$$Q = \lim_{\gamma\to 0^+} \frac{1}{2\pi}\int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx\, \frac{e^{iy(1-x)-\gamma|y|}}{(m-x)x(m-2)!} \times \sum_{r=0}^{m-2} \binom{m-2}{r}(m-x)^{m-2-r}(xe^{iy})^r$$

$$= \lim_{\gamma\to 0^+} \frac{1}{2\pi}\int_{-\infty}^{\infty} dy\, e^{-\gamma|y|} \int_{-\infty}^{\infty} dx \left[\frac{e^{iy(1-x)}}{(m-x)x(m-2)!}(m + x(e^{iy}-1))^{m-2}\right] \quad \text{(AIII-6)}$$

where we have summed the binominal series. The bracketed expression in eq AIII-6 has poles at $x = 0$ and $x = m$ on the real axis. We are integrating x on a line just below the real axis. When $y > 0$ we must close the contour in the lower half-plane so that the expression $e^{iy(1-x)}$ tends to zero as $|x| \to \infty$. In this case the poles are excluded from within the contour of integration. When $y < 0$ we must close the contour in the upper half-plane including the two poles within the contour. Thus the y integration can be limited to the range $(-\infty,0)$

$$Q = \lim_{\gamma\to 0^+} \frac{1}{2\pi}\int_{-\infty}^{0} dy\, e^{-\gamma|y|}(2\pi i(\text{Res }(x = 0) + \text{Res }(x = m)))$$

$$= \lim_{\gamma\to 0^+} i\int_{-\infty}^{0} e^{-\gamma|y|}\left[\frac{e^{iy}m^{m-3}}{(m-2)!} - \frac{e^{-iy}m^{m-3}}{(m-2)!}\right]$$

$$= -\frac{2m^{m-3}}{(m-2)!}\lim_{\gamma\to 0^+}\int_{-\infty}^{0} e^{-\gamma|y|}\sin y\, dy$$

$$= \frac{2m^{m-3}}{(m-2)!} \quad \text{(AIII-7)}$$

Q.E.D.

ARTICLES

Absorption Spectra and Photochemical Rearrangements of 1-, 2-, and 3-Chlorocycloheptatriene, 7-Chloronorbornadiene, and Benzyl Chloride Cations in Solid Argon

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Matrix photoionization of chlorocycloheptatriene (CCHT) during condensation with excess argon at 20 K produced new broad 484-, 517-, and 544-nm bands, a sharp 469.3-nm absorption, and weak 453- and 468-nm bands. The broad bands are assigned to the 1-, 2-, and 3-chlorocycloheptatriene cations. Photolysis with 500–1000-nm radiation decreased the broad bands and increased the sharp 469.3-nm absorption. The 469.3-nm band and a sharp 707.8-nm counterpart in benzyl chloride experiments suggest a conjugated triene cation identification with 6-chloro-5-methylene-1,3-cyclohexadiene cation (**3**) as the most reasonable possibility. The 453- and 468-nm bands, which markedly increased on near-UV photolysis in benzyl chloride experiments, were strong products in similar studies with 7-chloronorbornadiene. Photolysis with 470–1000-nm radiation decreased the 468-nm band and increased the 453-nm absorption; this interconversion was reversed with 370–460-nm radiation. The latter bands are probably due to *E* and *Z* isomers of 5-(chloromethylene)-1,3-cyclohexadiene cation (**6**), which isomerize upon photoexcitation.

Introduction

The ring-expanded chlorocycloheptatriene cation has been postulated as an intermediate in gas-phase rearrangment processes involving chlorotoluene cations.[1-3] This ring-expansion process is thought to be the rate-determining step for chlorine atom loss from chlorotoluene cations.[3]

Very recent matrix photoionization experiments have produced cycloheptatriene cation; photolysis into the cy-

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cloheptatriene cation absorption produced a sharp band first thought to be the toluene cation, but a more complete spectrum suggested the conjugated triene methylene cyclohexadiene cation.[4] Similar studies with methylcycloheptatriene (MCHT) gave broad absorptions for the four methylcycloheptatriene cation isomers; selective photolysis into the methylcycloheptatriene cation absorptions caused rearrangements among the different isomers and pronounced growth of a sharp new absorption.[5] A recent matrix isolation study of halotoluene cations provided evidence for rearrangements presumably involving a ring-expanded intermediate, although this intermediate was not detected in the matrix absorption spectrum.[6] The present series of experiments was performed on chlorocycloheptatriene to observe the intermediate ring-expanded cation absorption spectrum and to examine photochemical rearrangement processes in isomeric $C_7H_7Cl^+$ cations.

Experimental Section

The cryogenic apparatus for absorption spectroscopy and the windowless argon resonance lamp have been described previously.[7,8] Chlorocycloheptatriene was synthesized by the copper bromide catalyzed insertion of a methylene unit into chlorobenzene using diazomethane. Diazomethane was generated in situ by the addition of 28 g *N*-nitrosomethylurea, synthesized by standard methods,[9] to a mixture of 40% aqueous KOH and chlorobenzene at 0 °C.[10] The diazomethane solution was then dried over solid KOH and added to 50 mL of chlorobenzene and 3 g of CuBr at reflux with vigorous stirring over a period of 2.5 h.[11] After addition of $^1/_3$ of the diazomethane solution, an additional 3 g of CuBr was added. Approximately 1 mL of chlorocycloheptatriene remained as a pale, yellow residue after removal of the excess chlorobenzene by vacuum distillation. An NMR spectrum of the residue revealed signals appropriate for the 1-, 2-, and 3-chlorocycloheptatriene isomers due to the aliphatic CH_2 group at 1.6, 2.3, and 2.9 ppm and olefinic hydrogens in the 5.4–6.8 ppm range. In addition the NMR spectrum exhibited a signal due to residual chlorobenzene at 7.3 ppm (about 30% of the residue) and placed an upper limit of a few percent on benzyl chloride and chlorotoluenes in the sample. This synthesis has been reported to yield about 15% of the 1-chlorocycloheptatriene isomer, 43% of the 2-chloroisomer, and 42% of the 3-chloroisomer;[11] the same synthesis was used to prepare the 1-, 2-, and 3-chlorocycloheptatriene isomers for a mass-spectroscopic study.[12] The 7-chlorocycloheptatriene isomer is believed to be unstable, giving the tropylium chloride salt.[13]

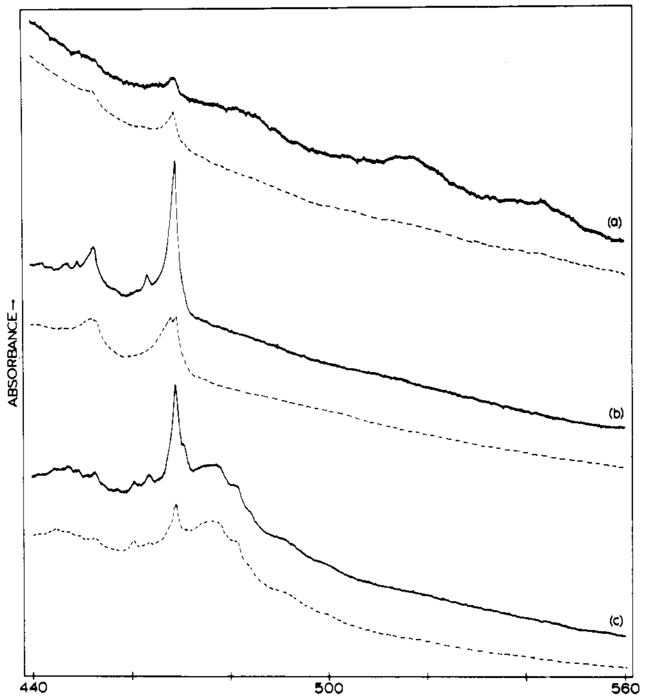

Figure 1. Absorption spectra of C_7H_7Cl samples subjected to matrix photoionization during condensation with excess argon at 20 K: (a) chlorocycloheptatriene (CCHT), dashed trace recorded after 470–1000-nm photolysis for 45 min; (b) benzyl chloride (ACT), dashed trace recorded after 420–1000-nm photolysis for 30 min; (c) *p*-chlorotoluene (PCT), dashed trace recorded after 470–1000-nm photolysis for 30 min.

The liquid product was evacuated for 2–3 min at room temperature in the apparatus to further reduce the more volatile chlorobenzene fraction before matrix deposition in each experiment. Chlorocycloheptatriene vapor, taken from the liquid at 0 °C, was introduced into the apparatus through a needle valve (set at one turn), mixed with argon emerging from a 3-mm orifice discharge tube, and condensed on a sapphire substrate at 20 K. A broad absorption from 300 to 230 nm with a 260-nm maximum is attributed to chlorocycloheptatriene. The growth rate of the 260-nm CCHT absorption in these experiments was similar to the 253-nm cycloheptatriene (CHT) absorption in earlier experiments using 1% CHT mixtures in argon;[4] accordingly the concentration of CCHT in the argon matrices used here was approximately 1%. The absorption minimum at 230 nm in the sample spectrum further indicates that chlorobenzene makes a minor contribution to the ultraviolet spectrum; similar matrix photoionization experiments with chlorobenzene in this laboratory show that much more chlorobenzene is needed to contribute to the product spectrum.[14] Codeposition of CCHT with argon was continued for 7 h with the argon excited by a microwave discharge operating at 75% power. Absorption spectra were monitored on a Cary 17 from 800 to 200 nm. After sample preparation, expanded scale spectra were recorded and the sample was subjected to photolysis with a high-pressure mercury arc[4] using glass short-wavelength cutoff filters (500 nm, 0.2% transmitting; 470 nm, 0.1% transmitting; 420 nm, 0.2% transmitting), followed by recording more spectra. Photon flux from the mercury arc, measured on a thermopile laser power meter arranged to match the experimental geometry, was 5 × 10^{16} photons/(cm^2 s) in the 420–750-nm range, 8 × 10^{16} photons/(cm^2 s) at 290–420 nm, and 10 × 10^{16} photons/(cm^2 s) at 220–290 nm.

Additional experiments were performed with the C_7H_7Cl isomers benzyl chloride (α-chlorotoluene, ACT), *p*-chlorotoluene (PCT), and 7-chloronorbornadiene (CNB) by using 1% samples in argon as described previously.[6]

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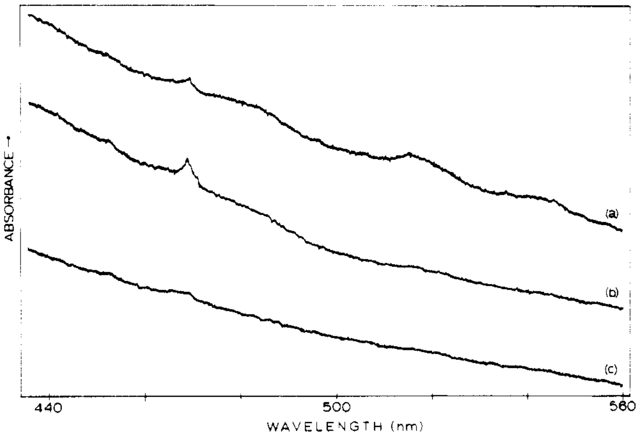

Figure 2. Absorption spectra of chlorocycloheptatriene subjected to argon resonance photoionization during condensation at 20 K: (a) spectrum after concurrent photoionization and condensation for 7 h; (b) spectrum after 500–1000-nm photolysis for 30 min; (c) spectrum after 420–1000-nm photolysis for 30 min.

The CNB sample was synthesized from 7-*tert*-butoxynorbornadiene[15] dissolved in ether with dry HCl bubbled through the solution at room temperature.[16] The sample, purified by preparative GC, was shown by NMR to be free of impurities.

Results

The first experiment codeposited argon at 175 mtorr (about 1 mM/h) with CCHT vapor (about 0.01 mM/h) for 7 h. New product absorptions observed at 544 nm (A = 0.010), 517 nm (A = 0.014), 484 nm (A = 0.006), 469.3 nm (A = 0.010), and 453 nm (A = 0.003) are shown in Figure 1 a. Photolysis with 470–1000-nm radiation for 45 min destroyed the three broad bands and *increased* the sharper 469.3-nm absorption (to A = 0.020) with a shoulder at 468 nm and the 453-nm band (to A = 0.006) as shown in the dashed trace in Figure 1a. The second experiment employed slightly higher flow rates (needle valve at 1.25 turns, argon at 200 mtorr) and the absorption spectrum is shown in Figure 2a. New broad bands were observed at 544, 517, and 484 nm, and a sharp new band appeared at 469.3 nm; absorbances are given in Table I. Photolysis with 500–1000-nm radiation for 30 m reduced the former three broad bands with unequal rates, doubled the sharp 469.3-nm band, and increased the 453-nm absorption, as shown in Figure 2b; in addition, a broad, weak band appeared at 708 nm. Continued photolysis with 420–1000-nm radiation destroyed the broad bands and reduced the sharp 707.8-, 469.3-, and 453-nm bands (Figure 2c). Exposure to 290–1000-nm radiation from the mercury arc completed destruction of the 469.3-nm band. A third CCHT experiment with a brighter discharge lamp (argon at 225 mtorr) gave an increased yield of the same absorptions, particularly the 453-nm band and the 468-nm shoulder, as listed in Table I; in addition a weaker 708-nm band was observed without absorption at 665 nm. Exposure of this sample to filtered photolysis caused the same general changes in band absorbances described above, which are given in Table I.

Another experiment was performed with benzyl chloride codepositing a 1% ACT sample in argon with argon discharge radiation for 5 h. The spectrum, contrasted in Figure 1b, contains sharp new bands at 469.3 nm (A = 0.10) and 452.7 nm (A = 0.02), and additional bands were observed at 665 nm (A = 0.007) and 708 nm (A = 0.012).

TABLE I: Absorption Bands Produced by Matrix Photoionization of 1-, 2-, and 3-Chlorocycloheptatrienes[a]

λ,[b] nm	A_i	A_{500}	A_{420}
708	0.00	0.002	0.00
544	0.006	0.000	0.000
517	0.010	0.002	0.000
484	0.008	0.004	0.000
469.3	0.008	0.016	0.004
453	0.001	0.004	0.002

λ,[c] nm	A_i	A_{500}	A_{470}
708	0.002	0.003	0.002
544	0.012	0.000	0.000
517	0.014	0.002	0.000
484	0.008	0.004	0.000
469.3	0.022	0.026	0.020
468	0.010	0.010	0.008
453	0.008	0.008	0.010

[a] Absorbances given before and after filtered mercury arc photolysis. A_i denotes initial absorbances produced by matrix photoionization; A_{500} denotes absorbances after 500-nm short wavelength cutoff photolysis; A_{470} and A_{420} denote absorbances after subscripted short wavelength cutoff photolysis; absorbance measurements are accurate to ±0.001 absorbance unit using 0.1 absorbance range of Cary 17. [b] Experiment used 200-μm argon; Spectra in Figure 2. [c] Experiment used 225-μm argon.

Photolysis with 590–1000-nm radiation had no affect on the spectrum, and 420–1000-nm light virtually destroyed the above absorptions and increased absorption at 467.7 nm (to A = 0.024) and 452.5 nm (to A = 0.033) as shown in the dashed spectrum. A subsequent 290–1000-nm photolysis further increased the 467.7-nm (to A = 0.032) and 452.5-nm bands (to A = 0.042), which are compared at the bottom of Figure 3 with the same bands produced from the CNB precursor. A final photolysis with the full arc, 220–1000 nm, decreased the 452.5-nm band by one-third (to A = 0.028) and the 467.7-nm band by one-tenth (to A = 0.029). A similar study with 1% PCT in argon subjected to argon discharge photoionization for 5 h revealed the spectrum in Figure 1c with sharp bands at 469.3 nm (A = 0.15) and 463.7 and 452.7 nm (A = 0.02) superposed on broad absorptions at 448 and 478 nm; additional bands were observed at 708 nm (A = 0.009) and 665 nm (A = 0.006). Photolysis with 470–1000-nm radiation reduced the 708-, 469-, 464-, and 453-nm absorptions by 66% and the 665-nm band by 85%.

Four additional photoionization experiments were done with ACT by adding CH_2Cl_2 to serve as an electron trap and using $Ar/CH_2Cl_2/ACT \approx 1000/3/1$ concentrations. After concurrent photoionization with the argon resonance lamp for 3 h of sample deposition, the spectrum illustrated in Figure 3a reveals a series of broad bands at 627, 580, 545 nm without absorption at 517 and 484 nm, sharp 469.3- and 452.8-nm bands, a broad 370–340-nm band, the 340-nm part of which is due to $CH_2Cl_2^+$ cation,[17] and a sharp 315-nm band assigned previously to α-chlorobenzyl radical;[6] these new bands, absorbances, and their changes on photolysis are listed in Table II. Photolysis with 590–1000-nm radiation for 10 min decreased the 627-, 580-, and 545-nm bands and the broad 370–340-nm band in unison, increased the sharp blue absorptions, and produced a broad new band at 303 nm. Figure 3b shows the spectrum after 520–1000-nm photolysis, which continued these trends. Photolysis with 290–400-nm radiation, however, decreased the 303-nm band, restored some of the 627-, 580-, 545-, and 370-nm absorbance, increased the 452.8-nm

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TABLE II: Absorption Bands Produced by Matrix Photoionization of Benzyl Chloride with Added Methylene Chloride[a]

λ, nm	A_i	A_{590}	A_{520}	$A_{290-400}$	A_{500}	$A_{370-460}$	A_{220}
707.8	0.008	0.008	0.01	0.01	0.01	0.01	0.00
686							0.007
652.1							0.020
627	0.036	0.027	0.002	0.014	0.002	0.014	0.00
469.3	0.065	0.072	0.084	0.084	0.096	0.088	0.00
467.4				0.050	0.064	0.072	0.20
452.8	0.014	0.018	0.032	0.056	0.078	0.074	0.31
303		0.03	0.20	0.07	0.17	0.07	0.06

[a] Absorbances given before and after filtered mercury arc photolysis.

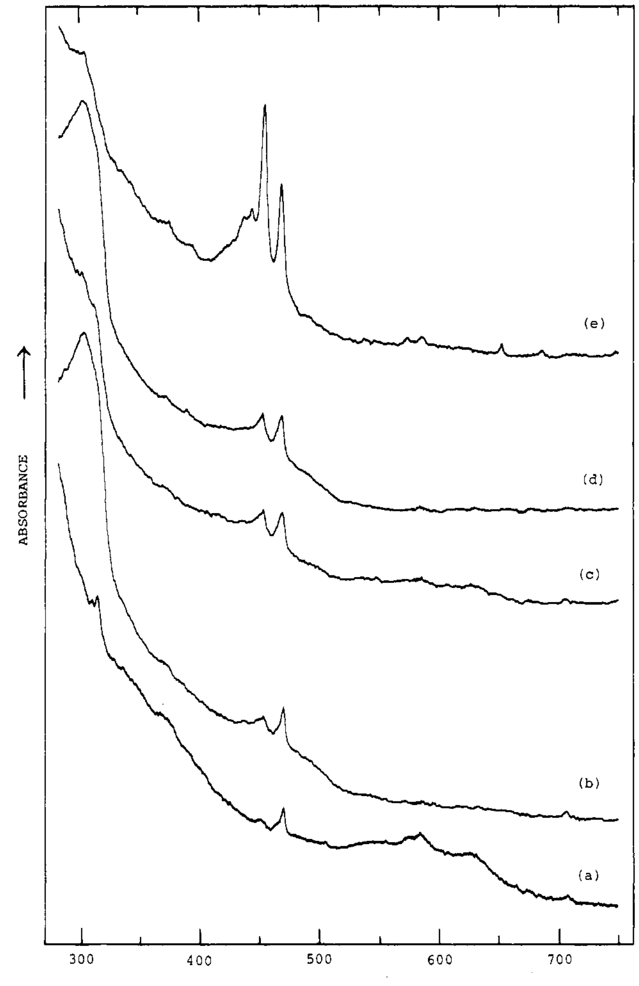


Figure 3. Absorption spectra of benzyl chloride and methylene chloride subjected to argon resonance photoionization during condensation at 20 K, Ar/CH_2Cl_2/ACT ≈ 1000/3/1: (a) spectrum after concurrent photoionization and condensation for 3 h; (b) spectrum after 520–1000-nm photolysis for 10 min; (c) spectrum after 290–400-nm photolysis; (d) spectrum after 500–1000-nm photolysis; and (e) spectrum after 220–1000-nm irradiation.

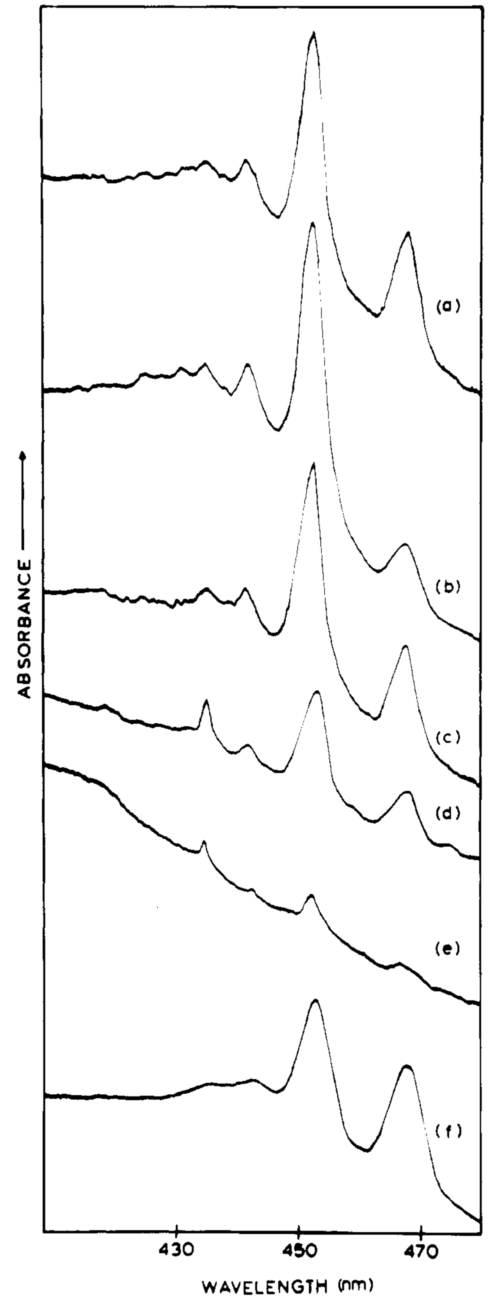


Figure 4. Absorption spectra of 7-chloronorbornadiene subjected to argon resonance photoionization during condensation with excess argon at 20 K: (a) spectrum after concurrent photoionization and condensation for 7 h; (b) spectrum after 470–1000-nm photolysis for 30 min; (c) spectrum after 370–460-nm photolysis; (d) spectrum after 290–1000-nm photolysis; (e) spectrum after 220–1000-nm photolysis; (f) product spectrum after 290–1000-nm photolysis of ACT sample from Figure 1b shown for comparison.

band, and produced a new shoulder at 467.4 nm, as shown in Figure 3c. Photolysis with 500–1000-nm radiation reduced the 627-, 580-, 545-, and 370-nm bands and increased the 303-nm absorption and the 452.8- and 467.4-nm bands (Figure 3d). Irradiation at 370–460 nm restored some 627-, 580-, 545-, and 370-nm absorption, reduced the 303- and 452.8-nm bands, and increased the new 467.4-nm band. A final 220–1000-nm irradiation (Figure 3e) destroyed the broad 627- and 370-nm bands leaving sharper 585-, 575-, 374-, and 390-nm bands, markedly increased the 452.8- and 467.4-nm bands, and revealed weaker 652.1- and 686-nm counterparts. The other experiments gave similar results and photolysis behavior. Irradiation with 380–1000-nm light in one study instead of 290–400-nm light gave a larger yield for the 467.4-nm absorption. A subsequent 240–400-nm photolysis markedly increased the 452.8- and 467.4-nm bands and destroyed the 469.3-nm band. A similar experiment with PCT and added CH_2Cl_2 gave the sharp 707.8- (A = 0.004) and 469.3-nm (A = 0.03) bands, along with a structured broad band near 475 nm, a broad 448-nm band, and a triplet at 310, 303, and 297 nm. Visible and near-UV photolysis had little effect on these bands; however, 220–1000-nm irradiation halved the 475-, 448-, 310-, 303-, and 297-nm bands and doubled the sharp 469.3- and 707.8-nm bands.

An experiment was done with p-fluoro-α-chlorotoluene and added CH_2Cl_2 with $Ar/CH_2Cl_2/FC_6H_4CH_2Cl \approx 1000/2/1$ concentrations. After 3 h of sample deposition with visible–UV irradiation, weak broad bands were observed at 600, 583, 560, 548, and 380 nm, and weak sharp bands were found at 480.7 and 465.9 nm (A = 0.01). Photolysis with 520–1000-nm radiation for 10 min destroyed the weak broad bands, did not affect the sharp 480.7- and 465.9-nm bands, and produced a strong broad 301-nm band like that in Figure 3b. Photolysis with 370–460-nm radiation for 20 min substantially reduced the 301-nm band, restored the broad red and 380-nm UV bands, and increased the 480.7- and 465.9-nm bands by a factor of 4. A 10-min irradiation with 290–1000-nm light halved the red bands, doubled the 301-nm band, tripled the sharp 480.7- and 465.9-nm bands, and produced new bands at 645.3 and 656 nm. A similar 220–1000-nm irradiation destroyed the broad red and 380-nm bands, reduced the 301-nm band, and doubled the 480.7-, 465.9-, 645.3-, and 656-nm bands. Vibrational structure was observed for the 480.7-nm (A = 0.154) band at 473.5 and 463.0 nm and for the 465.9-nm (A = 0.152) band at 453.7, 449.4, and 446.4 nm. A final 470–1000-nm irradiation for 10 min *increased* the 465.9- and 645.3-nm bands by 6% and *decreased* the 480.7- and 656-nm bands by 20%.

Two experiments were done with a 1% CNB sample in argon irradiated by the argon discharge tube (argon at 150 mtorr) for 7 h. The spectrum contained prominent absorptions at 467.7 nm (A = 0.035) and 452.5 nm (A = 0.075) with weaker satellite features at 442 nm (A = 0.03), 435 nm (A = 0.02), and 431 nm (A = 0.02). An extensive photochemical study was done in the first experiment, which is summarized in Table II. Sample photolysis with 630–1000-nm radiation for 30 min increased the 467.7- and 452.5-nm bands by 10% and 20%, respectively. A like treatment with the 590–1000-nm output of the mercury arc decreased the former and increased the latter band, whereas 500–1000-nm photolysis reversed this trend, increasing the former and decreasing the latter absorption. Continued photolysis with 470–1000-nm radiation, which falls within the 467.7-nm absorption band, reduced the 467.7-nm band substantially and increased the 452.5-nm band. The next irradiation with a 370–460-nm filter, which irradiated the 452.5-nm band but not the 467.7-nm band, increased the latter at the expense of the former. This cycle was repeated with the same result. Exposure of the sample to 290–1000-nm radiation reduced both bands and the weaker 442- and 431-nm absorptions to about 30% of their initial absorbances, left the sharper 435-nm band unchanged, and produced new bands at 325 nm (A = 0.006), 316 nm (weak) and 309 nm (A = 0.01), and 302 nm (A = 0.03). Irradiation with the full 220–1000-nm mercury arc further reduced the 467.7- and 452.5-nm bands to about 15% of their initital absorbances and increased the new bands at 325 nm (to A = 0.01), 316 nm (to A = 0.01), 309 nm (to A = 0.03), and 302 nm (to A = 0.04).

Spectra from the second CNB experiment are illustrated in Figure 3a. Again the prominent features were observed at 467.7 and 452.5 nm with weaker components at 442, 435, and 431 nm. Photolysis with 470–1000-nm radiation decreased the 467.7-nm band and increased the 452.5- and 442-nm bands, as can be seen in Figure 3b and Table III, produced a weak new band at 652 nm. Continued photolysis with 370–460-nm radiation reduced the 452.5- and 442-nm bands, increased the 467.7-nm band (Figure 3c), and produced a weak new 686-nm band. Irradiation with 290–1000-nm light reduced the 467.7-, 452.5-, and 442-nm bands (Figure 3d), reduced the 686- and 652-nm bands, left the 453-nm absorption unchanged, and produced new ultraviolet bands at 325, 309, and 302 nm as in the previous experiment. Finally, photolysis with the full arc, 220–1000 nm, reduced the major products to about 10% of their initital absorbances (Figure 3e) and increased the UV bands 325 nm (to A = 0.01), 309 nm (to A = 0.04), and 302 nm (to A = 0.05).

TABLE III: Absorption Bands Produced by Matrix Photoionization of 7-Chloronorbornadiene[a]

	467.7 nm	452.5 nm
A_i	0.035	0.075
A(630–1000 nm)	0.038	0.092
A(590–1000 nm)	0.032	0.095
A(500–1000 nm)	0.034	0.076
A(470–1000 nm)	0.016	0.090
A(370–460 nm)	0.035	0.079
A(470–1000 nm)	0.020	0.092
A(370–460 nm)	0.035	0.074
A(290–1000 nm)	0.011	0.028
A(220–1000 nm)	0.004	0.010
A_i	0.034	0.073
A(470–1000 nm)	0.014	0.092
A(370–460 nm)	0.029	0.065
A(290–1000 nm)	0.009	0.024
A(220–1000 nm)	0.003	0.008

[a] Absorbances given before and after filtered mercury arc photolysis.

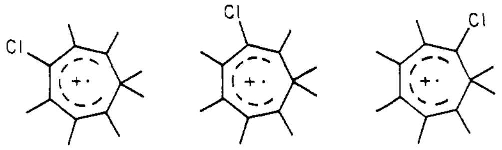
Discussion

The new absorptions will be assigned and molecular ion rearrangements will be considered.

Assignments. In the present experiments, CCHT vapor was codeposited with argon at 20 K and the argon stream was subjected to microwave discharge excitation. Accordingly, CCHT molecules were trapped in solid argon under a bath of 11.6–11.8-eV radiation[8] which is capable of direct photoionization of the precursor molecules, based on the 9-eV ionization energies[2] of chlorotoluenes. Since parent cations of simple substituted aromatic and cycloheptatriene molecules are photosensitive,[4-6] the present absorption bands are considered for assignment to parent cations.

The identification of the broad 544-, 517-, and 484-nm absorptions as isomers of chlorocycloheptatriene cation ($CCHT^+$) is based upon comparison with methylcycloheptatriene cation ($MCHT^+$) spectra.[5] Analogous studies with a mixture of the four MCHT isomers gave similar broad bands at 498, 494, 480, and 472 nm. In that work, the precursor synthesis produced primarily the 7-methyl isomer, and the 494-nm band dominated the spectrum. The use of thermally isomerized precursor molecules gave a different relative yield of the broad absorptions in subsequent matrix photoionization experiments. Photolysis with red mercury arc light decreased the 494-nm band and increased the 507-nm band; green radiation left the 507-nm band unchanged and destroyed the 494-, 480-, and 472-nm bands; prolonged blue photolysis destroyed the 507-nm band and produced marked growth in a sharp 440.6-nm band.

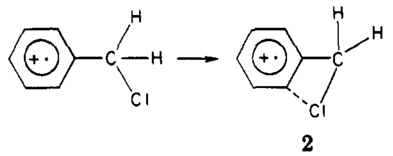
Although the 544-, 517-, and 484-nm bands cannot be individually identified with specific $CCHT^+$ isomers, the three photosensitive bands can be assigned to the 1-, 2-, and 3-chlorocycloheptatriene isomeric cations (1). A possible rearrangement product, the 7-chlorocycloheptatriene cation, is not likely to be trapped in the present experiments. Owing to the unusual stability of the tropylium cation, the 7-chlorocycloheptatriene cation is expected to eliminate chlorine readily to give the tropylium cation. Unfortunately, the tropylium cation could not be observed in these experiments since its 263-nm absorption[18] was masked by the totally absorbing CCHT band in this region. The photolysis data in Table I do show a decreasing CCHT$^+$ cation stability with increasing absorption wavelength; this indicates that the CCHT$^+$ isomer absorbing at lowest energy rearranges most readily.



1

The photolysis observations provide more information on the sharp 469.3-nm band believed to be a $C_7H_7Cl^+$ cation isomer; its growth on visible photolysis in CCHT experiments shows that it cannot be due to CCHT$^+$. Although the benzyl cation is an expected photolysis product, the benzyl cation absorbs strongly at 353 nm in solid argon.[18] Furthermore, the narrow bandwidth is not compatible with any of the substituted cycloheptatriene cation or ring-substituted chlorotoluene cation spectra. No evidence for the PCT$^+$ isomer[6] was found in the present CCHT experiments. Matrix photoionization experiments with ACT gave a substantially increased 469.3-nm band absorbance, with weaker satellites at 463.7 and 452.7 nm which have been attributed to vibrational structure,[6] and with weaker bands at 665 and 707.8 nm. The present CCHT experiments gave the 469.3- and 707.8-nm bands without absorption at 665 nm, which supports assignment of the latter band to a different species, whereas the 469.3- and 707.8-nm bands are due to the same species. In the previous chlorotoluene study,[6] the 469.3- and 707.8-nm bands were produced by 10.2-eV photoionization of a cold ACT sample, which characterizes the species as a $C_7H_7Cl^+$ cation with limited rearrangement from the ACT precursor structure. Similar experiments with PCT gave the same 469.3-nm band as ACT, which is shown in Figure 2, and in addition broad absorptions at 448 and 475 nm which have been assigned to the ring-substituted PCT$^+$ ion.[6]

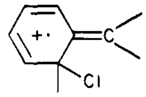
More recent ACT photoionization experiments doped with an electron trap produced a broad red absorption beginning at 627 nm and a broad 370-nm band. Photolysis with 590–1000-nm light slightly increased the 469.3-nm band at the expense of the broad 627- and 370-nm bands, and additional 520–1000-nm photolysis destroyed the 627- and 370-nm bands, slightly increased the 469.3-nm band and produced a strong, broad new 303-nm absorption. Further 240–400-nm photolysis reduced the UV band and regenerated part of the 627- and 370-nm bands. The present photosensitive broad 627-, 580-, 545-nm band is in sufficient agreement with the 595-nm band in the photodissociation spectrum (PDS) of ACT[19] to support assignment to ACT$^+$. Previous workers[6,19] have noted that this absorption is slightly higher in energy than predicted by the photoelectron spectrum,[19] which suggests relaxation of the parent ion structure as represented by structure 2.



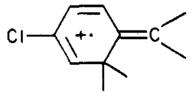
2

The red absorption is assigned to the $n_z \rightarrow \pi$ charge-transfer transition; the 627-, 580-, and 545-nm peaks decrease and increase together on photolysis so they are attributed to vibronic components of the same transition. The broad 370-nm band is in the region expected for $\pi \rightarrow \pi$ transitions of aromatic cations; its displacement to slightly higher energy than toluene cation[20] at 416 nm is probably due to interaction with the $n_z \rightarrow \pi$ transition. The absence of the stronger CCHT$^+$ bands at 517 and 484 nm verifies that 1 cations are not produced and trapped in ACT experiments. It follows that the broad band system beginning at 600 nm and the broad 380-nm band in p-$FC_6H_4CH_2Cl$ experiments are due to the p-F derivative of 2.

The species with the sharp photosensitive 469.3- and 707.8-nm absorptions is formed by argon-resonance photoionization of ACT and PCT, and red-green photolysis of 1 and 2. Since sharp bands in *blue* and *red* regions are characteristic of conjugated triene and not diene or aromatic cations,[20–23] the most reasonable $C_7H_7Cl^+$ isomeric structure for the single set of sharp 469.3- and 707.8-nm bands appears to be the 6-chloro-5-methylene-1,3-cyclohexadiene structure 3. A ring-opened species clearly would have too many isomeric possibilities for the single set of sharp bands. Although a similar methylene cyclohexadiene cation species with a 2-chloro substituent, 3a, can be suggested by formation of the 469.3-nm absorber from PCT$^+$, ring expansion of PCT$^+$ to CCHT$^+$ can occur[2,3] under the experimental conditions, followed by rearrangement to 1-CCHT$^+$, which can give 3 on photoexcitation. The absence of a 469.3-nm counterpart in the p-$FC_6H_4CH_2Cl$ experiment might also suggest the 2-chloro position, 3a; however, the aromatic fluorine substituent deactivates the meta position more effectively than the ortho position to electrophilic substitution, which might make transfer of the α-chlorine in 2 to the 6 position in 3 unfavorable. The present data cannot definitively determine the position of the chlorine substituent in the methylenecyclohexadiene product species, although the 6 position appears most reasonable. It is again suggested that the 440-nm band in the photodissociation spectrum of ACT[19] is due to the species responsible for the 469.3-nm matrix absorption, which from the matrix spectrum, is consistent with structure 3.



3



3a

Photodissociation of 2 is expected to give the benzyl cation and a chlorine atom trapped together in the matrix cage. Recent matrix isolation experiments have shown that the benzyl cation rearranges to the tropylium cation upon irradiation with a strong, broad benzyl cation absorption

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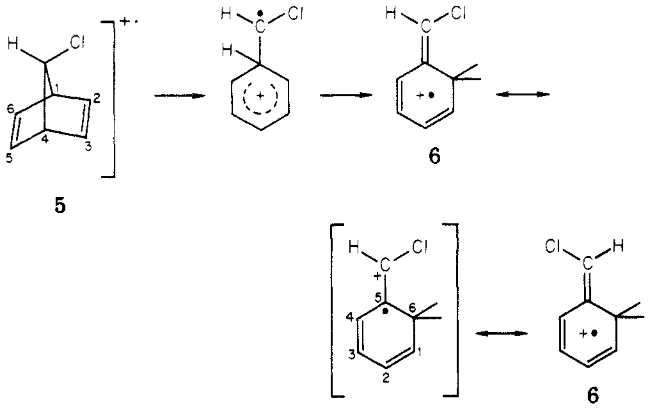
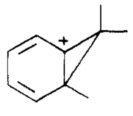
[23] Kelsall, B. J.; Andrews, L. To be submitted for publication.

Scheme I



peaking at 353 nm.[18] Theoretical calculations have suggested norcaradienyl cation 4 as an intermediate in the benzyl → tropylium rearrangement.[24] The strong, broad 303-nm band is attributed to 4 with an adjacent chlorine atom, which could give 2 and 3 as products of a photochemical reaction. Final 220–1000-nm photolysis that produced marked growth in the 452- and 467-nm bands also produced weak 374-, 390-, 575-, and 585-nm absorptions. These latter absorptions could be due to ring-opened conjugated polyene cations of formula $C_7H_7Cl^+$.



4

Weak bands at 453 and 468 nm in the CCHT experiments were produced in larger yield in CNB studies and in still larger yield upon near-UV photolysis in ACT studies. These absorptions, however, were not produced in the PCT experiments. Since the 452.5- and 467.7-nm bands were photolytically interconvertible, these two absorptions are probably due to structural isomers. The observation of a 652.1-nm band that is associated with the 452.5-nm band and a 686-nm counterpart for the 467.7-nm band suggests a conjugated triene cation assignment similar to that proposed above for 3.

Since the 452.5- and 467.7-nm bands were the major products in CNB experiments, possible isomeric triene structures that can readily be produced by rearrangement of CNB^+ will be considered first. Earlier argon matrix photoionization experiments with norbornadiene gave weak product bands for the isomeric cycloheptatriene and methylene cyclohexadiene parent cations with no evidence for norbornadiene cation itself,[4] expected to give a broad band near 630 nm on the basis of its observation at 635 nm in butyl chloride glass.[25] The observation of two photolytically interconvertible sets of bands in the region expected for conjugated trienes suggests the *Z* and *E* products 6 of Scheme I. The 452.5- and 467.7-nm bands cannot be assigned uniquely to one of the two structures; one band is due to the *Z* isomer and the other to the *E* isomer.

The formation of 6 from CNB^+ (5) requires simple cleavage of the 4–7 bond and formation of a π bond to C(1) with a concerted 1,2-hydrogen shift as depicted in Scheme I. A similar cleavage has been postulated in recent mass spectroscopic studies of 1,6-methano[10]annulene.[26] The formation of 6 in ACT photolysis experiments could proceed directly from 2 by transfer of an α-hydrogen to the ring or by further rearrangement of 4 to the tropylium cation followed by chlorine addition and formation of a 1–6 bond upon photoexcitation. Analogous photochemically interconvertible bands at 480.7 and 465.9 nm in the p-$FC_6H_5CH_2Cl$ experiment are attributed to the 2-fluoro derivative of the 6 isomers. These reasonable mechanisms for the formation of 6 from CNB and ACT support this assignment for the 452.5- and 467.7-nm bands.

TABLE IV: Summary of $C_7H_7Cl^+$ Product Absorptions, Precursors, and Assignments

absorptions, nm	precursors	assignments
544, 517, 484	CCHT	three $CCHT^+$ isomers (1)
627, 580, 545, 370	ACT	ACT^+ (2)
707.8, 469.3	ACT, PCT, CCHT	3
686, 467.7	ACT, CNB, CCHT	6 isomer
652.1, 452.5, 442, 431	ACT, CNB, CCHT	6 isomer
475, 310, 303, 297	PCT	PCT^+

Rearrangements. Molecular ion rearrangements have been observed in matrix photoionization experiments under two different circumstances. First, the $CCHT^+$ ion can be formed with excess internal energy, since the ionizing radiation exceeds the ionization energy by more than 2 eV. Rearrangement may occur during the condensation process while this excess internal energy is quenched by the matrix. Observation of the sharp 469.3- and 707.8-nm bands following argon resonance photoionization during condensation of ACT, PCT, and CCHT samples shows that rearrangement of parent cations occurs during sample formation. Second, upon photoexcitation in the absorption band, sufficient internal energy is provided to promote rearrangement of the molecular ion trapped in the 20 K matrix. The marked growth of sharp 452.5- and 467.7-nm bands on UV photolysis in ACT experiments and the interconversion of these two bands upon selective photolysis show that photochemical rearrangements occur in the cold matrix. Scheme II and Table IV summarize the $C_7H_7Cl^+$ cation rearrangements studied here.

The observation of 3 in PCT experiments suggests rearrangement through the ring-expanded $CCHT^+$ intermediates although 1 cations were not detected in PCT experiments. The matrix facilitates the formation of 3 and 6 from 1 by quenching internal energy and retarding chlorine atom elimination, which is the favored process in the gas phase.[3,19,27]

The results of the present matrix photoionization experiments are consistent with a recent mass-spectroscopic study of 1-, 2-, and 3-chlorocycloheptatriene cations.[12] Observation of the same normal ion spectra from the three different isomers suggested rapid hydrogen atom rearrangments to a common parent ion structure. Furthermore, ion kinetic energy release measurements confirmed that the reactive molecular ions have equilibrated before chlorine atom elimination. This rearangement was proposed to involve a series of random 1,2, 1,3, and 1,4 hydrogen migrations or rearrangements involving norcaradienyl-type intermediates to give the 7-chlorocycloheptatriene cation structure which can most readily eliminate chlorine to form the tropylium cation. The solid argon matrix, however, quenches internal energy and reduces the dissociation rate allowing rearrangement to cations 3 and 6 to be competitive processes. The role of

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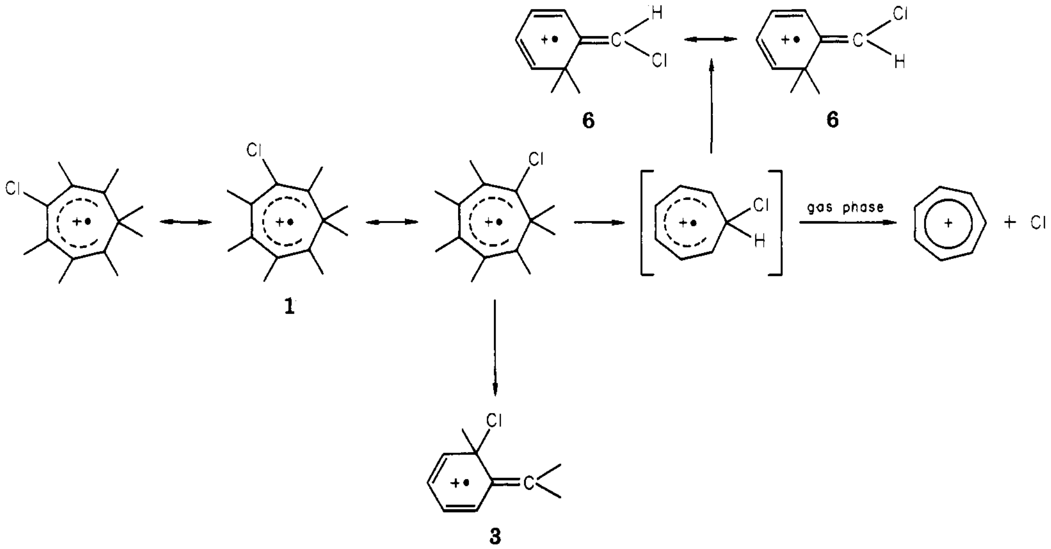
Scheme II



the matrix as a medium that enhances molecular ion rearrangements at the expense of decomposition has been demonstrated for cycloheptatriene, benzyl, and methylcycloheptatriene cations.[4,5,18]

The rearrangement of 7-chloronorbornadiene cation to **6** cations (Scheme I) takes place after photoionization during sample condensation and upon photolysis of the cold sample. Although no absorption was observed for the **5** cation, it is expected in the 630-nm region.[25] Photolysis with 630–1000-nm radiation increased the 452.5- and 467.7-nm bands, which is best explained by the Scheme I rearrangement. Finally, rearrangement between the *Z* and *E* structural isomers of the **6** cation proceeds through selective activation of one isomer by electronic absorption unique to that one isomer, followed by dynamic equilibrium between the two isomers, and deactivation of the other isomer by the cold matrix. On the basis of the molecular orbitals for hexatriene,[28] the blue $\pi \rightarrow \pi^*$ transition[22,29] decreases π bond order between the terminal carbon atoms, thus weakening the methylene–ring π bond enough to allow rotation and $Z \rightleftarrows E$ isomeric equilibration. Alternatively, the $E \rightleftarrows Z$ rearrangement could proceed by a simple 6, 4 hydride shift. The matrix is necessary for quenching internal energy to allow the $Z \rightleftarrows E$ rearrangement of this reactive species to be competitive with dissociation.

Conclusions

Matrix photoionization of chlorocycloheptatriene produced and trapped three CCHT$^+$ isomeric cations. Visible photolysis destroyed broad CCHT$^+$ absorptions at 544, 517, and 484 nm and produced weak sharp 469.3-, 467.7-, and 452.5-nm bands believed to be isomeric $C_7H_7Cl^+$ cations. The observation of sharp red absorptions for each blue absorption in more productive benzyl chloride experiments suggests chlorine-substituted methylenecyclohexadiene assignments for these $C_7H_7Cl^+$ species. The 469.3-nm band was also produced from *p*-chlorotoluene, which suggests that ring expansion to the CCHT$^+$ isomers is involved in the rearrangement. The photolytically interconvertible 452.5- and 467.7-nm bands were also produced by matrix photoionization of 7-chloronorbornadiene; these observations are in accord with *Z* and *E* isomers of 5-(chloromethylene)-1,3-cyclohexadiene cation, which is expected to isomerize upon selective photoexcitation.

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