August, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *53*, *2185—2187 (1980)* 2185

Photodissociation Spectroscopy and Photoreactions in *t*-Butylbenzene Cation and Its Daughter Cations

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(Received January 21, 1980)

Photodissociation spectra were observed for *t*-butylbenzene cation (*m/e* 134) and its daughter ion (*m/e* 119). Photoproduction spectra of the ions at *m/e* 119 and *m/e* 91 were observed in the visible region. It was shown that the photodissociation of *m/e* 134 yields *m/e* 119 almost 100% at wavelengths above 450 nm. Below 450 nm *m/e* 91 and *m/e* 57 appear as light-produced species. From pressure dependence and double resonance results, it was concluded that *m/e* 91 is a direct photoproduct from *m/e* 119, and that *m/e* 57 is produced in an ion-molecule reaction of *m/e* 91 with neutral *t*-butylbenzene. The photodissociation spectrum of *m/e* 119 is very similar to that of *m/e* 105 obtained by protonation of styrene, and it is reasonable to assume that *m/e* 119 has the protonated methylstyrene structure.

The photochemistry of gas-phase ions is conveniently studied using techniques of ion cyclotron resonance.[1–4] Aromatic radical ions have been particularly well explored, and many aspects of their spectroscopy and photochemical reactions have begun to be clarified, leaving a rich variety of unresolved and interesting questions.

The photodissociation spectrum of *t*-butylbenzene ion(I) was measured by Dymerski *et al.*[5] using steady-state ICR technqiues, showing, as is typical of alkylbenzene ions,[6] a broad photodissociation feature in the visible, and a peak near 270 nm. At wavelengths above about 400 nm, the only observed product was *m/e* 119, corresponding to loss of CH_3 (Eq. 1):

$$\underset{(m/e\ 134)}{\underset{\text{I}}{C_6H_5C(CH_3)_3^{+\cdot}}} \xrightarrow{h\nu} \underset{(m/e\ 119)}{\underset{\text{II}}{C_9H_{11}^{+}}} + CH_3\cdot \qquad (1)$$

However, at shorter wavelengths another product ion was observed at *m/e* 57 ($C_4H_9^+$). The possibility of this being a direct photodissociation product, formed in competition with the less energetic *m/e* 119 product channel, is an interesting one. The 57^+ product channel is about 7 kcal more endothermic than the 119^+ channel;[7] competitive fragmentation to both products would be interesting, and might turn out to be indicative of non-statistical (non-RRKM) dissociation. However, the steady-state ICR technique is well known to have difficulty in distinguishing between direct photoproducts and subsequent ion-molecule reaction products,[3] and it seemed desirable to reexamine this photodissociation chemistry using the more powerful methods of pulsed ICR spectroscopy.

Experimental

The application of ion cyclotron resonance (ICR) spectroscopic techniques to studying photodissociation spectroscopy and ion photochemistry has often been described.[1–4] For one-photon photodissociations, the photodissociation cross section is obtained in the pulsed ICR technique from the extent of ion disappearance following illumination for a time τ:

$$\sigma = -[1/(I\tau)]\cdot\ln[(M_0^+ - M^+)/M_0^+] \qquad (2)$$

where M_0^+ and M^+ are the signal intensities of parent ions respectively without and with light, and I is the photon flux. Equivalent information can be obtained by observing the appearance of photoproduct ions under illumination.[8] The instrument and techniques used have been described.[2,3]

Commercial *t*-butylbenzene was used without further purification with a sample pressure ranging from 8×10^{-9} to 4×10^{-8} Torr, ionizing electron energy of 12 eV, and trapping times in the range 1—3 s. The detection radio frequency was 137.4 kHz, and the magnetic field varied from 3 to 11 kG to observe mass numbers from 41 to 134. Light from a 2.5 kW Hg–Xe arc lamp was wavelength-selected with a Schoeffel GM-250 monochromator at a resolution (FWHM) of 14 nm.

The ratio of signal intensities $[119^+]/[134^+]$ was found very sensitive to electron beam parameters in the low-energy region used in this work, and varied from day to from about 1.2 to 1.8. The sum of $[119^+]$ and $[134^+]$ signal intensities was, however, kept constant within 20% in order to maintain constant ion density conditions in the cell. Representative photodissociation results are displayed in Fig. 1. All of the curves plotted in Figs. 2, 3, and 4 were obtained by measuring the extent of light-induced increase or decrease of the ap-

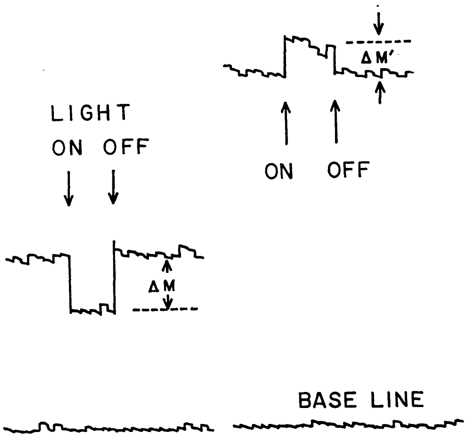

Fig. 1. Change under illumination of ICR signal intensities of *m/e* 134 (left) and *m/e* 119 for light at 440 nm. Neutral pressure was 3×10^{-8} Torr and reaction time τ was 3.0 s. ΔM denotes the signal decrease of *m/e* 134, and $\Delta M'$ denotes the signal increase of *m/e* 119.

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propriate ion, and dividing by (I) for photoproduction curves, or applying Eq. 2 for photodisappearance curves.

Results and Discussion

The visible-region photodissociation (photodisappearance) spectrum of the *t*-butylbenzene cation (m/e 134) is shown in Fig. 2, along with the photoproduction spectra of the ions at m/e 119 and m/e 91, whose abundance increases when the light is turned on. Above 450 nm m/e 119 is the only observed photoproduct under any conditions, and accounts quantitatively for all of the photolyzed parent ion, indicating that Eq. 1 is the only photodissociation process, and that the m/e 119 ion is stable against both photodissociation and ion-molecule reaction processes.

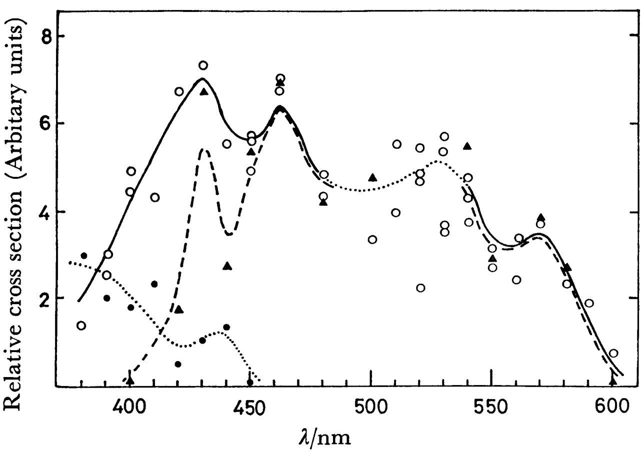


Fig. 2. Photodissociation spectrum of *t*-butylbenzene cation (m/e 134) (—○—), and the photoproduction spectra of its daughter ions m/e 119 (---▲---) and m/e 91 (···●···). While not absolute, the units for the three curves are consistent, so that the extent of parent-ion destruction and product-ion production may be directly compared. The pressure was 4×10^{-8} Torr, the reaction time τ was 3.0 s, and the errors of wave length are almost ±7 nm.

However, at shorter wavelengths the photochemistry becomes more complex, and ions at m/e 91 and m/e 57 become prominent as light-produced species. Figure 3 shows the complete photodisappearence spectrum of m/e 134, and shows that at shorter wavelengths, m/e 119 also decreases under illumination. Figure 4a shows that m/e 91 and m/e 57 increase under illumination parallel to the decrease in m/e 119.

The ion m/e 91 is evidently a direct photoproduct from m/e 119, but m/e 57 is not: at shorter times and lower pressure, as indicated in Fig. 4b, m/e 57 virtually disappears, and is apparently an ion-molecule reaction product from m/e 91. The photochemistry in this system is thus governed by three processes, Eqs. 1, 3, and 4.

$$\underset{(m/e\ 119)}{C_9H_{11}^+} \xrightarrow{h\nu} \underset{(m/e\ 91)}{C_7H_7^+} + C_2H_4 \tag{3}$$

$$\underset{(m/e\ 91)}{C_7H_7^+} \xrightarrow{C_{10}H_{14}} \underset{(m/e\ 57)}{C_4H_9^+} + \text{Neutral products} \tag{4}$$

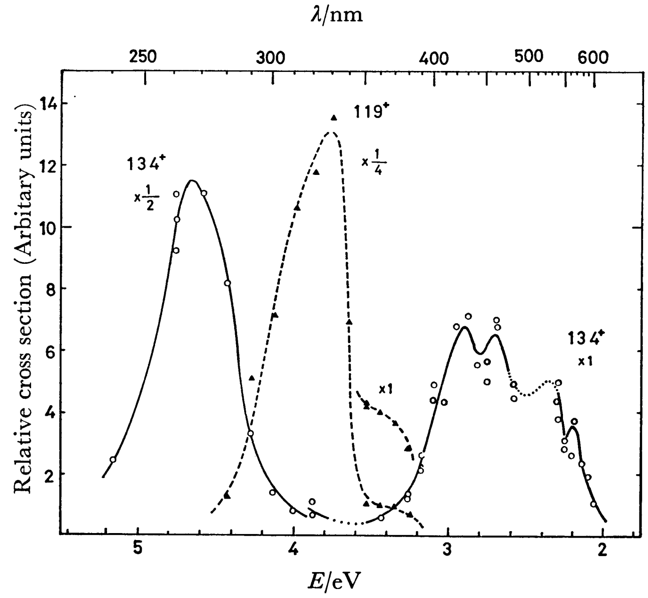
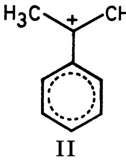


Fig. 3. Photodisappearance spectra of m/e 134 (—○—) and m/e 119 (---▲---). The intensity units are consistent for the two curves, and are also consistent with those of Fig. 2, (but note that this figure plots photodisappearance of m/e 119, while Fig. 2 plotted photoproduction of m/e 119 at the longer wavelengths involved). Pressure and τ as in Fig. 2.

Further confirmation of this sequence is provided by the double resonance results shown in Fig. 4b: the ejection of m/e 119 results in a large decrease in m/e 91, supporting the assignment of Eq. 3 as the immediate source of m/e 91. Ejection of m/e 134 gives a lesser, but still significant decrease in m/e 91, reflecting the two-reaction sequence connecting these two ions.

Under the conditions of Fig. 4a, about half of the m/e 91 ions are converted to m/e 57 over most of the wavelength range; the sharp increase in the [57]/[91] ratio near 320 nm (where both the photon flux and the m/e 119 photodissociation cross section are large) apparently reflects the extremely rapid conversion of m/e 119 to m/e 91 at this wavelength, giving, Eq. 4 more time to move further toward completion.

The photodissociation spectrum of the m/e 119 ion reflected in Fig. 3, while subject to some distortion by photoproduction of 119 by Eq. 1, is probably reasonably faithful from 3.3 to 4.3 eV. This spectrum, with a strong peak at 3.8 eV and a small peak around 3.4 eV, is very similar to the photodissociation spectrum of m/e 105 obtained by protonation of styrene[9] (showing a strong peak at 3.9 eV, and a weaker one near 3.1 eV). It is thus reasonable to assume that the m/e 119 ion produced by electron impact from *t*-butylbenzene has the protonated methylstyrene structure II. Since the



II

background of electron-impact-produced m/e 119 ions

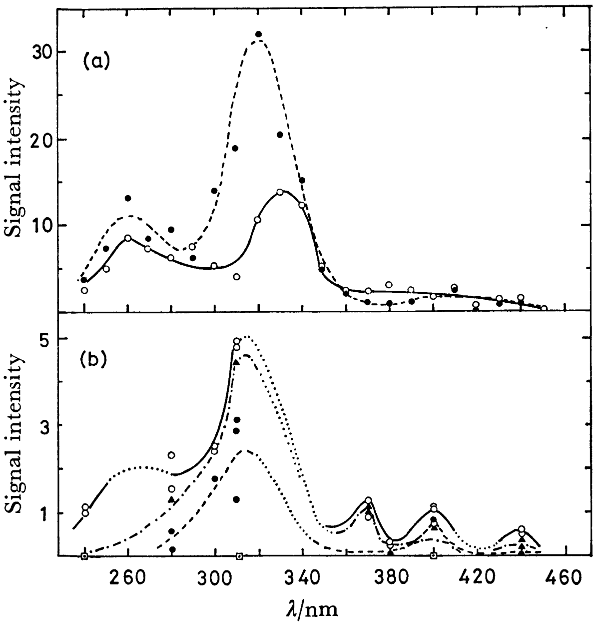


Fig. 4. a): Photoproduction curves for *m/e* 91 (—○—) and *m/e* 57 (---●---). Pressure and τ as in Fig. 2.
b): Photoproduction of *m/e* 91 using double resonance ejection of possible precursors: (—○—) shows *m/e* 91 production without double resonance; (--▲--) shows *m/e* 91 production with ejection of *m/e* 134, and (---●---) shows *m/e* 91 production with ejection of *m/e* 119. The pressure was 2.4×10^{-8} Torr, and τ was 1.0 s. Under these conditions of lower pressure and shorter τ, there was no observable signal for *m/e* (⊡).

was larger than the photoproduced *m/e* 119 ion, it was not possible to analyze separately the photoproduct ions of Eq. 1.

Reaction 4 can be visualized as a simple displacement of the *t*-butyl group by C_7H_7 on the neutral *t*-butylbenzene, although of course the present results give no information about the actual mechanism. Assuming the neutral product of this reaction to be diphenylmethane, the reaction is calculated to be exothermic by a few kcal/mol.

Conclusion

Considerable complexity has been found in the photochemistry of *t*-butylbenzene ions at shorter wavelengths, with the final product ion, *m/e* 57, terminating a sequence of two successive photodissociations and an ion-molecule reaction. No evidence was found for competitive dissociation of I into two different product channels, however, and the observed chemistry seems to be satisfactorily accounted for within the assumption that Reaction (1) is the only photoreaction of the parent ion I.

The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, the U. S. National science Foundation, and the U. S. Air Force Geophysics Laboratory is gratefully acknowledged. One of the authors, Yoshiya Takenoshita, thanks the Kitakyushu Mayor for the Kitakyushu Abroad Fellowship and Dr. Myung Soo Kim for his help at the beginning of this work.

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