\sim 31$ kcal/mol,<sup>6</sup> which results in a rearrangement among the 1a, 2a, 3a, and 4a isomers. This suggests that the first new rearrangement product absorption, 19.7, could be due to the 7-methylnorcaradiene cation, 5a, and that subsequent photochemical rearrangements give the methylcycloheptatriene cation isomers. The 19.7 absorption is, on this mechanistic evidence, tentatively assigned to the 7methylnorcaradiene cation, 5a.



The 7-ethylcycloheptatriene, **1b**, experiments gave similar but less extensive results. The initial broad 20.1 ab-

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 1982, 86, 2916.

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<sup>(21)</sup> The photoelectron spectrum of 7-methylcycloheptatriene provided by J. P. Maier revealed a sharp onset of ionization at 8.12 eV with structureless peaks centered at 8.55, 9.42, and 10.80 eV before the onset of strong, broad, presumably  $\sigma$ -orbital ionization at 11 eV.

sorption is probably due to the 1b cation. Following the above argument, the 19.7 band produced on red visible photolysis is tentatively assigned to the 7-ethylnorcaradiene cation, 5b, and the broad 21.3 band, which increased on 20-10 photolysis, is probably due to the 4b cation.

An intense 31.3 band and a weak 32.7 band were produced on prolonged 20-10 irradiation on methylcycloheptatriene cation (Figure 1c); the 31.2 band was substantially reduced by 45-10 photolysis for 15 min that markedly increased the 32.7 band. These product absorptions are in the region for daughter cations between benzyl cation at 28.3 and tropylium cation at 38.0 in solid argon.<sup>2</sup> Similar absorptions have been observed for diene derivatives of norbornane.<sup>22</sup> Although definite identification of the new UV bands cannot be made form the present data, the first product of parent cation photolysis at 31.2 could be due to a methyl-substituted norcaradienyl cation. The 31.1 counterpart in the 7-ethylcycloheptatriene experiments shows a small shift with the heavier alkyl substituent. The second product at 32.7 formed rapidly from the 31.1 absorbing cation upon 45-10 irradiation is suggested to be due to a second daughter cation formed by  $C_2H_2$  elimination, based on the observation of  $C_2H_2$ elimination from gaseous  $C_7H_7^+$  cations with irradiation in this energy range.<sup>23</sup>

The fifth group consists of sharp absorptions produced by mercury arc photolysis of group three and four parent cations. Figures 1 and 2 show that prolonged 21-10 photolysis destroys the broad alkylcycloheptatriene cation absorptions and produces sharp 22.7 and 22.6 absorptions; matrix two-photon ionization experiments with p-xylene (Figure 4) and similar experiments with *p*-ethyltoluene first produce the broad p-dialkylbenzene cation band and subsequent photolysis gives the sharp 22.7 and 22.6 absorptions. In all of the matrix experiments, photolysis limited to the region of the sharp 22.7 and 22.6 bands destroys these bands; hence, the absorbing species is photosensitive, which is characteristic of many isolated cations.<sup>2,3,12</sup>

The sharp 22.7 band in p-xylene, experiments (Figure 4) was accompanied by a sharp, weak 15.0 band; these two absorptions in the red and blue regions comprise an important diagnostic for conjugated triene cations as opposed to conjugated diene or aromatic cations.<sup>24-26</sup> The analogous sharp toluene cation photoproduct at 23.2 was accompanied by a sharp, weak 15.6 band.<sup>3b</sup> The model cis,trans,cis-hexatriene cation<sup>26</sup> exhibits a strong, sharp absorption at 23.2 and a weak, sharp absorption at 14.8. Hence, the spectroscopic evidence favors a conjugated triene cation identification for the fifth group of absorptions, which were formed by rearrangement of p-dialkylbenzene cations and alkylcycloheptatriene cations.

McLafferty, et al. have outlined the rearrangement pathways for gaseous toluene and cycloheptatriene cations; the only conjugated triene cation that appears in this scheme is the methylenecyclohexadiene cation.<sup>7</sup> The sharp 22.7 absorption is, therefore, assigned to methyl-substituted methylenecyclohexadiene cation produced by rearrangement from p-xylene cation and methylcycloheptatriene cation upon photoexcitation of the parent cations. The position of the substituent cannot be determined with certainty, although the ready formation of the 22.7 band from p-xylene cation suggests the 2-

TABLE IV: Photosensitive Absorptions (cm<sup>-1</sup>)<sup>a</sup> Assigned to Substituted Methylenecyclohexadiene Cations Produced from Alkylbenzene Cations in Solid Argon at 20 K

toluene <sup>b</sup>	<i>p</i> -xylene	$p$ -xylene- $d_{10}$	<i>p</i> -ethyl- toluene	ethylbenzene <sup>c</sup>
$23223^d$	$22696^d$	$22826^{d}$	22 620	
23 990 24 1 20	23500 23500	$23\ 600$	23 4 3 0	
15 640	14950			
			$22\ 050\ 21\ 600$	$22\ 660\ 22\ 260$

<sup>a</sup> Uncertainty,  $\pm 10$  cm<sup>-1</sup>. <sup>b</sup> Reference 3b. <sup>c</sup> Unpublished results from this laboratory. d Uncertainty,  $\pm 5$  $cm^{-1}$ 

methyl-5-methylene-1,3-cyclohexadiene cation structure, 6.



The two-photon ionization experiments with o-xylene and m-xylene produced sharp 22.7 and 22.5 bands with 40% and 10% of the intensity of the sharp 22.7 band in the analogous *p*-xylene two-photon ionization experiments. The sharp 22.7 band appears to be due to the most stable methyl-substituted methylenecyclohexadiene structure, suggested above to be 6, which is probably formed from the o- and m-xylene isomers by rearrangement through a norcaradiene cation species discussed in the next section. The sharp 22.5 band is likely due to a different methyl isomer produced in largest yield from o-xylene cation; this suggests the 4-methyl-5-methylene-1,3-cyclohexadiene cation structure for the 22.5 band.

Finally, the *p*-ethyltoluene experiments produced two sets of photosensitive bands, one at 22.6 with a vibronic component at 23.4, which was also formed in 1b studies, and the other at 22.0 with a weaker counterpart at 21.6. The first, more photosensitive set, which shows a 0.6 red shift from the set assigned to 6 cation, is assigned to the analogous ethyl-substituted methylenecyclohexadiene cation, 7. The second set is similar to 22.7 and 22.3 ab-



sorptions observed in identical experiments with ethylbenzene, which suggests that the two bands in the second set are due to E and Z isomers of the substituted methylenecyclohexadiene cations 8. The assignments to substituted methylenecyclohexadiene cations are collected in Table IV.

Photochemistry. The ultraviolet region of the spectrum for substituted benzenes contains a number of absorptions corresponding to different excited electronic states. When these states are excited in mercury arc photolysis experiments, a number of competing photophysical processes occur. The processes include photodissociation and relaxation to lower energy states. The photodissociation mechanism can lead directly to benzyl radical, a process requiring about 30.0. Although benzyl radical formation by loss of an available alkyl group from an  $\alpha$ -carbon is thermodynamically favored over hydrogen loss, the matrix data indicate that the great mobility of small hydrogen

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Scheme I



atoms in small argon leads exclusively to hydrogen-loss radicals when either a hydrogen or an alkyl can be lost. The substituted cyclohexadienyl type radicals are formed by H addition to the alkyl benzene precursors although the mechanism for this process in the present experiments is not clearly understood. Whether a parent anion abstracts a proton from a parent cation, similar to the radiolysis mechanism,<sup>15</sup> or a H atom is added directly to an excited precursor molecule cannot be determined from the present data.

A process competing with photodissociation is excitedstate relaxation. In accordance with Kasha's rule, the higher excited states relax rapidly to the relatively longlived lowest excited singlet and lowest triplet states. If the lifetimes of these excited states are sufficiently long enough to allow for absorption of a second photon, new excited states are reached, which can lead to new dissociation products or two-photon ionization. This two-photon mechanism is responsible for the production of parent ions in p-xylene and p-ethyltoluene experiments with added halocarbon electron traps. Although parent cations can be produced in all experiments involving the 45-10 irradiation of matrix samples containing the substituted benzene precursor molecules, the ions were observed only in experiments where stable anions could be formed to prevent neutralization of the newly formed cations. In argon resonance photoionization experiments, the 11.6-eV radiation<sup>9</sup> is capable of direct photoionization of the precursor molecules, which explains the formation of parent cations in these experiments.

Photodissociation studies have shown that decomposition of alkylbenzene cations occurs with both visible and UV photolysis<sup>18</sup> and dissociation of cycloheptatriene proceeds with visible radiation; 27 however, the argon matrix quenches internal energy and favors rearrangement photoprocesses. Since the two-photon ionization experiments used broad-band UV and visible light, some photoinduced rearrangement products of the parent ion are expected. Based on the rearrangements described by Berson and Willcott<sup>6</sup> for cycloheptatriene, the following rearrangement, Scheme I, is proposed for methylcycloheptatriene cations in the matrix photolysis experiments. Rearrangement i, the least endothermic process,<sup>6</sup> occurs first on red visible photolysis, followed by rearrangement ii with green irradiation, and presumably rearrangement iii also occur simultaneously. The subsequent blue photolysis effects rearrangement iv. The observation of only the 22.6 band and its 23.4 vibronic component due to the similar 7 cation in the 7-ethylcycloheptatriene cation photolysis studies, without the lower energy set of bands for the 8 cations, also observed with *p*-ethyltoluene, confirms the rearrangement mechanism involving a norcaradiene cation intermediate

Scheme II



9 for the formation of methylenecyclohexadiene cation species like 6 and 7. Finally, UV photolysis effects parent cation dissociation and the product is most likely a substituted norcaradienyl cation.

The rearrangement schemes proposed by McLaferty et al. for gaseous toluene and cycloheptatriene cations<sup>7</sup> provide a guide for the rearrangements observed in the pdialkylbenzene cation matrix photolysis experiments, Scheme II. Although no spectroscopic evidence was found for the o-methylnorcaradiene cation 9, its participation in Scheme II as an intermediate for the rearrangement to 6 is likely.

Finally, rearrangement of cations in these experiments proceeds after photoionization during the condensation process, Scheme II, with activation provided by the extra energy in the incident argon resonance photons (11.6 eV) in the ionization energy of the precursor (8.7 eV).<sup>20</sup> Rearrangements are also activated for ions trapped in the matrix by irradiation within an absorption band for the cation, Scheme I. Here the matrix quenches internal energy and allows structural rearrangements to be competitive with dissociation processes.

## Conclusions

Matrix photoionization studies have been done for several *p*-dialkylbenzenes and alkylcycloheptatrienes. Absorption spectra for the *p*-dialkylbenzene cations exhibit broad absorptions near 23.0 and 35.0 in very good agreement with photodissociation spectra and theoretical predictions, while spectra recorded for the alkylcycloheptatriene cations exhibit moderately broad absorptions near 20.0 in agreement with photoelectron data. Filtered mercury arc photolysis studies have been used to explore the extensive rearrangements of the alkylcycloheptatriene cations and alkylbenzene cations, which ultimately rearrange to a common conjugated triene cation. This triene cation is identified as a methyl-substituted methylenecyclohexadiene cation, like that proposed as an intermediate in gas-phase rearrangements of similar cations.<sup>7</sup>

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**Registry No.** p-Xylene, 106-42-3; p-xylene- $d_{10}$ , 41051-88-1; p-ethyltoluene, 622-96-8; m-xylene, 108-38-3; o-xylene, 95-47-6; 7-ethylcycloheptatriene, 17634-51-4; 7-methylcycloheptatriene, 4281-04-3; p-xylene cation radical, 34510-22-0; 7-methylcycloheptatriene cation radical, 34504-46-6; 7-ethylcycloheptatriene cation radical, 85251-39-4; 2-methyl-5-methylene-1,3-cyclohexadiene cation radical, 85251-40-7; 2-ethyl-5-methylene-1,3cyclohexadiene cation radical, 85251-41-8.