Threshold Formation of Benzylium (Bz^+) and Tropylium (Tr^+) from Toluene. Nonstatistical Behavior in Franck–Condon Gaps[†]

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Benzylium (Bz^+) and tropylium (Tr^+) ion formation from toluene-h_8 and toluene-α-d_3 were studied by time-resolved photoionization mass spectrometry (TPIMS). Bz^+ was distinguished from Tr^+ through its ion/molecule reaction with toluene, which converts it quantitatively to $C_8H_9^+$. The appearance energies (AE's) at 0 K of $C_7H_7^+$ without ion trapping (11.5 eV) and of Bz^+ with ion trapping (11.1 eV) are in excellent agreement with predictions by time-resolved photodissociation (TRPD). The structure observed at photon energies below 11.1 eV in the Bz^+ photoionization efficiency curve is ascribed to autoionizing Rydberg states converging to the third ionization energy in toluene. These states, which reside in a Franck–Condon gap, dissociate in competition with autoionization. This dissociation is a non-RRKM process forming Bz^+, in preference to Tr^+, and is made possible energetically by virtue of the thermal energy at the temperature of the experiment (298 K). H/D loss ratios for toluene-α-d_3 demonstrate complete isotopic scrambling and an energy dependent isotope effect. The H/D ratio stays constant below 11.1 eV, demonstrating that $AE_{0\,K}(Tr^+) = 11.1$ eV and that there is equality of the AE's of the two $C_7H_7^+$ isomers within experimental error. The preferential, nonstatistical, formation of Bz^+ over Tr^+ below $\sim$11.1 eV is given further proof by the observation of an increased direct CD_2^+ transfer probability from $C_6H_5CD_2^+$ to $C_6H_5CD_3$. These results, combined with previously published *ab initio* calculations which demonstrated a reverse activation energy for the Tr^+ exit channel, explain why there is no energy range in which there is pure Tr^+ formation from toluene, under either photoionization or electron ionization conditions, although Tr^+ is $\sim$11 kcal/mol more stable than Bz^+.

Introduction

The formation of $C_7H_7^+$ from toluene, reaction 1, has been one of the most widely studied reactions in mass spectrometry.

$$C_7H_8^{\bullet+} \rightarrow C_7H_7^+ + H^\bullet \qquad (1)$$

Nevertheless, the role of tropylium (Tr^+) versus benzylium (Bz^+) formation is still unclear. There has been the general belief, since the early work of Rylander et al.,[1] which demonstrated extensive hydrogen scrambling, that interconversion of the toluene ($TOL^{\bullet+}$) and cycloheptatriene ($CHT^{\bullet+}$) radical cations is rapid at the threshold for hydrogen atom loss. This should lead to the preferential formation of Tr^+ over Bz^+ cations at threshold, since Tr^+ has a lower ΔH_f° than Bz^+.[2] However, collisional activation (CA) experiments[3] led to the conclusion that toluene molecular ions do not generate Tr^+ at their dissociation limit. Rate–energy curves were obtained by time-resolved photodissociation (TRPD),[4] and RRKM fitting of the curves gave a critical energy $E_0 = 2.11$ eV in very good agreement with the thermochemical value[5,6] for $Bz^+ + H^\bullet$.

The role of Tr^+ versus Bz^+ formation from toluene remained unclear. This problem was resolved to a certain extent recently.[7] A time-resolved photoionization mass spectrometry (TPIMS) experimental determination of appearance energies combined with *ab initio* and RRKM/QET calculations demonstrated[7] the following: (1) Tr^+ is not formed at its thermochemical threshold owing to the presence of a reverse activation energy for the reaction leading from $CHT^{\bullet+}$ to $Tr^+ + H^\bullet$; (2) the critical energies required to form Bz^+ and Tr^+ from $TOL^{\bullet+}$ are very close, being 2.18 and 2.11 eV, respectively; (3) the appearance energies (AE's) of Tr^+ and Bz^+ at long (t = 40 ms) storage times are equal, within experimental error; (4) previous experimental results for the internal energy dependence of the Tr^+/Bz^+ abundance ratio for photodissociation[8] and charge exchange[9] were in excellent agreement with RRKM/QET calculations[7] appropriate for dissociations of isomerizing ions.[10]

The present study is part of an extension of the original short communication.[7] The emphasis in this part is on the experimental aspect of Bz^+ and Tr^+ formation at near threshold energies. The question why a large fraction of the $C_7H_7^+$ population at low energies under photoionization (PI) or electron ionization (EI) is in the form of Bz^+ will be raised and answered. Another extension of the earlier work will be a detailed report of the *ab initio* calculations.[11] The experiments employed involve TPIMS. This technique has several merits in studying the toluene problem: (a) It can overcome "conventional" kinetic shifts. The conventional kinetic shift (CS) is defined as the excess energy required to observe detectable (1%) dissociation within 10 μs, appropriate to conventional mass spectrometer appearance energy measurements.[4] The "intrinsic" kinetic shift (IS) is taken as the energy needed for 10% fragmentation in competition with radiative relaxation of the excited ion.[4] The latter definition is appropriate to an ion-trap appearance-energy experiment unlimited by ion containment time. (b) Ion/molecule reactions can take place in the ion trap. These, as will be discussed below, allow one to distinguish between isomeric ions such as Tr^+ and Bz^+ and to determine their time-resolved photoionization efficiency (PIE) curves and appearance energies separately.

Experimental Section

The experimental technique of TPIMS has been described in detail recently,[12] and only a brief description will be given here.

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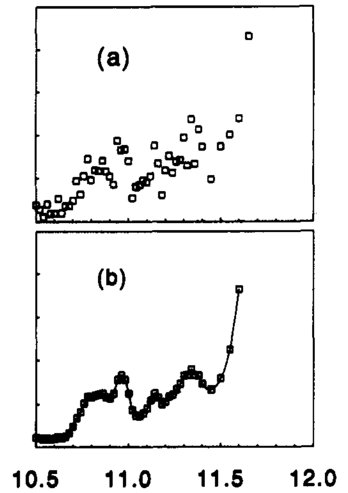

Figure 1. PIE (arbitrary units) versus photon energy (eV) for $C_7H_7^+$ from toluene using no ion trapping: (a) raw data; (b) smoothed data.

Photoionization is induced by a pulsed-vacuum UV light source, in the present case a Hinteregger discharge in hydrogen producing the many-line spectrum or the Hopfield continuum in He. Photoions are trapped in a cylindrical ion-trap (CIT). They are ejected into a quadrupole mass filter by a drawout pulse, following a variable delay time. In this study ions were stored from ~20 μs to ~40 ms. A pulse timing sequence is employed.[12,13] The creation pulse is a train of short pulses applied to the light source, the ejection pulse is applied to the end-cap electrode of the CIT nearest the mass filter, and the detection pulse is gating the ion counter. The radio frequency (rf) of the potential applied to the cylindrical barrel electrode of the CIT is 0.5 MHz ($\omega/2\pi$). The r.f. field is superimposed throughout the pulse sequence.

The effective wavelength resolution employed is 5.0 Å. This corresponds to an energy resolution near the fragmentation onset of toluene of ~0.05 eV.

Toluene (C_7H_8), 99.9+% HPLC grade from Aldrich, was purified further by preparative GC until there was no longer any observable impurity signal at m/z 106 (xylene or ethylbenzene). The ratio of abundances of (m/z 106):(m/z 92) was estimated to be ≤1:10^6. Toluene-α-d_3 was from Cambridge Isotope Laboratories with a stated isotopic purity of 98% D.

Results and Discussion

The onset region of the photoionization efficiency curve for $C_7H_7^+$ at ~20 μs is presented in Figure 1. The appearance energy (AE) is at 10.7 ± 0.05 eV, in excellent agreement with high-sensitivity PI values.[14,15] We have noticed before[12] a shallow plateau region, which is slightly above the background region, starting at ~10.7 eV up to ~11.3 eV. This is similar to the result of Traeger and McLoughlin,[14] which has been ascribed by Buschek et al.[3] to an ethylbenzene or xylene impurity. We have indeed observed in our original study[12] an impurity peak at m/z 106, which (as noted above) has been completely removed by gas chromatography. Nevertheless, the tailing region on the $C_7H_7^+$ PIE curve remained and demonstrates, in addition, some structure (Figure 1). We conclude, therefore, that the onset at 10.7 eV and the structure are real and are due to toluene itself. At this point it is impossible to tell whether this low-energy onset is due to Tr^+ or Bz^+.

We have recently increased the ion trapping times in the TPIMS experiment, without sacrificing sensitivity or mass resolution. Our previous work on toluene[7,12] and toluene-d_8[13] has demonstrated the feasibility of "titrating" Bz^+ ions through their ion/molecule reaction,[16-20]

$$C_7H_7^+(Bz^+) + C_7H_8 \rightarrow C_8H_9^+ + C_6H_6 \qquad (2)$$

under TPIMS conditions. Tr^+ ions do not undergo reaction 2, while Bz^+ ions are fully converted to $C_8H_9^+$. We have employed long ion trapping times to enhance the tailing region on the PIE curve, and in addition we have let the ion/molecule reaction 2 proceed, in order to titrate the Bz^+ ions. The resultant onset region, for t = 40 ms, of the $C_8H_9^+$ PIE curve is plotted in Figure 2, together with the parent PIE curve, $C_7H_8^+$ by Traeger and McLoughlin.[14] The two curves demonstrate similar structure. In particular, there is a maximum in the $C_7H_8^+$ PIE between ~10.7 and ~11.1 eV, ascribed to an unresolved autoionization structure, which has consistently been observed at approximately the same position for $C_8H_9^+$. The identical structure observed in the $C_7H_8^+$ and $C_8H_9^+$ curves is another clear indication that the tailing region on the $C_7H_7^+$ curve (Figure 1 and refs 12 and 14) is not due to an impurity. Autoionization is probably due to a series of Rydberg states converging to the third ionization energy (IE) of toluene,[14] which is at 11.22 eV. Rydberg series converging to the first and second IE's of toluene have been reported.[21] Autoionization can lead to highly vibrationally excited ground-state ions, which in addition contain the thermal vibrational energy distribution of the neutral. The predicted 0 K threshold for $C_7H_7^+$, which includes a 0.19-eV intrinsic kinetic shift, is[4] 2.3 eV. Adding 8.82 eV for the ground-state IE of toluene,[14] this corresponds to 11.12 eV. While we do observe a sharply rising onset at ~11.1 eV (Figure 2), the tailing, which includes the autoionizing structure, proceeds all the way down to at least 10.65 eV. Titration indicates quite clearly that the ion we are observing is Bz^+.

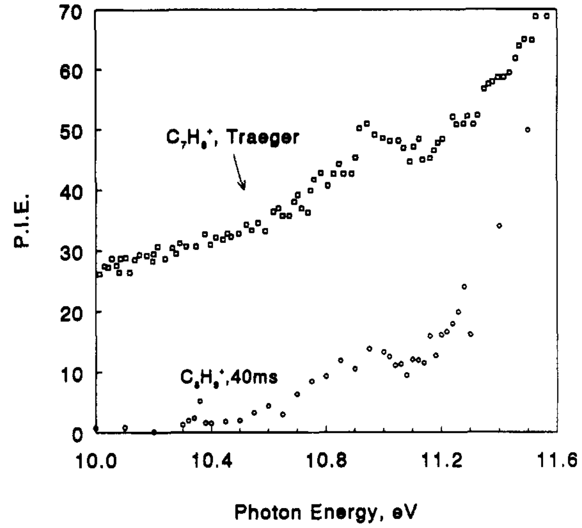

Figure 2. PIE curves for parent $C_7H_8^{\bullet+}$ from toluene[14] and $C_8H_9^+$ at an ion storage time of 40 ms (present data). The ion $C_8H_9^+$ is the product of reaction 2, and its PIE reflects that of Bz^+ (see text).

Two phenomena become apparent when comparing the PIE curve for Bz^+ at 40 ms with the one for $C_7H_7^+$ at 24 μs (Figure 3). (a) Some of the autoionization structure observed for the experiment in the microsecond region is reproduced by the experiment in the millisecond region. This is particularly true for the maximum at ~10.9 eV and the following minimum at ~11.1 eV. (b) There is a pronounced kinetic shift in the steeply rising part of the PIE curves which onsets at 11.5 eV for 24 μs and at 11.1 eV for 40 ms. This corresponds to thresholds of 2.7 and 2.3 eV, respectively, and to conventional and intrinsic kinetic shifts of 0.59 and 0.19 eV, respectively, as predicted by time-resolved photodissociation experiments.[4]

It is evident from our titration experiments that Bz^+ ions are not the only $C_7H_7^+$ ions formed, since a large $C_7H_7^+$ component, ascribed to Tr^+, is left unreacted. The autoionization structure is not as apparent in the Tr^+ PIE curve as in the Bz^+ PIE curve (Figure 4). The two curves are superimposable through a 2.5 multiplication factor (Figure 5) save for the autoionization maximum at ~10.9 eV which contributes much more strongly to Bz^+.

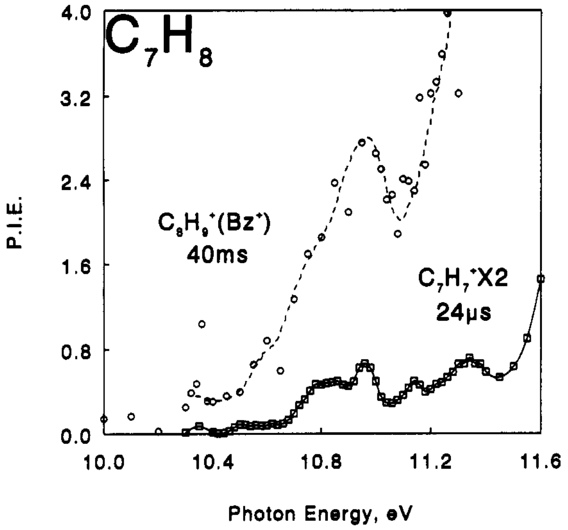

Figure 3. PIE curves for $C_7H_7^+$ (Tr^+ plus Bz^+) at 24 μs and for $C_8H_9^+$ (Bz^+ only) at t = 40 ms. The PIE's are in arbitrary units, to scale. The lines (—) and (- -) are drawn to lead the eye.

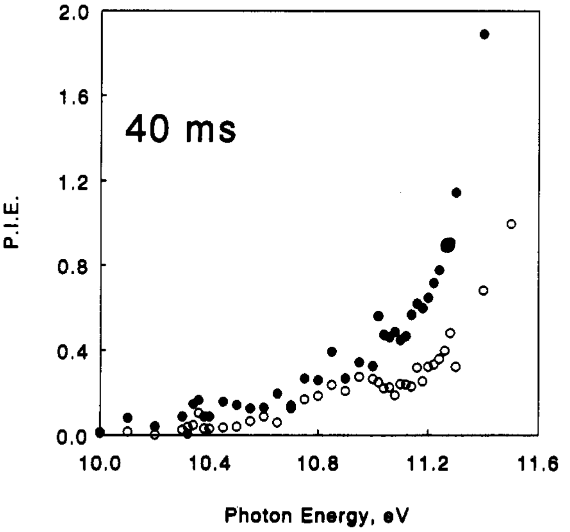

Figure 4. PIE curves for Bz^+ (○) and Tr^+ (●) at t = 40 ms.

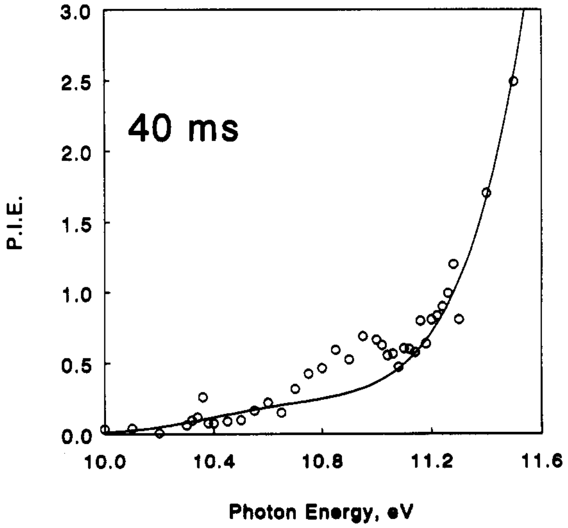

Figure 5. PIE curves for Bz^+ (○) and Tr^+ (—) at t = 40 ms. The Bz^+ data from Figure 4 were multiplied by a factor of 2.5 to normalize them to the Tr^+ data at the higher photon energies.

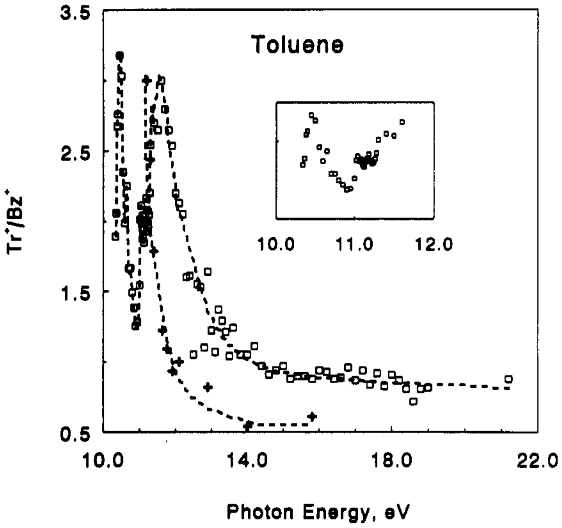

Figure 6. Tr^+/Bz^+ intensity ratio as a function of photon energy: (□) present photoionization data; (+) a photodissociation and charge exchange data from refs 8 and 9. The lines (- -) are drawn to lead the eye. The data in the inset show the ratio near the threshold on an expanded scale.

According to the NIST tables,[2] Tr^+ is ~11 kcal/mol more stable than Bz^+. If Tr^+ were formed at its thermochemical thresold, the critical energy would be E_0 = 1.6 eV, and the appearance energy for 0 K, 10.4 eV—provided there is no IS. If an IS in included, the thermochemical AE should be (at 0 K) ~10.6 eV, namely, 0.5 eV lower than that for Bz^+. Figure 4 shows a slight shift (~0.1 eV) to lower energies of the onset of the rapidly rising part of the PIE curve of Tr^+ compared to Bz^+. When the two curves are superimposed (as in Figure 5), this is no longer evident. The appearance energies of Bz^+ and Tr^+ were determined in a series of experiments to be equal, within experimental error: AE(Bz^+) = AE(Tr^+) = 10.7 ± 0.1 eV. The AE for Bz^+ makes full use of the thermal energy. We have calculated the thermal vibrational energy distribution of toluene at 298 K. The probability for 0.4 eV thermal energy is quite low (0.6% of the maximum, which is at 0.03 eV). Only if there is no IS is it possible to understand the onset of 10.7 eV for Bz^+ at 298 K. This point will be discussed below, in connection with the mechanism of Bz^+ production via the autoionizing states. The near equality of the appearance energies is in agreement with the results of *ab initio* calculations[7] which demonstrate almost equal dissociation barriers leading to Tr^+ and Bz^+. It also explains why there is no energy region for which the $C_7H_7^+$ ions are pure Tr^+. Even if the Tr^+ threshold is ~0.1 eV lower than that for Bz^+, this difference is washed out by the thermal energy distribution at 298 K and pure Tr^+ will only be seen at 0 K.

We have determined the Tr^+/Bz^+ ratio over a wide range and compared our results with previous photodissociation[8] and charge exchange[9] data in Figure 6. The ratio decreases with increasing energy, except for the local minimum at ~10.9 eV and the maximum at ~11.6 eV. The drop beyond 11.6 eV is as expected, if one takes into account that photodissociation and charge exchange are resonance processes while photoionization is not. The present experiment in fact integrates the data up to a certain energy point, leading to a more moderate decrease in the Tr^+/Bz^+ ratio. The minimum at 10.9 eV corresponds, as expected, to the autoionization structure, which becomes very pronounced in this presentation, reflecting nonstatistical behaviour. RRKM/QET calculations[7] reproduce the photodissociation and charge exchange data. The onsets of Tr^+ and Bz^+ which we observe at 298 K are in a Franck–Condon gap, between two photoelectron bands in the well-known photoelectron spectrum (PES) of toluene.[22] The original calculations by Bombach et al.[22] have predicted an increased production of Tr^+ in this energy range at extended reaction times. We observe, on the contrary, an increased production of Bz^+ which coincides with autoionizing Rydberg states converging to the exctied state, i.e., the one corresponding to the higher energy PES band. There are well-documented cases[23] for nonstatistical behavior in Franck–Condon

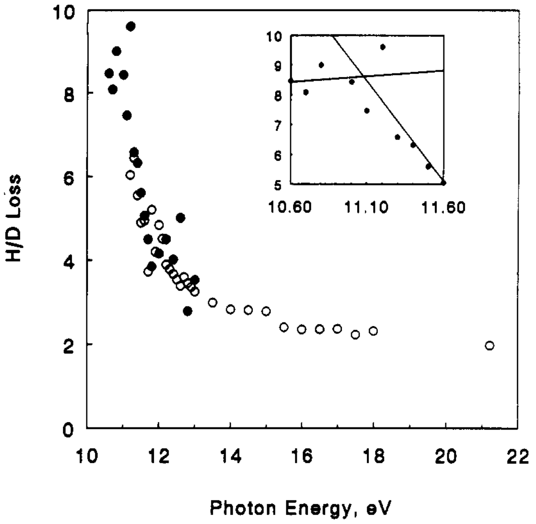

Figure 7. H/D loss ratio as a function of photon energy in $C_6H_5CD_3$: (○) ratio obtained by monitoring $C_7X_7^+$ (X = H or D) without ion storage; (●) ratio obtained by monitoring $C_7X_7^+$ (Tr^+, X = H or D) at t = 40 ms.

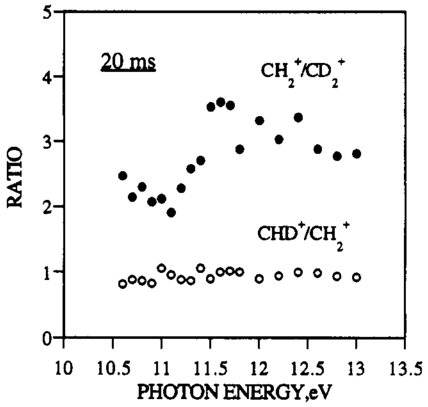

Figure 8. Methylene ion (CX_2^+, X = H or D) transfer ratios as a function of photon energy. The reaction products observed are due to reactions 6 and 7 (see text).

gaps. By analogy with the methane case,[23] we propose that the Rydberg states dissociate into $C_6H_5CH_2^* + H$ neutral fragments followed by autoionization of the benzyl radical into the benzyl cation, thus circumventing the production of Tr^+ from toluene molecular ions of sufficiently low energy. The dissociation of the Rydberg state competes with its autoionization to $C_7H_8^+$:

$$C_7H_8(E_{vib}>0) + h\nu(10.7\text{–}11.1\ \text{eV}) \rightarrow C_7H_8^*\ (\text{Rydberg}) \quad (3)$$

$$C_7H_8^* \rightarrow C_7H_7^*(\text{Bz}) + H^\bullet \quad (4)$$

$$C_7H_7^* \rightarrow C_7H_7^+(\text{Bz}^+) \quad (5)$$

We have studied next the H/D scrambling in $C_6H_5CD_3^+$ as a function of photon energy and ion trapping time. The H/D loss ratio is shown in Figure 7. For toluene-α-d_3 the scrambled ions give an H/D ratio of $5i/3$, where i is the isotope effect, and the unscrambled ions give exclusively D.[24] The isotope effect according to RRKM/QET is a theoretically decreasing function of the internal energy.[24] Our results (Figure 7) are in excellent agreement with previous electron impact data and with the RRKM/QET predictions,[24] providing evidence for complete scrambling. The inset of Figure 7 shows that the H/D loss ratio levels off below 11.10 eV. This forms additional evidence for a 0 K Tr^+ appearance energy, $AE(Tr^+)_{0\,K} \simeq 11.1$ eV. While dissociation at room temperature is observed at lower photon energies, the internal energy in the ion is constant and the isotope effect is constant as well.

We have next studied the ion/molecule reaction products. Two reactions are possible for the Bz^+ cation[20]

$$C_7H_5D_2^+ + C_6H_5CD_3 \rightarrow CD_3C_6H_4C(H,D)_2^+ + C_6(H,D)_6 \quad (6)$$

$$C_7H_4D_3^+ + C_6H_5CD_3 \rightarrow CD_3C_6H_4C(H,D)_2^+ + C_6(H,D)_6 \quad (7)$$

The benzyl ions can transfer CH_2^+, CHD^+, or CD_2^+, and the CX_2^+ group transferred reflects the isotopic CX_2 unit of the reactant ion, since no isotopic scrambling occurs in the collision complex of the ion/molecule reaction.[20] (The neutral $C_6H_5CD_3$ back-donates a ring H-atom to the neutral benzene formed.) The ratio of CHD^+/CH_2^+ transferred (Figure 8) was found equal to 1, irrespective of the photon energy. This is the statistical ratio expected for reaction 6.[20] The CH_2^+/CD_2^+ transfer ratio is between 3 and 4 above 11.5 eV (Figure 8) but drops to ~2 between 11.5 and 11 eV. This change corresponds to an increased CD_2^+ transfer in the Franck–Condon gap region, in agreement with a nonstatistical production of $C_6H_5CD_2^+$, without Tr^+, by direct D loss from the Rydberg state followed by autoionization of $C_6H_5CD_2^*$. Contrary to the ICR study,[20] we are unable to study reactions 6 and 7 separately. The statistically expected CH_2^+/CD_2^+ ratio for reaction 6 is 10 and for reaction 7 is 2.

Conclusion

The previous *ab initio* calculations[7] and the present TPIMS study have solved the long standing problem regarding Tr^+ and Bz^+ formation from toluene. Although Tr^+ is more stable than Bz^+ and although $TOL^{\bullet+}$ and $CHT^{\bullet+}$ interconvert below their dissociation limits, there is no energy range under either EI or PI under which pure Tr^+ is formed for two major reasons: (a) There is a reverse activation barrier in the exit channel leading from $CHT^{\bullet+}$ to $Tr^+ + H^\bullet$; (b) Bz^+ ions are formed, below the 0 K threshold, in a Franck–Condon gap, from Rydberg states which dissociate in a nonstatistical, non-RRKM fashion.

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References and Notes

(1) Rylander, P. N.; Meyerson, S.; Grubb, H. M. *J. Am. Chem. Soc.* **1957**, *79*, 842.
(2) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G.; *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.
(3) Buschek, J. M.; Ridal, J. J.; Holmes, J. L. *Org. Mass Spectrom.* **1988**, *23*, 543.
(4) Huang, F.-S.; Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 151.
(5) Baer, T.; Morrow, J. C.; Shao, J. D.; Olesik, S. *J. Am. Chem. Soc.* **1988**, *110*, 5633.
(6) Eiden, G.-C.; Weisshaar, J. C. *J. Phys. Chem.* **1991**, *95*, 6194.
(7) Lifshitz, C.; Gotkis, Y.; Ioffe, A.; Laskin, J.; Shaik, S. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, R7.
(8) Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382.
(9) Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259.
(10) Baer, T.; Brand, W. A.; Bunn, T. L.; Butler, J. J. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 45.
(11) Shaik, S.; Ioffe, A.; Gotkis, Y.; Lifshitz, C. To be published.
(12) Lifshitz, C. *Int. J. Mass. Spectrom. Ion Processes* **1991**, *106*, 159.
(13) Ohmichi, N.; Gotkis, I.; Steens, L.; Lifshitz, C. *Org. Mass Spectrom.* **1992**, *27*, 383.

(14) Traeger, J. C.; McLoughlin, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *27*, 319.

(15) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7351.

(16) Shen, J.; Dunbar, R. C.; Olah, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 6227.

(17) Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382.

(18) Ausloos, P.; Jackson, J.-A. A.; Lias, S. G. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 269.

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

(20) Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259.

(21) Bolovinos, A.; Philis, J.; Pantos, E.; Tsekeris, P.; Andritsopoulos, G. *J. Chem. Phys.* **1981**, *75*, 4343.

(22) Bombach, R.; Dannacher, J. J.; Stadelmann, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 4205.

(23) Dutuit, O. In *Fundamentals of Gas Phase Ion Chemistry*; Jennings, K. R., Ed.; NATO ASI Series C; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; Vol. 347, pp 21–54.

(24) Howe, I.; McLafferty, F. W. *J. Am. Chem. Soc.* **1971**, *93*, 99.