

the spectrum were measured with narrow spectral widths to obtain good digital resolution (ca. 0.001 ppm/point).

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94484-02-3; 13, 57344-16-8; 14, 41798-19-0; 15, 43022-03-3; 16, 18682-96-7; CH<sub>2</sub>=CHCHO, 107-02-8; CH<sub>3</sub>CH=CHCHO, 4170-30-3; CH<sub>2</sub>=CHCH(OMe)<sub>2</sub>, 6044-68-4; CH<sub>3</sub>CH=CHCH(OMe)<sub>2</sub>, 21962-24-3; HC(OEt)<sub>3</sub>, 122-51-0; D<sub>2</sub>, 7782-39-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 1,1-dimethoxycyclopentane, 931-94-2; 1,1-dimethoxycyclohexane, 933-40-4; 3,3-dimethoxycyclohexene, 1728-18-3; 3,3-dimethoxycyclopentene, 94484-03-4; 3,3-dimethoxy-d<sub>6</sub>-cyclohexene, 94484-04-5.

## Photochemical Rearrangements of *o*- and *m*-Dichlorobenzene Cations to *p*-Dichlorobenzene Cation in Solid Argon

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**Abstract:** Matrix photoionization experiments with *o*- and *m*-dichlorobenzene and 1,2,4-trichlorobenzene produced and isolated for spectroscopic study not only radical cations of the precursor compound but also rearranged cation products. It is postulated that a bridged chloronium ion is formed upon excitation to the lone pair hole state which serves as an intermediate in rearrangements among the excited-state di- and trichlorobenzene cation isomers. The chlorine lone pair hole excited state facilitates a "chloronium ion walk" around the aromatic ring.

Photochemical rearrangements of molecular cations in solid argon have been described, including the benzyl-tropylium cation transformation<sup>1</sup> and the rearrangement of alkylbenzene and cycloheptatriene cations to methylenecyclohexadiene cation species.<sup>2-4</sup> These rearrangements proceed following activation by irradiation into a cation absorption band. Thus, the presence of *p*-dichlorobenzene cation absorptions in matrix photoionization experiments using the *o*- and *m*-dichlorobenzene precursors could be due to intramolecular photochemical rearrangements of the precursor cations in the matrix. A viable mechanism for this rearrangement involves the formation of an excited bridged chloronium ion species as an intermediate. There is strong evidence for the existence of bridged halonium ions in SbF<sub>5</sub> solutions,<sup>5,6</sup> and ab initio molecular orbital studies have demonstrated the stability of the bridged intermediate in the addition of Cl<sup>+</sup> to ethylene.<sup>7</sup>

Rearrangements among halobenzenes have been observed in solution, for example, the transformation of 1,2,4-tribromobenzene to the 1,3,5-isomer upon treatment of potassium anilide in liquid ammonia.<sup>8</sup> However, it has been proposed that these occur via a series of nucleophilic displacements by aryl anions on an aryl halide.<sup>8</sup> The mechanism for the dichlorobenzene cation rearrangements observed in the matrix more closely resembles that seen in sigmatropic reactions; for example, a plausible explanation for the interconversion between 1,4,4-, 1,3,3-, and 1,2,2-trimethylcycloheptatriene involves sigmatropic carbon skeletal rearrangements between norcaradiene intermediates.<sup>9</sup> Specific experiments performed to characterize rearrangements between di- and trichlorobenzene cation isomers will be described in the following report.

### Experimental Section

The cryogenic apparatus and argon resonance photoionization sources have been described previously.<sup>10-12</sup> Room-temperature equilibrium vapors of the dichlorobenzenes and 1,2,4-trichlorobenzene were mixed with argon and CH<sub>2</sub>Cl<sub>2</sub> in a 2-L can to yield Ar/CH<sub>2</sub>Cl<sub>2</sub>/reagent ratios of 900-500/1/3-1. Due to the slightly lower volatility of 1,3,5-trichlorobenzene, the equilibrium vapor pressure at 35 °C was mixed with argon, and experiments were done with and without CH<sub>2</sub>Cl<sub>2</sub> added to serve as an electron trap. All the chlorobenzene mixtures were deposited onto a sapphire window (20 ± 2K) at a rate of 1 mmol/h for 3-5 h during exposure to argon-discharge 11.6-11.8 eV (vacuum ultraviolet) radiation from a 1- or 3-mm orifice discharge tube powered by a microwave discharge unit using maximum (80%) and minimum (20%) stable power. Mercury arc 220-1000-nm (UV-vis) lamp photolyses were subsequently performed for 15-30-min periods for all samples.

A Cary 17 spectrophotometer was used to record ultraviolet and visible spectra before and after vacuum ultraviolet irradiation and UV-vis photolyses. The uncertainty in the bands was ±0.2 nm unless otherwise indicated. All the chlorobenzenes were obtained from Aldrich Chemical Co., except for *o*-dichlorobenzene which was supplied by Matheson, Coleman, and Bell; no further purification was necessary.

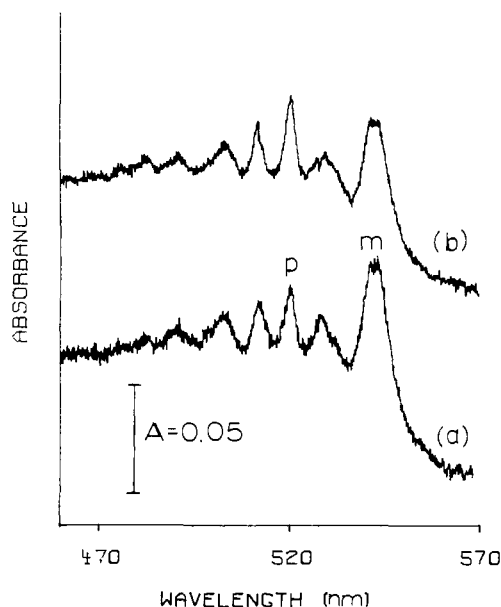
### Results

Experiments with different chlorine-substituted benzene precursors will now be described individually.

***m*-Dichlorobenzene.** Several experiments have been performed previously with *m*-dichlorobenzene (MDCB).<sup>13</sup> Additional experiments were conducted with less intense argon resonance photoionization in order to minimize secondary photoprocesses. Spectra following vacuum ultraviolet irradiation through a 3-mm orifice with maximum (80%) discharge power exhibited vibronic systems with origins at 542.8 (accompanied by a vibronic band at 529.5 nm) and 520.6 nm with band absorbances of 0.15 and 0.17, respectively, which have been assigned to the MDCB and *p*-dichlorobenzene (PDCB) cations.<sup>13</sup> Photolysis at 590-1000 nm had no effect on the absorptions; however, the 542.8-nm absorption

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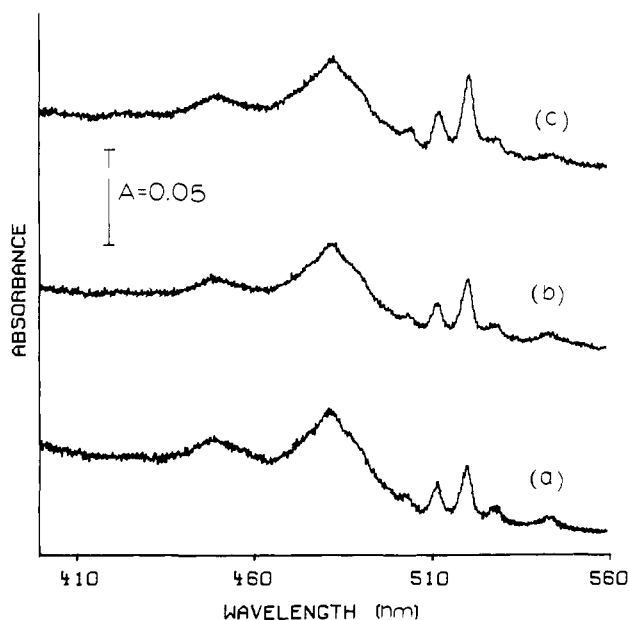


**Figure 1.** Absorption spectra of *m*-dichlorobenzene subjected to argon resonance photoionization during condensation: (a) Ar/CH<sub>2</sub>Cl<sub>2</sub>/MDCB = 500:1:2 matrix sample after 4 h of deposition and photoionization, (b) sample after two 30-min periods of 515–1000-nm photolysis.

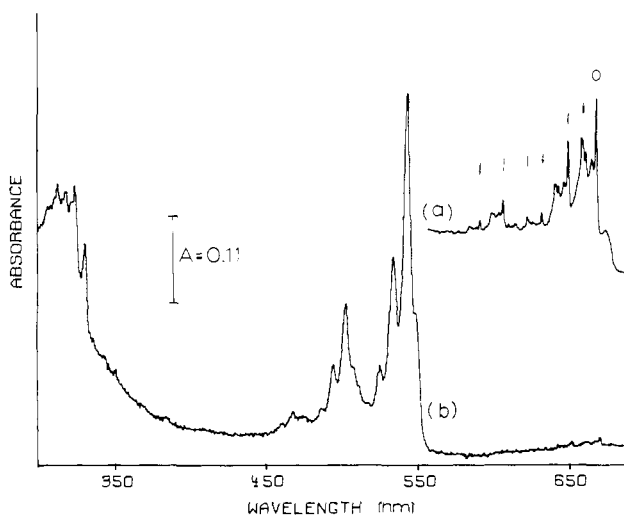
was reduced 25% and the 520.6-nm band increased 20% by 515–1000-nm photolysis. Spectra following vacuum ultraviolet irradiation at minimum stable (20%) power in another experiment displayed a 542.8-nm absorption significantly more intense than the 520.6-nm peak. The former band was decreased slightly, while the latter was increased slightly by 500–1000-nm photolysis. Figure 1 shows spectra from an experiment employing argon discharge irradiation from argon flowing through a 1-mm discharge tube at minimum power. Trace a displays the spectrum from a MDCB matrix sample after 4 h of deposition and concurrent photoionization; again the predominant peaks are the origins at 542.8 nm ( $A = \text{absorbance} = 0.09$ ) labeled m and at 520.6 nm ( $A = 0.05$ ) labeled p. Trace b was recorded after two 30-min periods of 515–1000-nm photolysis. The 542.8-nm band absorbance decreased 25% as the 520.6-nm band increased more than 20%.

Examination of the precursor used in the MDCB experiments showed only a trace (<2%) of *p*-dichlorobenzene contamination as determined from the sharp-resolved vibronic matrix UV spectrum.

***o*-Dichlorobenzene.** A previous experiment with *o*-dichlorobenzene (ODCB) as precursor gave primarily *p*-dichlorobenzene product bands.<sup>13</sup> Another 3-mm orifice argon discharge irradiation experiment was conducted at full power. Two band systems were observed, a sharp well-defined vibronic system originating at 520.6 nm ( $A = 0.28$ ) and a broad system with its origin at  $483 \pm 1$  nm ( $A = 0.12$ ). Two experiments were conducted by utilizing a 1-mm discharge orifice and minimum discharge power. In the first experiment, after 5 h of deposition and irradiation, vibronic systems with origins at 520.6 ( $A = 0.02$ ), 543 ( $A = 0.01$ ), and 483 nm ( $A = 0.03$ ) were observed. Irradiation at 360–470 nm for 30 min decreased the 483-nm band by 15% and increased the 543-nm band by 15%. A subsequent 420–1000-nm photolysis increased the sharp 520.6-nm band 40%, decreased the 543-nm band by 30%, and left the 483-nm band unchanged. There also appeared after argon photoionization a broad absorption at 334 nm ( $\pm 1$  nm) and a sharp vibronic system originating at 322.4 nm. Figure 2 shows spectra from the second experiment after 4 h of concurrent photoionization during sample condensation. The initial spectrum (a) displayed three vibronic band systems with origins at 543 ( $A = 0.006$ ), 520.6 ( $A = 0.028$ ), and 483 nm ( $A = 0.040$ , approximately  $A = 0.004$  of this peak is due to a vibronic component of the 520.6-nm system); a vibronic component of the 483-nm band was observed at 448 nm. Irradiation at 360–470 nm, Figure 2b, again reduced the 483-nm band by 15% and increased the 543-nm



**Figure 2.** Absorption spectra of *o*-dichlorobenzene subjected to argon resonance photoionization during condensation: (a) Ar/CH<sub>2</sub>Cl<sub>2</sub>/ODCB = 500:1:1 matrix sample after 4 h of photoionization during deposition, (b) sample after 30 min of 360–470-nm photolysis, (c) sample after 30 min of 515–1000-nm photolysis.



**Figure 3.** Absorption spectra of trichlorobenzenes after matrix photoionization: (a) Ar/1,3,5-trichlorobenzene = 300:1 without CH<sub>2</sub>Cl<sub>2</sub> after 3 h of photoionization and deposition, (b) Ar/CH<sub>2</sub>Cl<sub>2</sub>/1,2,4-trichlorobenzene = 900:1:3 after 4 h of photoionization and deposition followed by 50 min of 590–1000-nm photolysis.

band by 15% without changing the sharp 520.6-nm band. A subsequent 515–1000-nm photolysis, Figure 2c, reduced the 543-nm band by 20% and increased the 520.6-nm band by 40% without measurably affecting the broad 483-nm band. A final 320–1000-nm irradiation (not shown) reduced the broad 483-nm band another 15%, left the 543-nm band unchanged, and increased the sharp 520.6-nm band another 5%. Only a trace of PDCB and MDCB contamination was detected in the sharp resolved vibronic matrix UV spectrum of the ODCB precursor.

**1,3,5-Trichlorobenzene.** Similar argon resonance photoionization experiments were performed with 1,3,5-trichlorobenzene (1,3,5-TCB). In one experiment employing CH<sub>2</sub>Cl<sub>2</sub> as an electron trap, a sharp vibronic system with extensive structure was observed at 671.6 nm. Photolysis at 420–1000 nm did not significantly affect the visible absorptions, but 220–1000-nm photolysis decreased the 671.6-nm system by 60%. Figure 3a illustrates the spectrum from a matrix sample (Ar:1,3,5-TCB = 300:1, without CH<sub>2</sub>Cl<sub>2</sub>) exposed to 3 h of microwave discharge irradiation, which produced 67% of the yield in the above experiment with added

**Table I.** Wavelengths, Frequencies, Vibrational Intervals, and Vibrational Assignments for 1,3,5-Trichlorobenzene Cation in Solid Argon at 20 K

$\lambda$ , nm	$\nu$ , cm <sup>-1</sup>	$\Delta\nu$ , cm <sup>-1</sup>	assignment
671.6	14 890		origin
668.5	14 960	70	
664.9	15 040	150	$\nu_{17}$ (149) <sup>a</sup>
663.1	15 080	190 <sup>b</sup>	$\nu_{14}$ (191)
662.1	15 100	210	$\nu_{20}$ (215)
653.1	15 310	420 <sup>b</sup>	$\nu_{13}$ (429)
650.1	15 380	490	
646.5	15 470	580	$\nu_{17} + \nu_{13}$
644.8	15 510	620	$\nu_{13} + \nu_{14}$
644.0	15 530	640	
635.4	15 740	850 <sup>b</sup>	$2\nu_{13}$
625.9	15 980	1090	$\nu_{11}$ (1095)
618.4	16 170	1280	$3\nu_{13}$
617.5	16 190	1300	
613.6	16 300	1410	$\nu_{10}$ (1420)
609.9	16 400	1510 <sup>b</sup>	$\nu_9$ (1590)
607.4	16 460	1570	$\nu_{10} + \nu_{17}$
604.2	16 550	1660	
602.7	16 590	1700	$\nu_9 + \nu_{14}$
602.1	16 610	1720	$4\nu_{13}$
594.6	16 820	1930 <sup>b</sup>	$\nu_9 + \nu_{13}$

<sup>a</sup>Ground-state neutral frequencies in cm<sup>-1</sup> taken from ref 19.<sup>b</sup>These sharp bands are noted with a vertical line in Figure 3a.

CH<sub>2</sub>Cl<sub>2</sub>. Photolysis at 290–1000 nm reduced the intensity of the absorption system by 60%. Table I lists the wavelengths and frequencies of the visible absorptions produced with the 1,3,5-TCB precursor.

**1,2,4-Trichlorobenzene.** Two argon resonance photoionization experiments were performed with 1,2,4-trichlorobenzene (1,2,4-TCB), and a well-defined vibronic system appeared at 544.9 nm ( $A = 0.18$ ). Photolysis at 340–600 nm reduced the band 10%; warming the system to 40 K and recoiling to 20 K decreased the absorptions another 20%. A second, longer experiment produced vibronic band systems with origins at 544.9 ( $A = 0.49$ ), 331.4 ( $A = 0.12$ ), and 671.6 nm ( $A = 0.01$ ). The accompanying vibrational fine structure of the UV origin could not be identified with certainty due to the presence of bands from 1,2,4-TCB neutral precursor. The 671.6-nm band was accompanied by vibronic absorptions at 662.1 and 653.1 nm. Figure 3b illustrates the spectrum after the matrix sample was further subjected to 50 min of 590–1000-nm photolysis. The 544.9- and 331.4-nm origins were reduced 10%; the 671.6-nm origin was unaffected. Irradiation at 420–1000 nm had a similar effect on the band systems. Finally, 220–1000-nm photolysis reduced the three-band systems by half. Table II lists wavelengths and frequencies of the visible absorptions produced with the 1,2,4-TCB precursor, excluding those seen in the 1,3,5-TCB experiments. The matrix ultraviolet spectrum of the 1,2,4-TCB sample did not reveal any 1,3,5-TCB contamination.

### Discussion

Electronic and vibrational assignments will be discussed, and the relevant photochemistry of the chlorobenzene cations will then be analyzed with respect to possible photochemical rearrangements.

**Identification and Assignments.** The band systems previously described will be assigned to the dichloro- and trichlorobenzene radical cations for the following reasons: (1) The matrix photoionization (11.6–11.8 eV)<sup>11</sup> experiment is capable of ionizing the parent and trapping the radical cation in the solid argon matrix. A substantial fraction of the electrons removed by photoionization are captured by CH<sub>2</sub>Cl<sub>2</sub> to give CH<sub>2</sub>Cl radical and Cl<sup>-</sup>. Methylene chloride thus serves as an efficient electron trap, which accounts for a 50% increase in the yield of 1,3,5-TCB<sup>+</sup> in experiments with added CH<sub>2</sub>Cl<sub>2</sub>. (2) Emission spectra and photoelectron spectra (PES)<sup>14</sup> furnish independent evidence for the electronic origins observed for the dichlorobenzene cations. The radical cations will be discussed individually.

**Table II.** Wavelengths, Frequencies, Vibrational Intervals, and Vibrational Assignments for 1,2,4-Trichlorobenzene Cation in Solid Argon at 20 K

$\lambda$ , nm	$\nu$ , cm <sup>-1</sup>	$\Delta\nu$ , cm <sup>-1</sup>	assignment
550.0	18 180		origin
544.9	18 350	0	origin
535.2	18 680	330	$\nu_{19}$ (328) <sup>a</sup>
526.3	19 000	650	$\nu_{15}$ (677)
513.4	19 480	1130	$\nu_{11}$ (1132)
508.7	19 660	1310	$\nu_8$ (1264)
504.0	19 840	1490	$\nu_6$ (1461)
495.8	20 170	1820	$\nu_6 + \nu_{19}$
488.3	20 480	2130	$\nu_6 + 2\nu_{19}$
331.4	30 180	0	origin
325.0	30 770	590	$\nu_{16}$ (575)
322.5	31 010	830	$\nu_{14}$ (816)
319.1	31 340	1160	$\nu_{10}$ (1156)
313.5	31 900	1720	$\nu_{10} + \nu_{16}$

<sup>a</sup>Ground-state neutral frequencies in cm<sup>-1</sup> taken from ref 20.

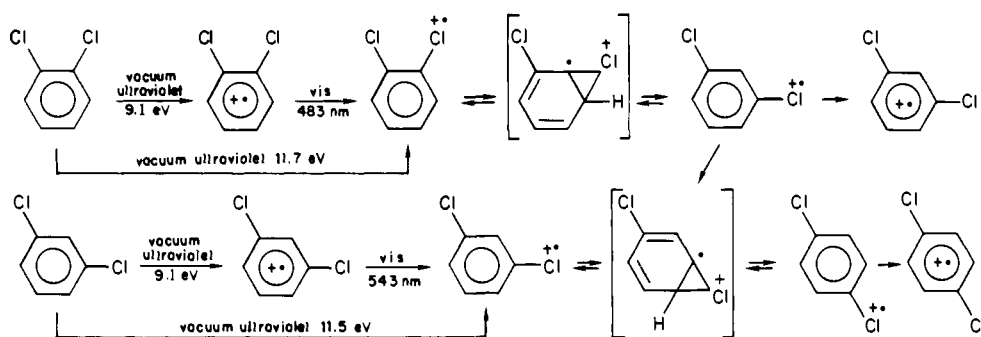
**m-Dichlorobenzene.** As previously described,<sup>13</sup> the 542.8-nm absorption is due to the  ${}^2B_1 \leftarrow {}^2A_2$  transition for the MDCB cation which is red-shifted 350 cm<sup>-1</sup> from the gas-phase emission origin for MDCB<sup>+</sup> at 533 nm.<sup>14</sup> The vibronic fine structure at 529.5 nm corresponds to a vibrational frequency CH<sub>2</sub>Cl<sub>2</sub> 460 cm<sup>-1</sup> and is tentatively assigned to the  $\nu_{10}(a_1)$  X sensitive vibrational mode (397 cm<sup>-1</sup> for neutral parent).<sup>15</sup> The 520.6-nm electronic origin appearing upon discharge irradiation has been previously identified as the  ${}^2B_{3u} \leftarrow {}^2B_{2g}$  absorption of the PDCB cation in solid argon,<sup>13</sup> which is red-shifted 410 cm<sup>-1</sup> from the gas-phase emission.<sup>14</sup>

**o-Dichlorobenzene.** There is good agreement between the optical absorption spectrum and a transition for the ODCB cation predicted from PES. The photoelectron spectrum shows bands at 9.06, 9.6, 11.24, and 11.7 eV due to ionization from  $a_2$ ,  $b_1$ ,  $b_2$ , and  $b_1$  orbitals, respectively.<sup>14</sup> The difference between the first and fourth bands predicts a symmetry-allowed transition in the visible region at 470 nm. The 483-nm absorption can be assigned to this  ${}^2B_1 \leftarrow {}^2A_2$  transition for the cation with a 590 cm<sup>-1</sup> red shift by the argon matrix. The observed band is broadened due to nonradiative transfer from the  ${}^2B_1$  to the  ${}^2B_2$  state, which likely prevents observation of emission from this ion in the gas phase.<sup>14</sup> Whereas the  ${}^2B_1$  state is generated by ionization of a chlorine  $\pi$ -type electron, the  ${}^2B_2$  state arises from ionization of a chlorine  $\sigma$ -type electron;<sup>14</sup> thus, the  ${}^2B_2 \leftarrow {}^2A_2$  transition, although symmetry-allowed, is not intense enough to be observed, but its presence is manifested by lifetime-broadening the  ${}^2B_1$  state. A vibronic band at 448 nm accompanied the 483-nm origin and represents a vibrational spacing of  $1620 \pm 40$  cm<sup>-1</sup>. It is assigned to the vibrational mode  $\nu_3(a_1)$  (C–C) which occurs at 1571 cm<sup>-1</sup> for the neutral parent.<sup>16</sup> The 334-nm absorption is probably due to a  $\pi^* \leftarrow \pi$  transition for the ODCB cation and is analogous to this transition for the MDCB cation which, although much sharper, appeared at the same wavelength.<sup>13</sup> The 542.8-nm band observed in the ODCB experiments has been identified as the MDCB cation and the 520.6- and 322.4-nm absorptions are due to the PDCB cation<sup>13</sup> produced by the rearrangements discussed below.

**1,3,5-Trichlorobenzene.** Photoelectron and emission spectra confirm the assignment of the electronic absorptions in the 1,3,5-TCB experiments to the 1,3,5-TCB radical cation. The PES for 1,3,5-TCB shows peaks at 9.34, 11.25, 11.51, 11.93, and 13.0 eV, which have been assigned to electrons removed from  $e''$ ,  $a_2''$ ,  $a_2'$ ,  $e'$ , and  $e''$  orbitals, respectively.<sup>14</sup> The electronic transition  ${}^2A_2'' \leftarrow {}^2E''$  is predicted to occur near 649 nm, and the gas-phase emission spectrum<sup>14</sup> reveals a strong sharp band at 15 410 cm<sup>-1</sup>. These confirm the assignment of the 671-nm absorption to the  ${}^2A_2'' \leftarrow {}^2E''$  transition of the 1,3,5-TCB cation. Furthermore, previous matrix emission work has assigned this electronic transition in the argon matrix at 14 886 cm<sup>-1</sup>, red-shifted 380 cm<sup>-1</sup>

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Scheme I



from the electronic origin in a neon matrix,<sup>17</sup> and in excellent agreement with the present 671.6-nm ( $14\,890\text{ cm}^{-1}$ ) absorption value. The argon matrix absorption contrasts with the earlier excitation spectrum<sup>17</sup> in that weaker bands appear (i.e., 677 nm) in the absorption spectrum due to minor matrix sites that are not sampled in the excitation study; however, the sharp vibrational intervals (denoted in Figure 3a) agree to within  $4\text{ cm}^{-1}$  for the absorption and excitation measurements and to  $\pm 9\text{ cm}^{-1}$  with gas-phase intervals.<sup>17,18</sup> The vibrational assignments for the visible vibronic system are given in Table I. The observed vibrational frequencies are also in excellent agreement with spacings in the excitation spectrum measured in solid neon<sup>17</sup> and with vibrational intervals of the neutral molecule.<sup>19</sup>

**1,2,4-Trichlorobenzene.** By analogy with the 1,3,5-TCB cation, it is reasonable to identify the 544.9-nm electronic origin in the 1,2,4-TCB spectra with a transition from the ground state of the 1,2,4-TCB radical cation (electron "hole" in the ring) to an excited state of the cation with a "hole" in a chlorine lone pair orbital. Unfortunately, photoelectron and emission spectra have not been reported for this species. The absorption at 331.4 nm is probably due to a  $\pi^* \leftarrow \pi$  transition of the 1,2,4-TCB cation, analogous to the 322.5-nm band for PDCB cation.<sup>13</sup> Table II gives vibrational intervals for the 1,2,4-TCB cation vibronic band system and compares vibrational assignments for the neutral molecule. It is seen that the vibrational fundamentals for the excited state 1,2,4-TCB cation are not changed significantly ( $2\text{--}46\text{ cm}^{-1}$ ) from the ground-state molecule.<sup>20</sup>

The weak absorptions that appeared at 671.6, 662.1, and 653.1 nm upon argon resonance photoionization in the 1,2,4-TCB experiments have been assigned above to the 1,3,5-TCB cation produced in this experiment from 1,2,4-TCB rearrangement after photoionization but before trapping in solid argon, as will be discussed below. Attempts to facilitate further rearrangement of the 1,2,4-TCB cation to the 1,3,5-TCB cation by warming the matrix to 40 K and photolyzing the warm sample were unsuccessful.

**Photochemistry and Rearrangement.** Observations from the matrix photoionization and photolysis experiments indicate that ODCB and MDCB radical cations rearrange to the PDCB cation and that the 1,2,4-TCB cation rearranges much less efficiently to the 1,3,5-TCB cation. A probable mechanism for this rearrangement involves the formation of an excited bridged chloronium ion species as an intermediate. Before the chloronium ion can form, however, a chlorine lone pair hole excited state must be created; this excited state can be formed in two ways. First, the argon resonance lamp (11.6–11.8 eV) is capable of producing the excited state of the radical cation directly, where an electron is removed from an orbital centered primarily on the chlorine. PES show that the necessary energies are 11.46 eV for MDCB, 11.7 eV for ODCB, and 11.25 eV for 1,3,5-TCB.<sup>14</sup> Therefore, the

rearranged species was formed quite efficiently upon argon resonance irradiation during sample condensation, and the yield increased markedly with vacuum ultraviolet light intensity as determined by lamp power and orifice size. Second, visible photolyses from the filtered high-pressure mercury arc are capable of exciting the radical cation from its ground state which is itself accessible by argon discharge irradiation. The energies necessary for formation of the ground state of the ion with the "hole" in the ring are 9.12 eV for MDCB, 9.06 eV for ODCB, and 9.34 eV for 1,3,5-TCB.<sup>14</sup> Therefore, an increase in the yield of the rearranged species was observed for dichlorobenzene cations upon visible irradiation which promotes the hole from the ring to the chlorine lone pair. The photochemistry and/or rearrangement of the individual chlorobenzene cations will now be analyzed.

**m-Dichlorobenzene.** Experiments with the MDCB precursor irradiated by intense vacuum ultraviolet light (3-mm discharge orifice tube operating at full power) gave a larger relative yield of PDCB<sup>+</sup> to MDCB<sup>+</sup> than the experiment using less intense vacuum ultraviolet (1-mm orifice with argon discharge at minimum power). This is consistent with the capability of the argon photoionization to directly produce the excited state of MDCB<sup>+</sup> with its subsequent rearrangement to PDCB<sup>+</sup> before trapping of the radical cation. Furthermore, as expected, visible photolysis (Figure 1) increased the yield of the rearranged product (PDCB<sup>+</sup>) and lowered the absorbance of the precursor cation (MDCB<sup>+</sup>). It is very important to note that the yield of PDCB<sup>+</sup> must be caused by rearrangement during the matrix experiment, as there was only a trace of PDCB contamination in the MDCB precursor.

**o-Dichlorobenzene.** Experiments with the ODCB precursor using a 3-mm orifice discharge tube resulted in a significantly greater yield of PDCB<sup>+</sup> than ODCB<sup>+</sup>, and no MDCB<sup>+</sup> was observed. In 1-mm discharge experiments conducted at minimum discharge power, vibronic band systems due to ODCB<sup>+</sup>, MDCB<sup>+</sup>, and PDCB<sup>+</sup> were all observed. However, in the latter case, the yield of the parent ODCB cation was greater than the yield of either rearranged product. Subsequent visible photolyses first increased the yield of the MDCB cation while reducing the band systems due to the ortho cation and then reduced the MDCB<sup>+</sup> absorbance and increased the PDCB<sup>+</sup> absorbance as described above. These observations are consistent with the proposition that ODCB<sup>+</sup> rearranges upon photoexcitation to MDCB<sup>+</sup>, which itself subsequently rearranges to the PDCB<sup>+</sup> product. It is again important to establish that trace PDCB and MDCB contamination in the neutral precursor cannot be responsible for the large yields of the meta and para cations detected in the spectrum.

Scheme I outlines the rearrangements proposed for the dichlorobenzene cation system. The necessary intermediate in this mechanism is the bridged chloronium cation species which is formed from the excited chlorine hole cation state. This mechanism is consistent with the observation of more PDCB<sup>+</sup> than ODCB<sup>+</sup> and no MDCB<sup>+</sup> in ODCB experiments with intense vacuum ultraviolet radiation. With a concerted 1,2-hydrogen shift, the bridged species allows a "chloronium ion walk" to the rearranged product, which relaxes to the ground cation state in the matrix.

**1,3,5-Trichlorobenzene.** Photolyses at 290–1000 and 220–1000 nm significantly reduced the absorbance of the 1,3,5-TCB cation

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while the 420–1000-nm photolysis failed to alter the band systems. The decrease in stable cation absorbance with UV photolysis is due to photodetachment of electrons from chloride ion traps (340-nm threshold)<sup>21</sup> and the resulting neutralization of trapped cations. Similar behavior has been observed for CF<sub>3</sub><sup>+</sup> in a matrix containing Cl<sup>-</sup> electron traps.<sup>22</sup>

**1,2,4-Trichlorobenzene.** Matrix photoionization experiments with 1,2,4-TCB produced a small but detectable yield of the 1,3,5-TCB radical cation. Visible photolysis did not increase the yield of rearrangement produced, and, as expected, 220–1000-nm photolysis reduced all band systems. The failure to observe significant rearrangement of 1,2,4-TCB<sup>+</sup> to 1,3,5-TCB<sup>+</sup> in the matrix may be due to some intrinsic stability of chlorines located para to one another in the cation, since, for instance, both MDCB<sup>+</sup> and ODCB<sup>+</sup> rearranged to PDCB<sup>+</sup>. Although the 1,3,5-TCB<sup>+</sup> yield was low, it could not be due to contamination in the 1,2,4-TCB neutral precursor.

### Conclusions

Dichlorobenzene and trichlorobenzene cation isomers have been produced and trapped in matrix photoionization experiments for observation of cation absorption spectra. The matrix absorption

bands are sharp, and the several different isomers can be identified from the spectra. This matrix study shows that the relative absorbances of the dichlorobenzene cation isomers depend on the intensity of vacuum ultraviolet photoionization and visible irradiation of the trapped cation products. It is proposed that *o*- and *m*-dichlorobenzene cations can rearrange to *p*-dichlorobenzene cation after argon resonance photoionization of the precursor molecule or upon filtered high-pressure mercury arc photolysis of the precursor cation. A plausible mechanism for this rearrangement involves a bridged chloronium ion intermediate that is formed from the lone pair hole excited state of the precursor dichlorobenzene cation. This excited state of the cation is accessible either from the argon resonance lamp directly (11.6–11.8 eV) or by visible irradiation of the ground-state cation in the matrix. The matrix cage may aid the formation of the bridged chloronium cation intermediate by quenching excess internal energy. Accordingly, the chlorine lone pair hole excited state provides the necessary conditions for a "chloronium ion walk" around the aromatic ring.

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**Registry No.** MDCB, 541-73-1; ODCB, 95-50-1; 1,3,5-TCB, 108-70-3; 1,2,4-TCB, 120-82-1.

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## Valence Transitions in *cis*- and *trans*-Hexatrienes

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**Abstract:** In this experimental investigation of the valence states of *cis*- and *trans*-hexatrienes, two triplet and two singlet valence transitions are observed in each isomer. Differences are observed between the *cis*- and *trans*-hexatriene spectra. A comparison of the *trans*-hexatriene results with the best ab initio and semiempirical calculations suggests that the B<sub>u</sub><sup>+</sup> and A<sub>g</sub><sup>+</sup> singlet states are observed and that the A<sub>g</sub><sup>-</sup> state, while not observed, is above the B<sub>u</sub><sup>+</sup> state. The relation of these results to the polyene problem will be discussed.

We have conducted an experimental investigation of the valence transitions of *cis*- and *trans*-hexatrienes. Various experimental techniques were used in an attempt to locate all singlet–triplet transitions below the first allowed singlet–singlet transitions as well as all other forbidden valence transitions. Previous investigations of hexatrienes include optical absorption,<sup>1–3</sup> electron energy loss,<sup>4–8</sup> electron attachment,<sup>9</sup> photoelectron,<sup>10</sup> resonant multiphoton ionization,<sup>11</sup> and excited-state absorption<sup>12</sup> spectroscopies. In most of these investigations, the two geometric isomers were separated and individually investigated, but in several of the electron energy loss investigations, mixed isomer samples were used and assumed to contain predominantly the *trans* isomer. In addition to these experimental investigations, both ab initio<sup>13</sup> and semiempirical<sup>3,14,15</sup> calculations have been carried out on the *trans* isomer.

The basic question which underlies the interest in these molecules is whether or not the valence manifold of polyenes can be

described solely in terms of one-electron transitions. It appears that for the longer polyenes (*n* > 3), in condensed phases, at least,

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