Absorption Spectra and Rearrangements of Halotoluene Parent Cations in Solid Argon

Brian W. Keelan and Lester Andrews*

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901. *Received February 25, 1980*

Abstract: Matrix photoionization of dilute fluorotoluene samples produced relatively sharp photosensitive absorptions in good agreement with gas-phase photodissociation spectra for ring-substituted fluorotoluene parent cations. The benzyl chloride parent cation form was observed as a sharp, photosensitive 469.3 nm band in both benzyl chloride and *p*-chlorotoluene experiments, whereas chlorotoluene cations gave broad absorptions with little photolysis. Experiments with *o*- and *p*-fluorotoluene produced parent cation absorptions, which were considerably sharper than the gas-phase PDS, and the matrix absorptions exhibited vibrational structure. Benzyl and substituted benzyl radicals were also observed in these experiments.

Introduction

Halotoluene parent cations have been studied in the gas phase by mass spectrometric techniques,[1-6] photoelectron spectroscopy (PES),[7,8] and photodissociation spectroscopy (PDS).[8,9] Rearrangement between the benzyl halide and ring-substituted halotoluene structural forms is of particular interest; recent PDS observations with benzyl chloride showed two distinct $C_7H_7Cl^+$ populations.[9] Several studies have suggested that ring-expanded halocycloheptatriene cations are intermediates in these isomerization processes.[1,4,6]

Molecular ions can be produced and trapped in solid argon for absorption spectroscopic and photochemical studies which are complementary to gas-phase work.[10] In a recent matrix photoionization study, the toluene parent cation was observed in solid argon at 2.88 eV (430 nm),[11] in very good agreement with the gas-phase PDS band peak at 2.97 eV[8] and 3.0-eV difference between the adiabatic first and vertical second ionization energies from the PES.[7] In a following matrix investigation, cycloheptatriene cation was found to rearrange to toluene cation upon visible photolysis.[12] The present halotoluene study was undertaken to explore the relationship between gas-phase PDS and matrix absorption spectra and to further examine the rearrangements of the halotoluene parent cations.

Experimental Section

The cryogenic apparatus for optical absorption studies and the windowless argon resonance lamps have been described previously.[13,14] The hydrogen resonance lamp consisted of a 12-mm o.d. Pyrex tube, with a 6-mm o.d. side arm, vacuum sealed by a $^1/_2$ in. ultra-torr fitting to the outside of a brass flange with a 1 in. × 2 mm thick diameter MgF_2 window sealed by an O-ring on the inside, similar to that used by Milligan and Jacox.[15] Either 2% or 5% samples of hydrogen in argon were pumped through the tube and excited by a microwave discharge. Samples of benzyl fluoride, *p*-, *o*-, and *m*-fluorotoluene, benzyl chloride, *p*-, *o*-, and *m*-chlorotoluene, benzyl bromide, and *p*-bromotoluene (all Aldrich) were distilled from glass beads following outgassing and then diluted with argon to matrix/reactant (M/R = 100/1, 200/1, 300/1, or 400/1). A sample of benzyl chloride-d_7 was synthesized by photolysing toluene-d_8 (Merck, Sharpe and Dohme) vapor (20 torr) and Cl_2 (26 torr) in a 2-L Pyrex bulb for 2 h which formed liquid on the bulb wall. The product was cooled to -63 °C and evacuated for 60 min to remove Cl_2 and most of the unreacted toluene. Prior to sample preparation, the bulb was evacuated at room temperature for 1 min to remove the last traces of toluene; dilution with argon produced an M/R = 100/1 sample. Samples were condensed at about 1 mM/h for 3-5 h on a sapphire window at 20 K (argon resonance photoionization experiments) or 12 K (hydrogen resonance photoionization studies). In the argon resonance photoionization experiments, simultaneous irradiation and argon deposition from the windowless discharge tube caused the final sample concentrations in the matrix to be roughly half that of the original sample. The hydrogen resonance lamp was used only *after* sample deposition, generally 10 min of irradiation per hour of sample deposition followed by more sample and more irradiation in turn. All species produced with this technique were formed in a "cold" matrix that allowed little fragment mobility. Spectra were taken with a Cary 17 spectrophotometer from 800 nm down to the parent absorptions, generally near 270 nm. Samples of the precursors were deposited without discharge radiation to determine precursor absorptions. Photolyses were performed with a high-pressure mercury arc (1000-W, BH-6-1, Illumination Industries, Inc.) by using an ultraviolet mirror and Corning glass cutoff filters. High-resolution spectra were recorded at 0.2 nm/s and 3 nm/in before and after each photolysis. Band positions reported to 0.1 nm are accurate to ±0.1 nm; others are accurate to ±0.5 nm.

Results

Matrix photoionization experiments performed with fluoro-, chloro-, and bromotoluenes will be described.

Fluorotoluenes. The optical spectrum of a 1% benzyl fluoride-argon sample subjected to continuous argon resonance irradiation from an 8-mm i.d. orifice discharge tube is shown in Figure 1a. A broad 442-nm band (A = 0.005) was destroyed by 10 min of 420-nm photolysis, while a 437.9-nm absorption (A = 0.010) was substantially decreased; 30 min more of 420-nm photolysis destroyed the latter feature, as shown in Figure 1b. Absorptions at 449.6 and 430 nm resisted even full-arc photolysis. The photolysis behavior of the strong sharp band at 310.4 nm with satellite features at 305.2, 301.0, and 297.7 nm could not be determined due to light scattering by the sample.

The spectrum from a *p*-fluorotoluene experiment, shown in Figure 1c, contained a series of absorptions at 437.9 (A = 0.09), 431.5 (A = 0.01), and 423.5 nm (A = 0.02) which were destroyed by 420-nm light, as indicated in Figure 1d. The strong 437.9-nm absorption bandwidth is 104 cm^{-1} at half-maximum. A band at 329.8 nm was destroyed by full-arc photolysis, whereas bands at 465.4, 308.0, 303.5, and 296.2 nm were unaffected by the photolyses. A hydrogen resonance photolysis experiment yielded only the 437.9 ($A \approx$ 0.005) and 308.0 nm (A = 0.01) absorptions. The

---

(1) Tait, J. M. S.; Shannon, W. T.; Harrison, A. G. *J. Am. Chem. Soc.* **1962**, *84*, 4.

(2) Brown, P. *J. Am. Chem. Soc.* **1968**, *90*, 4459, 4461.

(3) Brown, P. *Org. Mass Spectrom.* **1970**, *3*, 639.

(4) Yeo, A. N. H.; Williams, D. H. *Chem. Commun.* **1970**, 886.

(5) Jackson, J. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.

(6) Stapleton, B. J.; Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1219.

(7) Baker, A. D.; May, D. P.; Turner, D. W. *J. Chem. Soc. B* **1968**, 22.

(8) Dymerski, P. P.; Fu, E. W.; Dunbar, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 4109.

(9) Fu, E. W.; Dymerski, P. P.; Dunbar, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 337.

(10) Andrews, L. *Annu. Rev. Phys. Chem.* **1979**, *30*, 79.

(11) Andrews, L.; Miller, J. H.; Keelan, B. W. *Chem. Phys. Lett.* **1980**, *71*, 207.

(12) Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1980**, *102*, 5732.

(13) Andrews, L. *J. Chem. Phys.* **1975**, *63*, 4465.

(14) Andrews, L.; Tevault, D. E.; Smardzewski, R. R. *Appl. Spectrosc.* **1978**, *32*, 157.

(15) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1974**, *47*, 5146.

0002-7863/81/1503-822$01.00/0

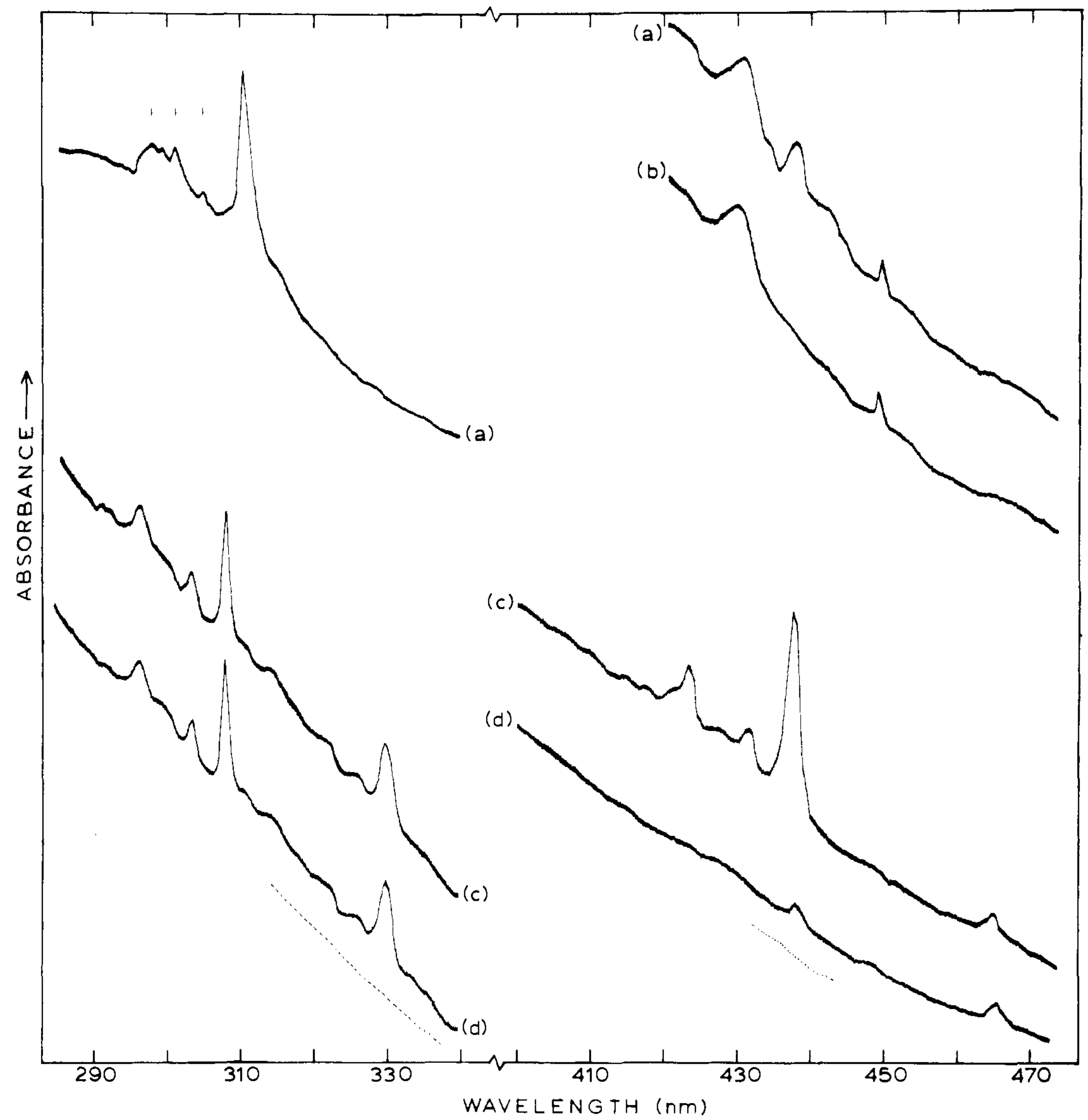


Figure 1. Absorption spectra of fluorotoluene samples subjected to argon resonance photoionization from windowless lamp during condensation. (a) Ar/benzyl fluoride = 100/1 after deposition and (b) after 40 min of 420–1000-nm photolysis. (c) Ar/*p*-fluorotoluene = 100/1 after condensation and (d) after 30 min of 420–1000-nm photolysis. Dashed trace shows changes after 220–1000 nm photolysis.

Table I. Absorptions (nm) and Intensities (Absorbance Units) Observed in Fluorotoluene Experiments[a]

benzyl fluoride					*p*-fluorotoluene				
absorptns	(I_0)	I_1	I_f	ID[b]	absorptns	(I_0)	I_1	I_f	ID[b]
449.6	(0.005)	0.005	0.005	B	465.4	(0.01)	0.01	0.01	PFB
442	(0.005)	0.000	0.000	AFT$^+$					
437.9	(0.010)	0.000	0.000	PFT$^+$	437.9	(0.090)	0.01	0.00	PFT$^+$
					431.5	(0.015)	0.00	0.00	PFT$^+$
					423.5	(0.024)	0.00	0.00	PFT$^+$
430	(0.01)	0.01	0.01	?	329.8	(0.08)	0.08	0.00	R
					326	(0.02)	0.02	0.00	R
310.4	(0.38)	*c*	*c*	B	322	(0.02)	0.02	0.00	R
305.2	(0.01)	*c*	*c*	B	308.0	(0.14)	0.14	0.14	PFB
301.0	(0.10)	*c*	*c*	B	303.5	(0.04)	0.04	0.14	PFB
297.7	(0.08)	*c*	*c*	B	296.2	(0.03)	0.03	0.03	PFB

[a] (I_0) indicates product band absorbance units, I_1 is after 420- or 380-nm photolysis, I_f is after final full-arc photolysis, and ID denotes identification. [b] B denotes benzyl radical, PFB denotes *p*-fluorobenzyl radical, and R denotes another type of free radical discussed in the test. [c] Not recorded.

new absorptions observed in α- and *p*-fluorotoluene experiments are summarized in Table I.

The spectrum from a second *p*-fluorotoluene study, compared in Figure 2 with spectra from the other ring-substituted isomers, is almost identical with the first study. This sample was subjected to 500-nm photolysis for 30 min which caused no changes in the absorptions; 420-nm photolysis had the same effect listed in Table I. Photolysis with 290-nm cutoff light eliminated the last trace of 437.9-nm absorption and halved the 330-nm band system without affecting the 308-nm system. As before the 330-nm band was destroyed and the 308-nm absorption was not changed by full-arc irradiation.

Another *p*-fluorotoluene experiment was done in krypton by using krypton discharge radiation for a 3-h period, and the

Table II. Absorptions (nm) and Intensities (Absorbance Units) Observed in Fluorotoluene Experiments[a]

o-fluorotoluene					*m*-fluorotoluene				
absorptns	(I_0)	I_1	I_f	ID[b]	absorptns	(I_0)	I_1	I_f	ID[b]
459.1	(0.026)	0.020	0.036	OFB	464.2	(0.007)	0.014	0.014	MFB
450.8	(0.005)	0.004	0.004	OFB	454.8	(0.002)	0.004	0.004	MFB
444.5	(0.010)	0.008	0.008	OFB					
429.5	(0.026)	0.005	0.000	OFT$^+$	444	(0.004)	0.000	0.000	MFT$^+$
416.6	(0.008)	0.000	0.000	OFT$^+$	437.9	(0.006)	0.004	0.000	PFT$^+$
326.0	(0.06)	0.06	0.00	R	318.4	(0.010)	0.010	0.000	R
311.7	(0.27)	0.20	0.16	OFB	310.5	(0.030)	0.06	0.06	MFB
309.0	(0.14)	0.10	0.08	OFB	307.8	(0.015)	0.03	0.03	MFB
305.0	(0.08)	0.06	0.04	OFB					
300.8	(0.12)	0.08	0.06	OFB					
298.2	(0.11)	0.07	0.05	OFB					

[a] (I_0) indicates product band absorbance units, I_1 is after 420- or 380-nm photolysis, I_f is after final full-arc photolysis, and ID denotes identification. [b] OFB and MFB denote the *o*- and *m*-fluorobenzyl radical isomers. R denotes another type of free radical discussed in the text.

spectrum is illustrated in Figure 2a. The product absorptions were red-shifted 2–4 nm from their argon matrix counterparts, and the relative yields of the several product species were altered. The 441.8-nm band was reduced to 20% of its 437.9-nm argon matrix counterpart whereas the 332.5-nm band was doubled and the 467-, 310.3-, 305.7-, and 298.2-nm bands were increased fourfold over their argon matrix counterparts.

Two experiments were performed with meta isomer and two with the ortho isomer; product bands and intensities are given in Table II. The *o*-fluorotoluene experiments gave band patterns and photolysis behavior similar to the para isomer. New bands at 429.5 (A = 0.026) and 416.6 nm (A = 0.008) were virtually destroyed by 380-nm photolysis, as shown in Figure 2c. A new 326.0-nm absorption was destroyed by 220-nm photolysis whereas new band systems beginning at 459.1 and 311.7 nm were decreased 20% by 380-nm irradiation and another 20% by the full arc.

The *m*-fluorotoluene studies gave lower product yields. A new weak 444-nm (A = 0.004) band was destroyed upon 420-nm photolysis that reduced a 437.9-nm band, Figure 2d. A new 318.4-nm feature was unaffected by 420-nm light but destroyed by the full arc. New bands at 464.2, 454.8, 310.5, and 307.8 nm were doubled by 420-nm photolysis and unchanged upon exposure to the full arc.

Chlorotoluenes. The spectrum after argon resonance irradiation of a benzyl chloride (α-chlorotoluene) sample (Ar/C_7H_7Cl = 100/1) during deposition is shown in Figure 3a. New product bands at 707.8 (absorbance = A = 0.15), 664.7 (A = 0.010), 469.3 (A = 0.15), 463.7 (A = 0.01), 452.7 (A = 0.03), 449.5 (A = 0.01), and 447.3 nm (A = 0.01) were destroyed on full-arc (220–1000-nm) photolysis, as illustrated in the dashed trace in Figure 3a, which revealed broad bands at 453 and 467 nm. The strong 469.3-nm absorption bandwidth is 68 cm^{-1} at half-maximum. Bands at 314.7 and 302 nm were each reduced by full-arc photolysis, whereas the dominant absorption in this region at 310.4 nm was unaffected. The product bands and absorbances in this benzyl chloride experiment are listed in Table III. Two other similar experiments produced the sharp 469.3-nm band (A = 0.10) and the sharp structure on the short wavelength side, and the 664.7- and 707.8-nm bands with the same relative intensities. In one of these studies, photolysis with 520-nm cutoff radiation had no effect on the spectrum, but 420-nm photolysis almost destroyed the 469.3-nm band (to A = 0.01), destroyed the sharp associated structure and the 664.7- and 707.8-nm bands, and produced new absorption at 453 (A = 0.033) and 467 nm (A = 0.024); 290-nm photolysis increased the latter bands, 453 (to A = 0.042) and 467 nm (to A = 0.032). In the other experiment, 380-nm photolysis destroyed the red and blue product bands and produced new 453- (A = 0.044) and 467-nm (A = 0.035) absorption, and final photolysis with the full arc reduced both bands, 453 (to A = 0.029) and 467 nm (to A = 0.032).

Hydrogen resonance photolysis of an argon/benzyl chloride = 400/1 sample after deposition produced the stronger 469.3-, 463.7-, and 452.7-nm bands, as shown in Figure 3b, with absorptions reduced to 25% of their values produced by continuous argon resonance photolysis. In addition the 708-nm absorption was detected ($A \approx 0.005$), but the 665-nm band was not observed above the noise level in the hydrogen resonance photolysis experiment.

Table III. Absorptions (nm) and Intensities (Absorbance Units) Observed in Chlorotoluene Experiments[a]

benzyl chloride			*p*-chlorotoluene				
absorptns	(I_0)	I_f	absorptns	(I_0)	I_1	I_f	ID[b]
707.8	(0.02)	0.00	707.8	(0.015)	0.00		ACT$^+$
664.7	(0.01)	0.00	664.7	(0.010)	0.00		ACT$^+$
			500	(0.02)	0.02	0.01	PCT$^+$
			492	(0.04)	0.04	0.02	PCT$^+$
			483	(0.08)	0.08	0.04	PCT$^+$
			475	(0.13)	0.13	0.07	PCT$^+$
469.3	(0.15)	0.00[c]	469.3	(0.12)	0.00		ACT$^+$
463.7	(0.01)	0.00	463.7	(0.01)	0.00		ACT$^+$
452.7	(0.03)	0.00[c]	452.7	(0.01)	0.00		ACT$^+$
449.5	(0.01)	0.00	449	(w)	0.00		ACT$^+$
447.3	(0.01)	0.00	447	(w)	0.00		ACT$^+$
			335.0	(0.06)	0.06	0.00	R
			331.0	(0.01)	0.01	0.00	R
			327.1	(0.01)	0.01	0.00	R
314.7	(0.04)	0.02					*b*
			312.7	(0.10)	0.10	0.12	PCB
310.4	(0.09)	0.09					B
301.7	(0.03)	0.02					*b*

[a] (I_0) indicates product band absorbance, I_1 is after 420–1000-nm photolysis, and I_f is absorbance after final 220–1000-nm photolysis. [b] See text for possible identifications. PCB is *p*-chlorobenzyl radical and B is benzyl radical. [c] Broad 453-nm band remaining after photolysis (A = 0.02) suggests that 452.7-nm peak (A = 0.01) on top of 453-nm band represents the change on photolysis; broad 467-nm band (A = 0.02) also remains on photolysis. These broad bands, unique to the benzyl chloride experiments, cannot be identified from the present information.

The spectrum from a *p*-chlorotoluene M/R = 100/1 argon resonance experiment is shown in Figure 3c which is similar to the α-chlorotoluene spectrum in many respects. Absorptions observed at 707.8, 664.7, 469.3, 463.7, and 452.9 nm were not affected by 520-nm photolysis but were destroyed with 420-nm light, as shown in Figure 3d and given in Table III. An absorption system at 335.0, 331.1, and 327.1 nm and a broad 310-nm band were destroyed upon 220-nm photolysis which more clearly revealed a new 312.7-nm band. Broad bands at 475, 481, and 492 nm unique to the *p*-chlorotoluene study were approximately halved in intensity by 220-nm photolysis. A similar 300/1 experiment gave a reduced yield of the sharp 469.3-nm (A = 0.08) and the 664.7- and 707.8-nm bands and increased broad bands at 492 (A = 0.03) and 500 nm (A = 0.01). Photolysis with 520–1000-nm radiation had no effect on the spectrum; 420–1000-nm light virtually destroyed the sharp 469.3-nm band and the weaker 664.7- and 707.8-nm bands and reduced the broad bands by 25%; a final 220–1000-nm photolysis reduced the broad bands to half of their original absorbances. In another experiment with a similar yield

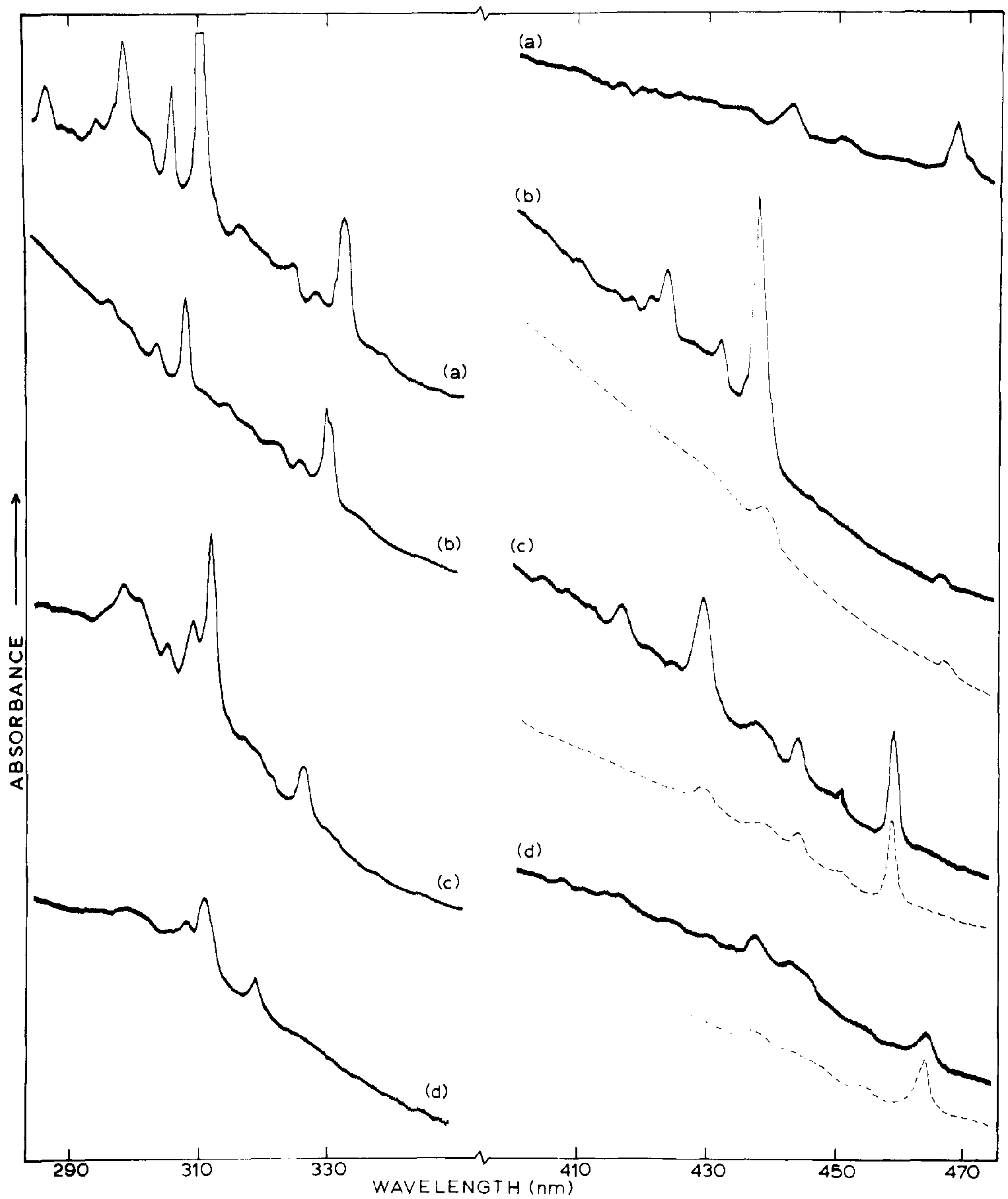


Figure 2. Absorption spectra of fluorotoluene cations and fluorobenzyl radicals prepared by matrix photoionization of 1% fluorotoluene samples: (a) krypton, para; (b) argon, para, dashed trace after 30 min of 420–1000-nm photolysis; (c) argon, ortho, dashed trace after 380–1000-nm photolysis; (d) argon, meta, dashed trace after 420–1000-nm photolysis.

of product absorptions, 470-nm cutoff photolysis reduced the 707.8-nm band (A = 0.009–0.003), the 664.7-nm band (A = 0.006 to 0.001), and reduced the sharp 469.3-nm absorption (A = 0.15 to 0.05) and its associated bands. A 380-nm photolysis eliminated the above features without producing any new absorption and decreased the broad 475-nm feature about 20%; final 220-nm photolysis had little additional effect.

A hydrogen resonance experiment with *p*-chlorotoluene, illustrated in Figure 4b, produced a series of broad bands at 500 (A = 0.01), 492 (A = 0.02), 483 (A = 0.02), 475 (A = 0.03), 468 (A = 0.02), and 461 nm (A = 0.01), and broad features were observed at 300 and 310 nm; the sharp 469.3-nm absorption and 665- and 708-nm bands were not observed.

Two *o*-chlorotulene experiments with argon resonance photolysis produced a broad band with maxima at 470 and 480 nm (A = 0.03), a broad band at 442 nm, a sharp, weak band at 469.3 nm (A = 0.005), and new absorptions at 327.7 (A = 0.03), 320.7 (A = 0.04), and 310.6 nm (A = 0.02), which are shown in Figure 4d. Full-arc photolysis halved the broad bands and destroyed the sharp 327.7-nm feature, as illustrated in the dashed trace of Figure 4d. In a similar *m*-chlorotoluene experiment, a broad band was observed with maxima at 466 and 482 nm, a sharp band appeared at 326.3 nm (A = 0.20), and weak features were found at 319 and 310 nm as shown in Figure 4c. Photolysis with 290-nm radiation destroyed the 326-nm band and slightly decreased the broad visible bands.

Several experiments were performed with α-chlorotoluene-d_7 in an attempt to observe deuterium counterparts of the weaker bands above the strong 469.3-nm absorption in C_7H_7Cl studies. The only product was a sharp band at 467.8 nm (A = 0.01) in three experiments; this absorption was decreased 50% by 420-nm photolysis in all three studies.

Bromotoluenes. All bromotoluene experiments were done with equilibrium vapor diluted by 100 torr of argon to give approximately 1% gas mixtures, and the argon photolysis experiments employed a 3-mm i.d. orifice discharge tube. The benzyl bromide

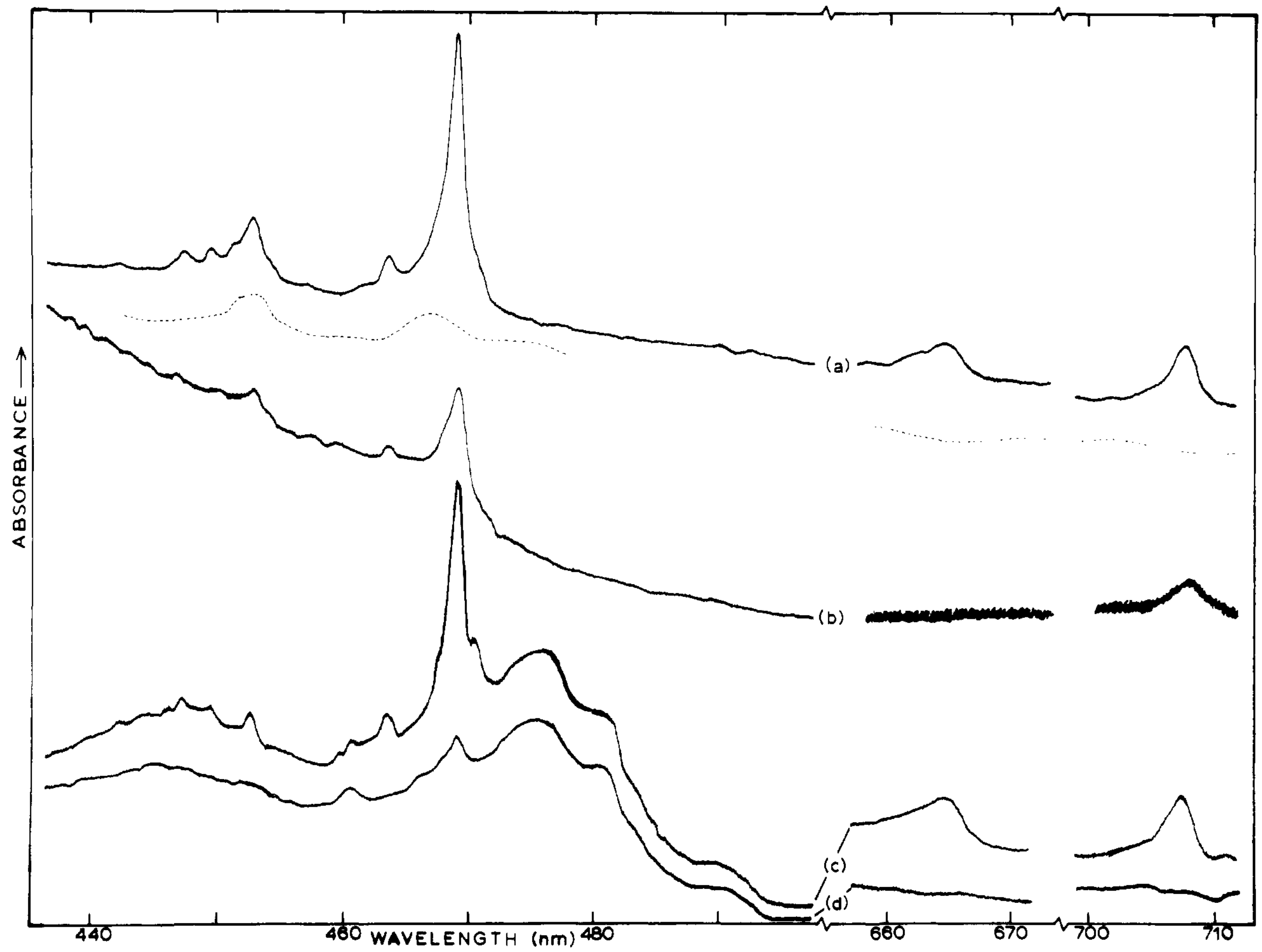


Figure 3. Absorption spectra of chlorotoluene samples subjected to matrix photoionization: (a) Ar/benzyl chloride = 100/1 sample photoionized by argon discharge radiation *during* condensation and diluted by argon from the discharge, dashed spectrum recorded after 220–1000-nm photolysis; (b) Ar/benzyl chloride = 400/1 sample subjected to hydrogen resonance photoionization *after* deposition; (c) Ar/*p*-chlorotoluene = 100/1 sample subjected to argon resonance photoionization from 3-mm orifice discharge tube; (d) sample from (c) after 520–1000-nm *and* 420–1000-nm photolysis.

spectrum revealed broad absorptions at 338 ($A \approx 0.4$), 495 ($A \approx 0.03$), and 540 nm ($A \approx 0.04$), which were decreased by 520-nm photolysis at 25 K. In a *p*-bromotoluene experiment, a weak 743-nm absorption ($A = 0.01$) was destroyed by 420-nm photolysis and a broad band at 495 nm ($A = 0.15$) was decreased, whereas a band at 314 nm was unaffected by the same treatment. A broad band ($A = 0.15$) with partially resolved peaks at 548, 541, 534, and 526 nm exhibited a 250-cm^{-1} average spacing and decreased upon 420-nm photolysis. The unresolved progression peaking at 540 nm and broad 495-nm band ($A = 0.01$) were also observed in a hydrogen resonance photolysis experiment with *p*-bromotoluene.

Discussion

Identification of Product Absorptions. The product absorptions in this study are conveniently divided by their photolysis behavior into four groups: (1) sharp photosensitive absorptions in the 400–800-nm region, (2) broad structured absorptions in the 400–600-nm region which exhibit some photolysis, (3) sharp bands in the 290–315-nm region stable to photolysis, and (4) band systems at 320–335 nm which photolyze with the full arc.

In previous matrix isolation studies, parent cations have been found to be photosensitive as elimination of a hydrogen or halogen atom is a favorable process,[11,12,16,17] since appearance potentials of daughter cations are usually 1–3 eV higher than the ionization energy of the precursor.[18] The photosensitive bands in group (1) are considered for assignment to parent cations produced by photoionization of precursor molecules (ionization ~9 eV)[15] with argon resonance radiation (11.6–11.8 eV)[14] during sample condensation at 22 K, which entraps the product cation in solid argon.

The *p*-fluorotoluene experiments in argon produced a strong sharp 437.9-nm absorption which photolyzed with 420-nm light, and the *o*-fluorotoluene studies gave a similar photosensitive band at 429.5 nm. Weak photosensitive absorptions were found at 444 nm in the *m*-fluorotoluene studies and at 442 nm with benzyl fluoride. These photosensitive absorptions in solid argon are near the PDS bands observed for fluorotoluenes in the 420 ± 5-nm region,[9] and accordingly the matrix absorptions are assigned to the parent cations (hereafter called PFT$^+$, OFT$^+$, MFT$^+$, and AFT$^+$, respectively). It is noteworthy that the 437.9-nm absorption was observed following hydrogen resonance photoionization of a cold matrix sample, which prevents the departure of large fragments from the site of photolysis. The 431.6- and 423.2-nm absorptions in the *p*-fluorotoluene experiments and the 416.6-nm band in *o*-fluorotoluene studies are probably due to vibrational structure, which will be discussed later.

Since the fluorine lone pairs do not interact with the aromatic system, in contrast to the chlorine case, the α- and ring-substituted species absorb in the same region involving a $\pi \rightarrow \pi$ transition.[19] The major absorptions for PFT$^+$ and OFT$^+$ are relatively sharp in these experiments, which suggests that the relatively sharp, extremely photosensitive 469.3-nm absorption in benzyl chloride and *p*-chlorotoluene experiments is also a $\pi \rightarrow \pi$ transition. This contrasts ring-substituted chlorine species, which involve interaction

---

(16) Andrews, L.; Prochaska, F. T. *J. Phys. Chem.* **1978**, *83*, 368.

(17) Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 9.

(18) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. No. 1.

(19) Dunbar, R. C.; Teng, H.; Fu, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 6506.

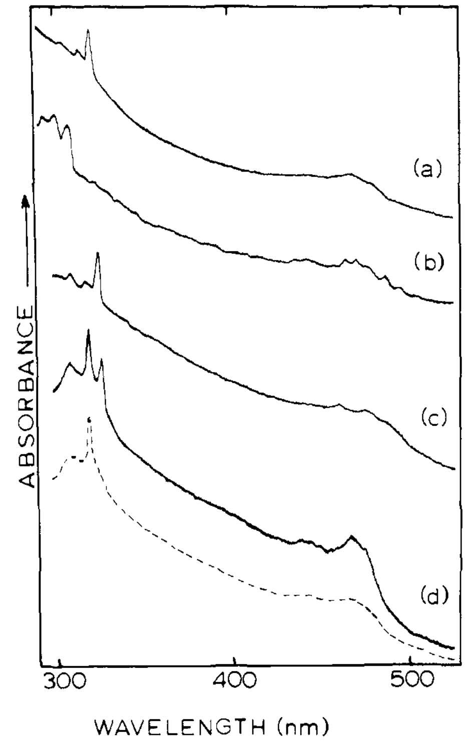


Figure 4. Absorption spectra of chlorobenzene and chlorotoluenes after matrix photoionization of Ar/precursor = 100/1 samples: (a) chlorobenzene subjected to simultaneous argon discharge photoionization; (b) *p*-chlorotoluene sample photoionized by hydrogen lamp *after* deposition; (c) *m*-chlorotoluene simultaneous argon discharge photoionization; (d) *o*-chlorotoluene, simultaneous argon discharge photoionization, dashed trace recorded after 220–1000-nm photolysis.

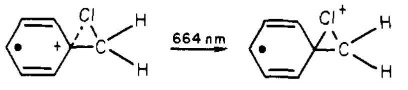
between the chlorine lone pairs and the aromatic ring and produce the broad $n_z \rightarrow \pi$ charge-transfer absorptions (Figure 4), which will be assigned below to the ring-substituted parent cations.

Possible $C_7H_7Cl^+$ structures *without* chlorine conjugated to the π system include benzyl chloride and 7-chlorocycloheptatriene, an intermediate postulated in gas-phase rearrangement processes.[1,4,6] Recent experiments with methyl cycloheptatriene cations in this laboratory gave different broad absorptions for the four methyl cycloheptatriene isomers.[20] This observation, coupled with the cycloheptatriene cation spectrum,[12] casts doubt on a chlorocycloheptatriene assignment for the sharp 469.3-nm absorption, which is therefore believed to be due to the $\pi \rightarrow \pi$ transition of benzyl chloride cation itself.

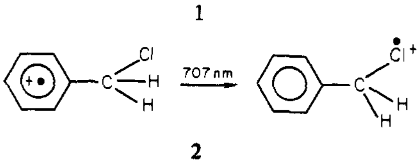
These identifications are supported by comparison of the hydrogen resonance (10.2 eV) photoionization of *cold samples* with results from argon resonance (11.6–11.8 eV) photoionization *during condensation.* The former process should favor photoionization and minimize rearrangement and fragmentation whereas the latter process can allow more rearrangement and fragmentation. The former experiment with *p*-chlorotoluene produced only the broad structured spectrum (Figure 4b), which will be assigned to PCT^+, and the same treatment of benzyl chloride gave ACT^+ (Figure 3b). The latter experiment with *p*-chlorotoluene produced the PCT^+ absorption and the ACT^+ isomer; this technique imparts more internal energy to the parent cations and removal of this energy by the condensing matrix requires a longer time interval, hence more extensive rearrangement is possible.

The gas-phase PDS of benzyl chloride cation gave peaks at 595 and 440 nm, and exhaustive photodissociation in the red band destroyed only 30% of the $C_7H_7Cl^+$ population, which suggested the presence of two different structural modifications. This PDS observation demonstrates that the benzyl chloride cation structure responsible for the 595-nm absorption is not responsible for the 440-nm absorption, which was thought to be due to a ring-substituted structure, although it was noted that the PDS for the latter species peaked near 460 nm.[9] The matrix photolysis behavior and constant relative intensities in α- and *p*-chlorotoluene experiments show that the 707.8, 664.7, and 469.3 nm absorptions could be due to similar species, the former of which will also be assigned below to benzyl chloride cation. It is suggested here that the 440-nm PDS band is due to the same ACT^+ isomer giving the sharp 469-nm argon matrix band.

The two most productive chlorotoluene isomers used in these studies, α and para, also gave new red absorptions at 664.7 and 707.8 nm; these bands were not affected by 520–1000-nm photolysis, but 420–1000-nm radiation destroyed the red bands and the sharp 469 nm absorption discussed above. The proximity of the 664-nm matrix band to the PDS peak at 595 nm in benzyl chloride ICR studies, where the latter was attributed to benzyl chloride cation,[9] suggests that the 664-nm matrix absorption is also due to the benzyl chloride cation (ACT^+). The 707-nm absorption appeared with the 664-nm band and exhibited similar photolysis behavior, so it could also be due to a similar cation. The PES of benzyl chloride exhibited a very strong band at 1.8 eV (689 nm) above adiabatic ionization,[9] which is somewhat lower energy than the PDS band peak (595 nm) but in reasonable agreement with the 708-nm matrix absorption, allowing for a red matrix shift of 391 cm^{-1}. This blue shifting of the PDS peak from the PES band could indicate different geometries for the ions observed in the PDS and PES; in fact the two matrix bands at 664 and 708 nm could be due to benzyl chloride cation involving slightly different geometries, i.e., the 664-nm band being due to a distorted structural form observed in the PDS, such as **1**, and the 469- and 708-nm bands due to the cation with the same geometry as the neutral, **2**. Since the red transition probably involves charge transfer from chlorine to the benzene ring and the chlorine hole is a reactive site, a chloronium structure like **1** could be attained with the excess energy available upon excitation.



1



2

The three ring-substituted chlorotoluene precursors gave broad absorptions in the 460–500-nm region with some structure (group 2), which is common with the major product from chlorobenzene itself[21] (Figure 4a). Since PDS bands for the chlorotoluene and chlorobenzene cations peak in the 459–474-nm range, the broad group (2) matrix bands in this region are probably due to the three ring-substituted chlorotoluene cations. These bands exhibited photolysis, but at a much slower rate than benzyl chloride cation, as might be expected. The maximum dissociation observed for PCT^+ in solid argon was about 50% with 30 min of full-arc irradiation whereas ACT^+ was destroyed by a like exposure to 420-nm photolysis.

The broad PCT^+ absorption exhibited vibrational peaks with intervals near 360 ± 10 and 280 ± 10 cm^{-1}. Although definitive vibrational assignments cannot be made, the neutral molecule[22] has chlorine deformation modes in this region and the $n_z \rightarrow \pi$ charge-transfer transition could excite such vibrations. Broad bands were observed at 495 and 540 nm in the *p*-bromotoluene experiment, which decreased on 420-nm photolysis; the 540-nm band exhibited four vibrational peaks with a 250-cm^{-1} average spacing which is reasonable for a bromine deformation mode based on the spectrum of the neutral molecule. Since the PDS band for *p*-bromotoluene peaks near 520 nm, the broad 495- and 540-nm

---

[20] Kelsall, B. J.; Andrews, L., to be published.

[21] Keelan, B. W.; Andrews, L. *J. Am. Chem. Soc.* **1981**, *103*, 99.

[22] Green, J. H. S. *Spectrochim. Acta* **1970**, *A26*, 1503, 1913.

matrix absorptions are attributed to PBT$^+$. This identification is supported by observation of the 495- and 540-nm bands in a hydrogen resonance photolysis experiment with *p*-bromotoluene.

A weak 743-nm band in the *p*-bromotoluene experiment is probably due to the bromine counterpart of **2**. A shift of 0.3 eV has been noted between the 660-nm PDS band and the PES for benzyl bromide which suggested that the molecular ion does not retain the neutral molecular structure;[6] it is further suggested here that the 660-nm PDS band is due to a structure like **1**. The 743-nm argon matrix band energy position is greater than ionization by an amount in reasonable agreement with the 10.74-eV PES band[8] and is probably associated with the **2** structure. In fact a tail out to 660 nm was observed on all of the ring-substituted bromotoluene PDS bands, indicating rearrangement to the α isomer cation.

The sharp, strong group (3) bands in the 290–315-nm region, which exhibit little if any photolysis behavior, are due to benzyl and substituted benzyl radicals; hydrogen photodetachment is a favorable process in these experiments. The α-fluorotoluene experiment produced the highest yield of benzyl radical observed in this laboratory; the strong 310.4-nm band and associated structure to higher energy have the same profile as the spectrum of benzyl radical in MP glass at −197 °C.[23] The vibrational intervals of 549, 1007, and 1375 cm^{-1} above the 310.4-nm origin are in very good agreement with the MP glass values. The sharp weak 449.6-nm band is the strongest vibronic component of the weaker visible transition of benzyl radical.[11,23] The α-chlorotoluene experiment produced a small yield of benzyl radical as evidenced by the weak 310.4-nm band.

The band system at 308.0, 303.5, and 296.2 nm and the weak 465.4-nm absorption in the *p*-fluorotoluene experiment are due to the *p*-fluorobenzyl radical; comparison of the strong origin band for this radical in EPA glass at 77 K[24] shows that *p*-fluoro substitution *blue* shifts the origin about 3 nm, which is compatable with the matrix result. The visible system, however, is red shifted 16.4 nm from benzyl radical in adamantane[25] which associates the 465.4-nm matrix absorption with *p*-fluorobenzyl radical. The *p*-fluorobenzyl radical (PFB) absorptions are compared in Table I with the benzyl radical (B) absorptions. The *m*- and *o*-fluorobenzyl radical (MFB and OFB) bands are compared in Table II. In the argon matrix studies, the origins of MFB and B are nearly the same, which may help locate this band in the glassy matrix studies. The strong origin and four vibrational intervals for OFB are in excellent agreement with the adamantane spectrum; the vibrational intervals correspond closely to spacings in the emission spectrum of the radical and the vibrational spectra of the precursor.

By comparison to earlier radiolysis work, the 314.7-nm band in benzyl chloride experiments is due to α-chlorobenzyl radical[26] and the 312.7-nm absorption in the para experiments is due to *p*-chlorobenzyl radical.[24] Likewise, the 314-nm band in the *p*-bromotoluene experiment is due to the *p*-bromobenzyl radical. The *o*-chlorotoluene experiment produced a new 320.7-nm absorption, which is probably due to *o*-chlorobenzyl radical, along with a weak 310-nm band probably due to benzyl radical. The meta isomer produced a new 319-nm absorption, which is likely due to *m*-chlorobenzyl radical.

Additional band systems (group 4) were observed in the *p*-fluorotoluene experiment beginning at 330 nm (Figure 1c) and in the *p*-chlorotoluene experiment starting at 335 nm with similar structure on the high energy side (not shown). Both band systems resisted 420-nm photolysis but were destroyed by 220-nm radiation. Analogous bands were observed at 326 and 328 nm in the *o*-fluorotoluene and *o*-chlorotoluene experiments and at 318 and 326 nm in *m*-fluorotoluene and *m*-chlorotoluene studies. A similar band observed at 322 nm in the chlorobenzene experiments, which was destroyed by 290-nm photolysis,[21] shows that the methyl substituent is not involved in a diagnostic manner. The increase in this species with *p*-fluorotoluene in a krypton resonance photolysis experiment, which was accompanied by an *increase* in PFB and a *decrease* in PFT$^+$, suggests a free-radical identification. These bands could be due to a cyclohexadienyl type of radical[27] (extra hydrogen atom attached to a ring carbon) observed at 310 nm in benzene experiments[28] and 317 nm in toluene studies;[11] this type of radical should be more photosensitive than substituted benzyl radicals. Sufficient information is not available for a definitive identification of these absorptions.

Vibrational Assignments. The strong, sharp PFT$^+$ band at 437.9 nm and OFT$^+$ absorption at 429.5 nm rise abruptly and are assigned to the electronic band origins for this $\pi \rightarrow \pi$ transition. The major satellite peak for PFT$^+$ is 777 ± 5 cm^{-1} higher energy, and the next OFT$^+$ peak is 721 ± 5 cm^{-1} above the origin. These intervals are in reasonable agreement with 733- and 747-cm^{-1} polarized Raman bands for the precursor molecules[22] to support assignment to this fluorine-dependent vibrational mode of the parent cation. The weaker 431.5-nm PFT$^+$ band is 339 ± 5 cm^{-1} above the origin which compares favorably with a 313-cm^{-1} deformation mode of the precursor;[22] this photosensitive band is probably due to a PFT$^+$ excited-state vibration.

The sharp, strong 469.3 ± 0.1-nm ACT$^+$ band shifts to 467.8 ± 0.1 nm for the deuterated species. This small blue shift (69 cm^{-1}) in the electronic origin is typical of hydrocarbons and arises from differences in zero-point vibrational energy for the heavy and light isotopes. The sharp weaker bands at 463.7 and 452.7 nm are associated with the ACT$^+$ species; these features could be due to vibrational structure. The band at 452.7 ± 0.1 nm is 782 ± 5 cm^{-1} above the origin, and a symmetric ring-breathing vibration at this energy is appropriate.

Parent Cation Rearrangements. Strong evidence for several parent cation rearrangements has been presented as a basis for identification of the particular parent cation. In argon resonance photoionization experiments with *p*-chlorotoluene, PCT$^+$ is formed with sufficient excess internal energy to rearrange to ACT$^+$ presumably involving a ring-expanded chlorocycloheptatriene intermediate. The ACT$^+$ species was also detected in OCT experiments. This rearrangement requires an activation energy of about 2.8 eV in the gas phase[4] which is provided by one 11.8-eV argon resonance photon in the photoionization process. In this regard, it is important that 10.2-eV hydrogen resonance photoionization of PCT did not produce ACT$^+$. Clearly insufficient energy is available in one 10.2-eV photon to activate this rearrangement upon photoionization to give PCT$^+$. It is also noteworthy that the *p*-fluorotoluene matrix photoionization experiment produced only the para cation. In this case, the argon resonance radiation is only 2.5 eV above ionization[4] and is apparently insufficient to form the fluorocycloheptatriene cation intermediate. However, with benzyl fluoride, the ring-expanded intermediate is apparently formed, since the major product ion in the matrix study is the *p*-fluorotoluene cation. Benzyl bromide cation was also observed in the *p*-bromotoluene experiment; the red tail in the bromotoluene PDS out to about 660 nm[9] is also likely due to benzyl bromide cation.

Strong evidence in support of this rearrangement mechanism has recently been obtained in similar matrix photoionization experiments with toluene and cycloheptatriene. These precursors yield both cycloheptatriene *and* toluene parent cations, as observed by their characteristic absorption spectra. Also noteworthy, the cycloheptatriene cation rearranges to the toluene cation with visible photolysis.[12]

Gas-Phase Comparisons. A most interesting comparison between the matrix absorption and gaseous PDS spectra of *o*-fluorotoluene and *p*-fluorotoluene cations is the relatively sharp bandwidth in the matrix (about 100 cm^{-1}) where the corresponding PDS bands[9] are at least 2000 cm^{-1} wide. The thresholds for the PDS bands for both of these species begin at least 2000 cm^{-1} above the band peaks, whereas the sharp matrix bands are electronic

---

(23) Porter, G.; Strachan, E. *Spectrochim. Acta* **1958**, *12*, 299.

(24) Hodgkins, J. E.; Megarity, E. D. *J. Am. Chem. Soc.* **1965**, *87*, 5322.

(25) Lloyd, R. V.; Wood, D. E. *J. Chem. Phys.* **1974**, *60*, 2684.

(26) Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *54*, 1595.

(27) Shida, T.; Hamill, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 3689.

(28) Miller, J. H.; Andrews, L.; Lund, P. A.; Schatz, P. N. *J. Chem. Phys.* **1980**, *73*, 4932.

origins with thresholds about 100 cm^{-1} above the band peaks. The matrix absorptions for PFT$^+$ and OFT$^+$ are sufficiently sharp to determine which isomer is present. Although the gas-phase PDS peaks for these isomers show PFT$^+$ at 0.04 eV higher energy than OFT$^+$, the large bandwidths prevent as accurate a determination of the PDS band peak as can be made in the solid argon matrix. Similar bandwidth observations have been noted for toluene cation although the differences were not quite as pronounced.[12]

A major affect of the solid argon matrix is to quench internal energy from the parent ions in the condensing layer after photoionization. The presence of excess internal energy may account, in part, for the greater width of the PDS bands. Finally, and of most interest, quenching of internal energy by the matrix allows rearrangement to compete with dissociation, particularly in the case of chlorotoluenes where gas-phase work gives dissociation before rearrangement.[5] A similar enhancement of rearrangement has been found in recent toluene–cycloheptatriene matrix studies.[12]

Acknowledgment. The authors gratefully acknowledge financial support for this research by the National Science Foundation under Grant CHE 79-10966 and the gift of fluorotoluene samples by Professor R. C. Dunbar.

Visible Absorption Spectra and Two-Photon Photodissociation of Halobenzene Cations in Solid Argon

Brian W. Keelan and Lester Andrews*

Contribution from the Chemistry Department,
University of Virginia, Charlottesville, Virginia 22901. *Received July 7, 1980*

Abstract: Matrix photoionization experiments with bromobenzene, chlorobenzene, and fluorobenzene precursors produced absorptions due to bromobenzene cation at 505 ± 5 nm, chlorobenzene cation at 470 ± 2 nm, and fluorobenzene cation at 431 ± 1 nm, respectively, in excellent agreement with gas-phase photodissociation and photoelectron spectra. Two-photon dissociation of the bromobenzene and chlorobenzene cations in solid argon was affected by photolysis in the very strong visible $n_z \rightarrow \pi$ charge-transfer electronic transition, as found in earlier gas-phase work. The lack of significant two-photon dissociation of fluorobenzene cation is attributed to lower oscillator strength for the $\pi \rightarrow \pi$ transition corresponding to absorption of the first photon.

Introduction

Gas-phase studies of molecular ions by photoelectron and photodissociation spectroscopies (PES and PDS, respectively) are nicely complimented by visible–ultraviolet absorption spectroscopy of the transients isolated in inert gas matrices at cryogenic temperatures, as demonstrated by very recent matrix-isolation work with substituted aromatic precursors. A matrix photoionization study of several halotoluene isomers[1] gave absorptions in very good agreement with previous gas-phase work[2] and provided new evidence for parent cation rearrangement. Toluene and cycloheptatriene cations have been observed in solid argon,[3,4] in very good agreement with the gas-phase data;[5,6] cycloheptatriene cation was isomerized to toluene cation in the matrix environment with visible photolysis.[4] This unique result, in conjunction with evidence for the reverse rearrangement in the gas phase,[7] lends strong support to the postulated equilibrium between the two isomeric cations at low internal energies.[8,9]

One particularly interesting photochemical phenomenon involving aromatic precursors, studied recently in the gas phase, is the two-photon dissociation of benzene, cyanobenzene, and halobenzene cations.[10-13] The purpose of this study is to compare gas-phase and matrix observations of the halobenzene cations and examine their photochemistry in a matrix environment.

Experimental Section

The cryogenic apparatus and windowless argon resonance lamp have been described previously.[14,15] Samples of fluorobenzene (Aldrich), chlorobenzene, and bromobenzene (both Baker) and C_6D_5Br (Aldrich) were outgassed and vacuum-distilled from glass beads and then used undiluted or diluted to M/R (matrix/reactant) = 100/1 or 200/1 concentrations. Samples were condensed through a needle valve at about 1 mM/h for several hours on a sapphire window at 20 K. Simultaneous deposition of argon from the 3-mm i.d. orifice discharge tube caused the final matrix concentrations to be approximately half that of the original sample. Spectra were taken on a Cary 17 spectrophotometer from 800 nm to parent absorptions near 270 nm. Each compound was deposited without discharge radiation to determine precursor absorptions. Photolyses were performed with a high-pressure mercury arc (1000-W, BH-6-1, Illumination Industries, Inc.) using an ultraviolet mirror and Corning glass short-wavelength cutoff filters; high-resolution spectra were recorded at 0.2 nm/s and 6 nm/in. before and after each photolysis.

---

[1] Keelan, B. W.; Andrews, L. *J. Am. Chem. Soc.* **1981**, *103*, 99.
[2] Fu, E. W.; Dymerski, P. P.; Dunbar, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 337.
[3] Andrews, L.; Miller, J. H.; Keelan, B. W. *Chem. Phys. Lett.* **1980**, *71*, 207.
[4] Andrews, L.; Keelan, B. W. *J. Am. Chem. Soc.* **1980**, *102*, 5732.
[5] Dymerski, P. P.; Fu, E.; Dunbar, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 4109.
[6] Dunbar, R. C.; Fu, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 2716.
[7] Jackson, J.-A. A.; Lias, S. G.; Auloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.
[8] McLafferty, F. W.; Winkler, J. *J. Am. Chem. Soc.* **1974**, *96*, 5182.
[9] Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382.
[10] Freiser, B. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *35*, 35.
[11] Orlowski, T. E.; Freiser, B. S.; Beauchamp, J. L. *Chem. Phys.* **1976**, *16*, 439.
[12] Dunbar, R. C.; Fu, E. W. *J. Phys. Chem.* **1977**, *81*, 1531.
[13] Dunbar, R. C.; Teng, H. H-I.; Fu, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 6506.
[14] Andrews, L. *J. Chem. Phys.* **1975**, *63*, 4465.
[15] Andrews, L.; Tevault, D. E.; Samardzewski, R. R. *Appl. Spectrosc.* **1978**, *32*, 157.

0002-7863/81/1503-829$01.00/0