

# The Photodissociation and High Resolution Laser Photodissociation of Halogen-Substituted Toluene Cations

Emil W. Fu,\* Paul P. Dymerski, and Robert C. Dunbar<sup>1</sup>

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106. Received January 27, 1975

**Abstract:** The photodissociation of isomeric halotoluene and benzyl halide cations was studied in the visible region with an ICR spectrometer. The peaks of the photodissociation spectra shift progressively toward longer wavelength from fluoro- to iodotoluenes. Benzyl chloride and benzyl bromide show strikingly different spectra from the corresponding halotoluenes. High resolution laser photodissociation was carried out on *o*- and *p*-iodotoluenes, and a small isomer shift was observed in good agreement with the filter results. The photodissociation pathways appear to be thermochemically determined while the peak positions are spectroscopic in origin. A time-resolved photodissociation technique was used to probe the structure of a number of ions. The results indicate partial rearrangement of the initially formed parent ion structure in several cases, most notably in benzyl chloride and benzyl bromide. Comparison of photodissociation spectra with photoelectron spectra shows excellent agreement in peak positions for the out-of-plane halogen p orbital for all the species examined except those which are postulated to rearrange. This supports the presumption that, in general, these parent ions do not rearrange.

Photodissociation of the molecular ions of aromatic compounds has been the subject of several recent ICR studies.<sup>2,3</sup> There is reason to hope that information concerning both the spectroscopic and the structural characteristics of such ions can be drawn from such photodissociation spectra; in the work described below, the possibilities and limitations of the ion photodissociation approach have been explored in some detail with attention to both of these aspects, using a series of halogen-substituted toluenes as a well-behaved series of related ions. These systems have also served in the development of a most promising alternative approach to ion-structure questions, making use of exhaustive photodissociation to probe the spectroscopic homogeneity of a population of trapped ions. This approach will be described, along with evidence for spectroscopic inhomogeneity of the parent ion population of several substituted toluenes.

The photodissociation process of isotopically labeled toluene has been thoroughly studied,<sup>2a</sup> the toluene cations showing complete hydrogen scrambling prior to dissociation, and a large deuterium isotope effect. The photodissociation of isomeric C<sub>7</sub>H<sub>8</sub><sup>+</sup> cations from toluene, norbornadiene, and cycloheptatriene was carried out<sup>4</sup> with the hope that this technique might yield structural information not accessible through other methods. It was indeed found that the three isomeric ions could very easily be distinguished by their photodissociation spectra.

Study of a variety of mono- and dialkyl-substituted benzene cations showed that several isomeric cations are readily distinguished by their spectra,<sup>2b</sup> and it was argued that the photodissociation thresholds for all but cumene are spectroscopically determined. The relative onset energy for the cations was taken to be a quantitative measure of the relative energies of excitation from the cation ground state to a low-lying excited state. In a recent study,<sup>3</sup> the photodissociation spectroscopy of a wide range of substituted benzene cations in the near-uv and visible showed at least two distinct relatively sharp peaks for each ion. A comparison of the photodissociation spectra with corresponding photoelectron spectra was made. Recently, a time-resolved photodissociation technique was used to study the C<sub>7</sub>H<sub>7</sub><sup>+</sup> ions produced in a photochemical reaction sequence of toluene ions,<sup>5</sup> and the formation of two distinct isomers of C<sub>7</sub>H<sub>7</sub><sup>+</sup> was considered highly probable.

Several mass spectrometric studies of the possibility of molecular ion rearrangement in halotoluenes and benzyl halides have been reported. Using a kinetic approach and comparing metastable ion abundances, Brown studied the

P-H decomposition reaction of substituted toluenes.<sup>6,7</sup> He suggested that the meta and para pairs of isomers of chlorotoluene and bromotoluene parent ions have unrearranged and distinct structures, although the transition state for the fragmentation process appeared to have the same energy for the two members of each pair. He concluded that the parent ions of *m*- and *p*-fluorotoluene have the same energy, while the structures may or may not be distinct.

On the other hand, a separate study by Brown of the P<sup>+</sup> → [P-Cl]<sup>+</sup> fragmentation suggested a common structure for the parent ions of *m*- and *p*-chlorotoluene.<sup>8</sup> These contradictory sets of evidence have apparently not been reconciled.

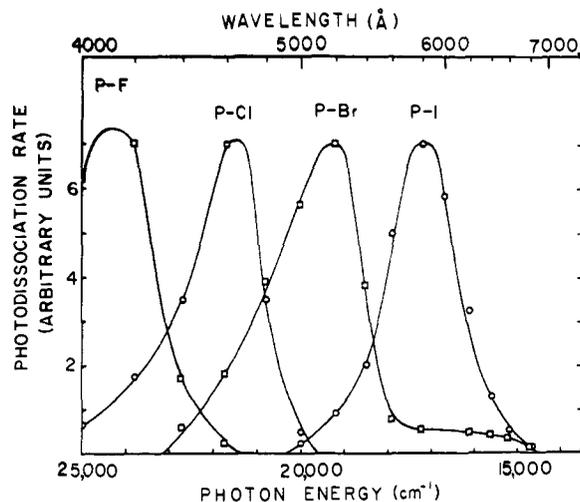
By measuring the appearance potentials and ionization potentials and comparing the ion intensities of the mass spectra of isomeric ions, Williams and Yeo studied the possibility of rearrangement for the molecular ions of halotoluenes and benzyl halides.<sup>9</sup> A ring-expansion rearrangement mechanism that leads to a cycloheptatriene or benzyl halide structure was postulated for the fragmentation of fluorotoluenes and chlorotoluenes. Bromo- and iodotoluenes, however, appeared not to undergo such rearrangement prior to fragmentation.

## Experimental Section

The experimental approach to photodissociation studies was the same as used previously.<sup>2,3</sup> A standard square cell was used to trap the cations with a trapping voltage of 2–3 V, and near zero drift potentials. The electron energy was usually about 1 eV above the reported ionization potential of the ions. The marginal oscillator frequency was usually 153 kHz. Sample pressures were varied from 7 × 10<sup>-8</sup> to 6 × 10<sup>-7</sup> Torr to keep the trapping time of the ions comparable.

Light was generated with a 2.5 kW xenon arc, and the wavelength was selected using Baird-Atomic interference filters. The filters have a bandwidth of 100 Å, spaced 200 Å apart from 4000 to 7000 Å, and a bandwidth of 150 Å at 7500 and 8100 Å. An Eppley thermopile was used to measure the relative light intensities. The photodissociation rates at different wavelengths were normalized to the same photon intensity. In some of the time-resolved photodissociation experiments, Corning long-wavelength-pass filters were used instead to give high wideband light intensities.

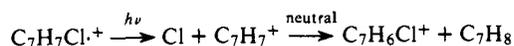
For cases where the three ortho, meta, and para isomeric cations showed little wavelength shift for the photodissociation peaks a Schoeffel monochromator was used to confirm the order of the peak wavelength of the isomers. The monochromator slit width was 4 mm giving a nominal band-pass (full width at half-maximum) of 132 Å. It was possible in some cases, such as for *o*-, *m*-



**Figure 1.** Comparison of the photodissociation spectra of the four *p*-halotoluene cations shows that the peaks shift toward longer wavelength from fluoro- to iodotoluene. The vertical scales for each curve were adjusted to give the same maximum value, and the rates for different ions should not be compared directly.

and *p*-chlorotoluenes, to obtain better isomer differentiation using the monochromator.

In all cases, the photodissociation path was confirmed by ICR double resonance methods. Some photodissociation product ions reacted with the neutral to generate secondary ions, giving signals which increased with the decrease of the parent ion signal. In addition to double resonance methods, a trapping plate ejection technique was found convenient to differentiate the secondary products from the initial photodissociation products. In this technique, a periodic negative voltage pulse was applied to the trapping plates in order to eject all the ions repetitively. The pulse interval was 0.5 to 1.5 sec, and the pulse width was several milliseconds. The intensities of all ion signals decreased with decreasing pulse interval, but as expected the reactively produced secondary ions were suppressed more drastically than the primary photodissociation products, making it easily possible to determine the initial photodissociation product ion or ions. One such example is the  $P-1^+$  ions in the benzyl chloride system, which were produced by the following sequence:



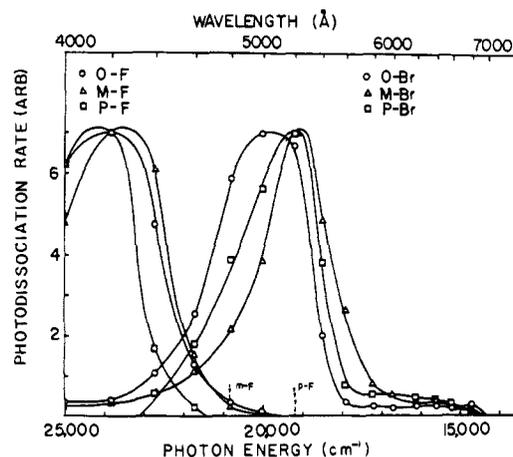
When the trapping ejection was applied with a pulse interval of  $\sim 1.3$  sec, the  $P-1^+$  ions were not observed at all.

For the high resolution laser study a pulsed liquid-dye laser was used as a light source to produce monochromatic light (fwhm  $< 5$  Å) from 5000 to 7500 Å. The laser was wavelength calibrated with a 15-Å band-pass monochromator. Laser resolution is better than 0.02 eV at 2.0 eV. Light and ion signal intensities were monitored and light intensity corrections were made with a PDP-11 computer.<sup>10</sup> The laser was pulsed at a rate of 10–30 pulses/min. The Synergetics dye laser was specified by the manufacturer to produce power levels near 100 mJ/pulse for the dyes used. Approximate measurements suggested that the actual power levels achieved were somewhat lower than this. The photodissociation rate constant was measured by integrating the ion intensity of the product ion ( $C_7H_7^+$ ) produced by each laser flash. (Ion lifetimes were found to be constant over long periods so that the integrated product ion signal is a direct measure of ion production.)

There was some difficulty in the matching of intensity measurements for the three different dyes used. Accordingly, the Rhodamine B and sodium fluorescein intensity measurements were corrected by small amounts, in order to bring the points measured with them into coincidence with corresponding points from Rhodamine 6-G in the regions of 6100 and 5700 Å, respectively.

#### Time-Resolved Photodissociation Technique

The experimental procedures for time-resolved photodissociation were similar to those used in the study of  $C_7H_7^+$



**Figure 2.** The photodissociation spectra of *o*-, *m*-, and *p*-fluorotoluenes and *o*-, *m*-, and *p*-bromotoluene cations. The dotted lines on the energy scale designate the thermochemical onsets of the dissociation for *m*- and *p*-fluorotoluenes. The vertical scale for each curve is arbitrary.

ions.<sup>5</sup> The ICR square cell was used to produce the ions and trap them for a period usually longer than 30 sec. While the parent ion signal was continuously monitored by the marginal oscillator, the decay curve of the ion was obtained by turning off the filament to terminate the ion production. The decay curve for a particular ion, while often deviating from simple exponential behavior, was found to be reproducible. After obtaining this decay curve, a second decay curve was obtained under the same conditions, by simultaneously turning off the filament and turning on the light. The light-on decay curve was normalized for the light-off ion loss processes by dividing point-by-point by the measured light-off decay curve; the result was taken to represent the extent of photodissociation of the parent ion population as a function of time.

In the case of benzyl chloride, there was some difficulty with photochemical regeneration of the parent ion via secondary reactions of photochemically produced  $C_7H_7^+$ . These problems were avoided by continuous efficient cyclotron ejection of  $m/e$  91 during the course of the time-resolved study of this system.

The high-resolution photoelectron spectra were obtained from a Varian photoelectron spectrometer with a uv source. These spectra were scanned from below the first IP to about 20 eV. We are indebted to Dr. C. McFarland and Dr. G. Mateescu for obtaining these spectra for us using the facilities of the Major Analytical Instrument Facility at CWRU.

We are also indebted to Dr. G. A. Olah for providing us the benzyl fluoride, benzyl chloride, *o*-chlorotoluene, and *o*-iodotoluene. The *o*-fluorotoluene, *m*- and *p*-chlorotoluenes, and benzyl bromide were obtained from Matheson Coleman and Bell Co. The *m*- and *p*-fluoro-, *m*- and *p*-bromo-, and *m*- and *p*-iodotoluenes were from Eastman Kodak Co. The purities of *m*- and *p*-chlorotoluenes and benzyl chloride were checked by NMR spectra. Compounds were used without further purification.

#### Results and Discussion

The photodissociation peak energies of halotoluene parent ions were found to decrease in the order:  $F > Cl > Br > I$ . Going from F to I, the peak shift amounted in all to about 0.3 eV toward longer wavelength. The photodissociation spectra of the parent ions are shown in Figures 1–4. The vertical scales for each curve in a figure were adjusted to give the same maximum value, and the photodissociation rates for different ions should not be compared directly. In the single resonance spectra, the only major peaks without

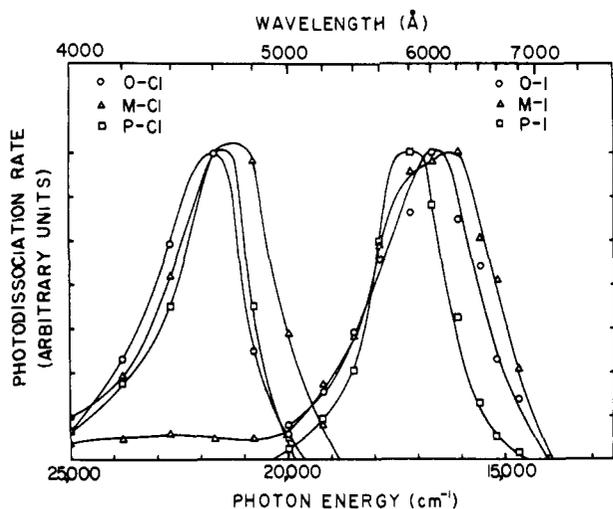
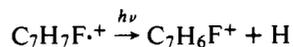


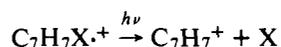
Figure 3. The photodissociation spectra of *o*-, *m*-, and *p*-chlorotoluenes and *o*-, *m*-, and *p*-iodotoluene cations.

illumination at these low electron energies were the parent ions. With the irradiation, most of the systems showed no more than one secondary ion-molecule reaction product in addition to the primary photodissociation product ion. Except for the iodotoluene system, the presence of high mass ions (to  $m/e$  250) was ruled out in each case.

The photodissociation reactions observed were the following:

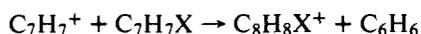


for *o*-, *m*-, and *p*-fluorotoluene and benzyl fluoride;



where X is Cl, Br, or I, and isomers examined were all the *o*-, *m*-, and *p*-halotoluenes, benzyl chloride, and benzyl bromide.

Numerous secondary photochemical reactions were seen. The reaction



was confirmed for the chlorotoluenes, and the product ion presumed to come from this sequence was observed in *p*-bromotoluene. Reactions not elucidated led among other products to  $\text{C}_8\text{H}_8\text{F}^+$  in fluorotoluenes and to  $\text{C}_8\text{H}_9^+$  and  $\text{C}_9\text{H}_{11}^+$  in benzyl bromide.

As is clear from the figures, the important question of whether the various isomers of these compounds retain their distinct identities in the parent ions can be answered in only a partial way. It is plain that the benzyl chloride and benzyl bromide parent ions remain very different from the corresponding halotoluene isomers, as the spectra are qualitatively different. The situation is less clearcut otherwise, but it would be reasonable to say that the differences found in the peak positions and curve shapes between isomers are reproducible and probably real, providing evidence against rearrangement to common structures. Such a conclusion is stronger for the bromo- and iodotoluenes than for the fluoro- and chlorotoluenes. The largest isomer shifts occur in the iodotoluene spectra, which is not surprising since the iodine substituent gives the largest perturbation from the toluene ion spectrum.

The effect of internal energy on photodissociation spectra has been discussed several times.<sup>2a,3,11,12</sup> It was found in most cases that the addition of buffer gases (such as  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ) to quench the internal energy did not significantly change the spectra. However, the possibility that the

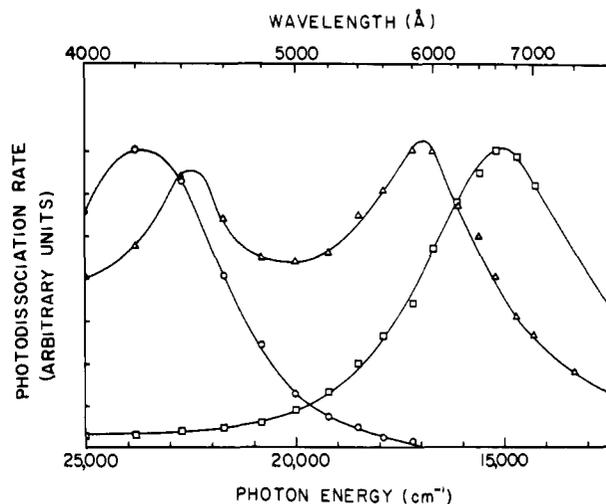


Figure 4. The photodissociation spectra of benzyl fluoride (O), benzyl chloride (Δ), and benzyl bromide (□) cations.

Table I. Photodissociation Onsets and Maxima and Thermochemical Onsets of Halotoluenes

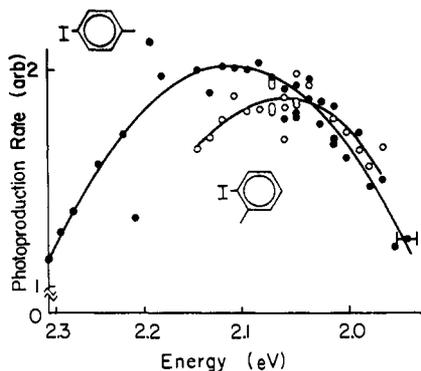
Halogen substituent	Photo-dissociation onset, eV <sup>a</sup>	Thermo-chemical onset, eV <sup>b</sup>	Photo-dissociation maxima, eV <sup>c</sup>
<i>α</i> -F	2.1		2.94
<i>o</i> -F	2.5	2.7	2.95
<i>m</i> -F	2.5	2.7, 2.6	2.91
<i>p</i> -F	2.7	2.9, 2.4	2.99
<i>α</i> -Cl	<1.5	1.1	2.10, 2.78
<i>o</i> -Cl	2.5	1.6	2.69
<i>m</i> -Cl	2.4	1.7	2.63
<i>p</i> -Cl	2.5	1.8, 2.7	2.67
<i>α</i> -Br	<1.5	0.6	1.86
<i>o</i> -Br	1.8	1.1	2.45
<i>m</i> -Br	1.8	1.1	2.36
<i>p</i> -Br	1.8	1.2	2.39
<i>o</i> -I	1.8	0.6	2.07
<i>m</i> -I	1.8	0.7	2.03
<i>p</i> -I	1.8	0.8	2.13

<sup>a</sup>The energies of the wavelengths where photodissociation began to be observable were taken to be the onsets. The estimated uncertainties are  $\pm 0.1$  eV. <sup>b</sup>For *m*-fluoro-, *p*-fluoro-, and *p*-chlorotoluenes, the second thermochemical onsets are for the *p*-H dissociation pathway. <sup>c</sup> $\pm 0.05$  eV is the estimated uncertainty for the maxima of photodissociation.

observed small photodissociation peak shifts merely reflect the internal energy differences of a common ion rearranged from different precursors deserves closer examination. If this were the case, the ordering of the photodissociation onsets and peaks of the isomeric ions would be expected to correspond to the internal energies of the ions. The heats of formation of the halotoluene parent ions are all in the order  $o > m > p$ . Rearranging to a common structure, the ortho isomers would have  $\sim 0.17$  eV higher internal energy than the para isomers. Consequently, the onsets and peaks of the ortho isomers would be expected to lie at lower wavelength. As is clear from Table I, the observed spectra show no such correlation with ion internal energies.

In addition to this, further evidence comes from the photoelectron spectra of the neutral compounds, which correspond in a well understood way to the visible-region photodissociation spectra of substituted toluene cations.<sup>3,13</sup>

The photodissociation peak energies of isomeric chloro-, bromo-, and iodotoluenes were estimated from photoelectron spectra, and the peak ordering obtained this way agrees very well with the photodissociation results (with the exception of *p*-iodotoluene, for which the photodissociation



**Figure 5.** Laser photodissociation results for production of  $C_7H_7^+$  from *p*-iodotoluene cation (solid circles) and *o*-iodotoluene (open circles). The photoproduction rate scale is arbitrary but consistent for the two compounds. Three overlapping laser dyes were used: sodium fluorescein (5400–5700 Å), Rhodamine 6-G (5700–6100 Å), and Rhodamine B (6100–6400 Å).

peak is shifted by about 0.2 eV from the photoelectron peak, so that an ordering  $p > o > m$  is found for photodissociation as compared with the  $o > m > p$  ordering of the photoelectron peaks). It seems clear that the evidence from both spectroscopic and thermochemical considerations does not favor rearranged common structures for the parent ions of these isomeric series of compounds.

#### Thermochemical Considerations

Only two kinds of photodissociation pathways were observed for the molecular ions. The fluoro-substituted toluene ions lose a hydrogen atom, while all the other ions lose halogen; apparently the heats of reaction determine the preferred channel of dissociation. The available thermochemical data are summarized in Table I for direct comparison with the photodissociation results. Heats of formation of Franklin et al.<sup>14</sup> will be accepted. Comparison of the energetics for the two most reasonable pathways shows that for *m*- and *p*-fluorotoluenes, the loss of H is favored over loss of F by about 0.1 and 0.5 eV, respectively, and the loss of Cl is favored by about 0.8 eV for *p*-chlorotoluene. Hence, for the compounds for which data are available, the photodissociation pathway appears to be determined thermochemically. Although the other path was energetically possible at the photodissociation peak wavelength, little, if any, of the other product was observed.

The energy of the longest wavelength where photodissociation of the parent ions was observed in these experiments was taken as the photodissociation onset in Table I. The observed photodissociation onsets of *o*-, *m*-, and *p*-chloro-, bromo-, and iodotoluenes are all more than 0.5 eV above the thermochemical onsets. Except for fluorotoluenes, the thermochemical onset in each halogen system shows a general order of benzyl  $< o < m < p$ . There is no correlation between this ordering and the observed order of peak wavelengths for these isomers. This lends weight to the supposition that the observed photodissociation peaks are spectroscopic in origin, and are not primarily determined by the thermochemistry of the dissociation reaction. However, the photodissociation onsets of *m*- and *p*-fluorotoluenes are close to the thermochemical onsets, and the peaks in these cations may well be shifted and distorted by the dissociation thermochemistry.

It should be mentioned that, as an approximation to the activation energy, the AP – IP values measured by Williams show fairly good correlation with the photodissociation peak energies of chloro- and bromotoluenes. However, the AP – IP values for iodotoluenes are appreciably higher

(~0.3 eV) than the photodissociation peak energies of iodotoluenes.

#### Laser Photodissociation Spectra

The photodissociation spectra of *p*- and *o*-iodotoluenes were reexamined at high resolution using laser photodissociation techniques, both as a check on the low-resolution results and also to explore the possibility of vibrational structure in the spectra. A pulsed dye laser was used as the light source with single-pulse data acquisition and analysis,<sup>10</sup> giving optical resolution better than 5 Å. The results are shown in Figure 5, which displays the observed rate of photoproduction of  $C_7H_7^+$  product ion from  $C_7H_7I^+$  precursor as a function of photon energy. The scatter of the data reflects the currently less than desirable signal-to-noise of this new approach to photodissociation. (The wide scatter of several points in the region of crossover from sodium fluorescein to rhodamine 6-G near 2.2 eV is probably instrumental, and not due to structure in the peak.) Several conclusions may be drawn from these results.

The peak position in *p*-iodotoluene lies at 2.11 eV and the width is about 0.4 eV (fwhm). This may be compared with the corresponding peak in the uv photoelectron spectrum,<sup>15,3</sup> which has its maximum at 1.93 eV above the ion ground state, with a width of 0.15 eV. The cation optical absorption peak leading to photodissociation is thus shifted to higher energy and broadened relative to the photoelectron peak of neutral iodotoluene. However, as expected, the two methods agree in the position of the low-energy onset of the peak. The extreme narrowness and sharp rise of the 1.93-eV peak in the photoelectron spectrum indicate excellent Franck-Condon overlap of the relevant excited ion electronic state with the neutral ground state. We conclude from the shift and broadening of the photodissociation peak that the overlap of this state with the ion ground state is much less favorable, as would be expected for a  $\pi \rightarrow n$  transition.

The isomer shift between *p*- and *o*-iodotoluenes is clearly seen in the laser photodissociation results, with *o*-iodotoluene peaking at 2.06 eV, 0.05 eV lower in energy than the para isomer. This is in agreement with the filter results, and lends confidence to the small isomer shifts assigned from filter results for other cases.

There is no evidence for pronounced vibrational structure in the curves. The region from 1.9 to 2.2 eV in *p*-iodotoluene has been particularly well covered (the data are more extensive than shown in Figure 5) and certainly shows no local structure much greater than 10% of the peak intensity.

#### Homogeneity of Ion Populations. Time Resolved Photodissociation

The doubly peaked visible-region spectrum of benzyl chloride parent ion is unique in our experience with substituted toluene cations, and seemed likely to be due to two distinct isomers of the ion coexisting in the cell. This was shown to be the case by the time-resolved approach to photodissociation. A population of parent ions was prepared in the cell by operating the electron beam for a period and then shutting it off. Irradiation was then commenced at either 4400 or 6000 Å at an intensity sufficient to effect complete dissociation of all the susceptible ions in a time short compared with the residence time of the trapped ions. It has been shown in previous work,<sup>5</sup> and was reconfirmed in a number of cases in the present study, that if all of the ions present are susceptible to dissociation, the normalized ICR signal decays in smooth exponential fashion to the baseline. By contrast, the decay curve for benzyl chloride parent ions

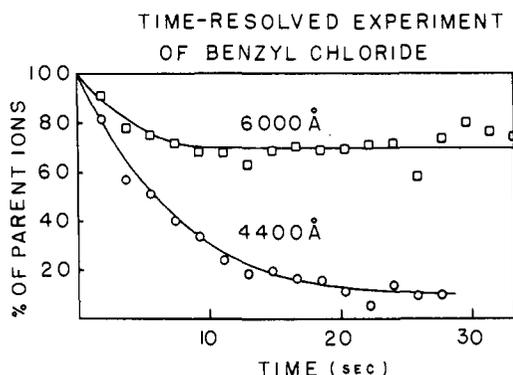


Figure 6. Time-resolved photodissociation results for benzyl chloride ions. The 6000-Å light dissociates only ~30% of the parent ions.

under irradiation at 6000 Å shown in Figure 6 falls rapidly to 70% of its initial value and then levels off, indicating that only 30% of the ion population absorbs light and dissociates at 6000 Å. Irradiation at 4400 Å gives dissociation with a lower cross section, but apparently leads to dissociation of essentially all of the ions.

As is discussed further below, the 6000-Å peak of the benzyl chloride system can reasonably be assigned to the unrearranged benzyl chloride ion structure. Accordingly we conclude that 30% of the parent ions from benzyl chloride have a structure, probably the unrearranged parent structure, which is rapidly photodissociated by light in a band centered near 6000 Å. The remaining 70% of the parent ions have a different structure with a photodissociation peak near 4400 Å. This peak is near the peaks observed for the chlorotoluene ions, so that the rearranged ions may well have the same structure as the chlorotoluene parent ions.

Measurement of the dissociation rate constant from the time-resolved photodissociation of a particular ion species at a given wavelength gives a value for the photodissociation rate for the *dissociating* species at that wavelength. For benzyl chloride parent ions at 4400 Å, a photodissociation rate of  $0.21 \text{ sec}^{-1}$  was found, while *o*- and *m*-chlorotoluene parent ions gave values of 0.17 and  $0.27 \text{ sec}^{-1}$ , respectively (after making a small correction for the differing light intensities at 4400 and 4600 Å). The photodissociation rate for rearranged benzyl chloride parent ions is thus equal within a reasonable error to the rates for either *o*- or *m*-chlorotoluene ions, which is consistent with the hypothesis that the benzyl chloride ion rearrangement yields the chlorotoluene structure.

There are, however, two areas of difficulty with such an interpretation: first, the 200 Å blue shift in the benzyl chloride peak relative to the chlorotoluene peak at 4600 Å would not be expected in this interpretation, and does not appear to be readily reconcilable with this rearrangement hypothesis. And second, the interpretation of the time-resolved results advanced here would indicate that irradiation at 4400 Å would lead to dissociation of only 70% of the parent ions, rather than the  $\geq 95\%$  observed. A quantitatively reasonable explanation of this latter observation is possible by assuming that the rapid photodissociation of the unrearranged ions, which peaks near 6000 Å, has a substantial short-wavelength tail such that these ions are still dissociated slowly by 4400-Å light. Alternatively, postulation of a small photodissociation peak for unrearranged benzyl chloride ions at about 4200 Å would be sufficient to account for both the blue shift and the excess extent of ion photolysis for the 4400-Å peak.

To summarize the conclusions reached concerning benzyl chloride ions, there is strong evidence for two distinct ion structures resulting from ionization. The 30% of the ions

Table II. Time-Resolved Photodissociation Results

Mol-ion	% photo-dissociated	Wavelength, Å
Benzyl-F	85	3850 high pass filter
Benzyl-Cl	$\geq 95$	4400
	30	6000
Benzyl-Br	65	6600
P-F	$> 95$	4200
O-Cl	$\sim 95$	4600
M-Cl	$\sim 95$	4600
P-Cl	95	4600
P-Br	100	5200

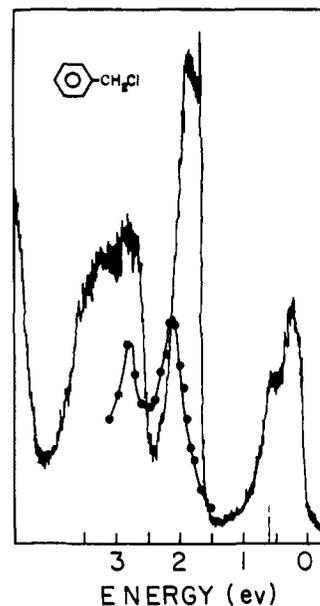


Figure 7. The photodissociation spectrum (●) and photoelectron spectrum of benzyl chloride plotted with arbitrary vertical scale. The adiabatic first ionization potential from PES is assigned as zero on the photodissociation energy scale. The dotted line represents the thermochemical onset for dissociation.

which dissociate with 6000-Å light most probably have the original benzyl chloride structure; the remaining 70% of the ion population may have a chlorotoluene structure, although the evidence for this is not conclusive.

Similar time-resolved exhaustive photodissociation experiments were performed on many of the other parent ions, with the results shown in Table II. (Only those cases are listed for which satisfactory and conclusive data could be obtained.) Not surprisingly, both benzyl fluoride and benzyl bromide, in addition to benzyl chloride, show evidence that a substantial fraction of the parent ions are not dissociated by light in the observed photodissociation band. Fifteen percent of the benzyl fluoride population is not dissociated by *any* visible wavelength, and this may suggest a structure absorbing light below the thermochemical dissociation threshold.

The halotoluene parent ions listed in Table II show little spectroscopic inhomogeneity, with 95% or more of the ions being dissociated at the peak wavelength. However, it is noteworthy that the chlorotoluene parent ions show about 5% of the nondissociated ions. This effect is real and is well outside experimental uncertainty, suggesting strongly that about 5% of these ions rearrange to a spectroscopically distinct structure.

In conclusion, for a number of the compounds studied, rearrangement of the parent structure occurs upon electron impact ionization, to the extent of about 70% for benzyl chloride, 35% for benzyl bromide, 15% for benzyl fluoride, and  $\sim 5\%$  for the chlorotoluenes.

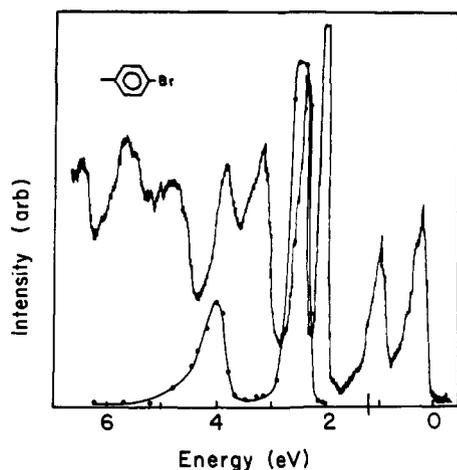


Figure 8. The photodissociation spectrum (●) and photoelectron spectrum of *p*-bromotoluene. Mark at 1.3 eV indicates the thermochemical dissociation onset.

### Photoelectron Spectra

The high resolution photoelectron spectra of the four *p*-halotoluenes and benzyl chloride and bromide were taken for the comparison of these two methods<sup>3</sup> (Figure 7 and 8). To each photodissociation peak there corresponds a photoelectron peak, except for benzyl bromide, where there is a difference of about 0.3 eV to the nearest PES peak (10.74 eV). Since the correspondence is so good in the other cases, this might suggest that this molecular ion does not retain the neutral molecule structure, but it seems more likely that this shift is due to extreme Franck-Condon broadening and blue shifting of the photodissociation peak, similar to but more extreme than that observed for benzyl chloride. The sharp PES peaks that correspond to the photodissociation peaks are those generally considered as arising from largely localized lone pair *p* electrons of the halogen atoms.<sup>15</sup> These lone pair electron peaks have been considered to be split by the unequal interaction with the aromatic ring.

It is interesting to find that only one of the split PES peaks was observed in the photodissociation spectra; in each case the peak observed is the one which has been assigned in PES work as corresponding to the *p* orbital that is vertical to the plane of the aromatic ring.<sup>15</sup> That only one of the split peaks was observed is well illustrated in the *p*-bromotoluene case (Figure 8), where both split PES peaks should

be observable in the photodissociation spectrum from an energetic point of view, but only the one with higher energy was actually observed. Since transitions from the  $\pi$  ground state of the ion to the excited state involving the in-plane halogen *p* orbital are not optically allowed, while transitions to the state involving the out-of-plane *p* orbital are symmetry allowed, this observation is not surprising, and gives strong support to the assignment of the two halogen *p* orbitals in the photoelectron spectra.

It has been argued that the uv peak in the photodissociation spectrum of toluene cation is an electron-excitation type of transition having no counterpart in the photoelectron spectrum.<sup>13</sup> Since the same is likely to be true of the substituted toluene spectra considered here, consideration of the uv peaks seems unlikely to be fruitful. The very good match obtained between the visible photodissociation peaks and the corresponding photoelectron peaks for chlorotoluenes and bromotoluenes in particular, is strong evidence that the parent ions retain the structure of the neutral compound. The same argument applies in the case of the 6000-Å peak of benzyl chloride (Figure 7). The match is less good in the case of iodotoluene, although the lack of perfect agreement is not more than can be accounted for by differing Franck-Condon envelopes for the peaks in the two different types of spectra.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for partial support of this research.

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