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Tropylium Ion Formation from Toluene: Solution of an Old Problem in Organic Mass Spectrometry[†]

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The Early Years (1957–1968) of Tropylium Ions in Mass Spectrometry

The formation of $C_7H_7^+$ from toluene, reaction 1, has been one of the most widely studied reactions in mass spectrometry. Originally, it was considered to be a

$$C_7H_8^{\bullet+} \rightarrow C_7H_7^+ + H^{\bullet} \tag{1}$$

simple bond cleavage leading to formation of the benzylium ion (Bz^+). In 1957 Rylander, Meyerson, and Grubb published[1] what has become a landmark in organic mass spectrometry: the suggestion that the $C_7H_7^+$ ion formed from toluene by electron impact ionization has the seven-membered-ring tropylium ion (Tr^+) structure. The hypothesis was based on the observation of hydrogen scrambling in deuterated toluenes and was able to explain several other observations including appearance energies and thermochemical information available at the time. The hydrogen atom cleavage from $C_6H_5CD_3^{\bullet+}$ was at a D/H ratio of $\sim 3/5$, indicating that all hydrogens lose positional identity and become equivalent. Furthermore, consecutive acetylene elimination, from the $C_7X_7^+$ (X = H or D) ions formed, demonstrated again that hydrogens in the $C_7X_7^+$ ion are equivalent. The suggested mechanism involved an irreversible isomerization of the toluene radical cation ($TOL^{\bullet+}$) to cycloheptatriene radical cation ($CHT^{\bullet+}$), preventing formation of Bz^+. An interesting conclusion was that Tr^+ is formed from $CHT^{\bullet+}$ in an $H^{\bullet}$ loss reaction having a reverse activation energy of at least 0.7 eV.

In the early days of Tr^+ in mass spectrometry there was a boom of publications. Many other C_7H_8 isomers were studied in addition to toluene.[2] They all demonstrated $H^{\bullet}$ loss reactions leading to $C_7H_7^+$ ions via what seemed to be a common intermediate: the excited $CHT^{\bullet+}$. Much of that information has been reviewed.[3,4] An important general criterion was established for the involvement of a common intermediate in mass spectral fragmentations:[3,4] the constancy of the sum of the formation enthalpy, ΔH_f, of the neutral precursor and the appearance energy of the $C_7H_7^+$ ion (see, for example, ref 4, Figure 3). Isotope labeling experiments with ^{13}C provided additional support for the ring expansion mechanism in toluene.[4] The idea that formation of Tr^+ via $CHT^{\bullet+}$ occurs at the exclusion of Bz^+ was adopted at the time. Although there was some indication of an apparent preference for loss of a methyl hydrogen from toluene, this was interpreted as an incomplete randomization of the hydrogens in the cycloheptatriene intermediates, rather than as a competitive direct dissociation process.[5]

Application of Modern Mass Spectrometric Methods for Ion Structure Elucidation: The Reemergence of Benzylium (1969–1974)

The techniques available in the 1950s and 1960s were limited to mass spectral fragmentation patterns, appearance energies, isotope labeling studies, and so-called "metastable ions".[3,6] Two much more powerful methods for elucidating ion structures were developed in the late 1960s and early 1970s: Ion/molecule reactions were demonstrated to be structure sensitive, as were collisionally activated mass spectra. An ion cyclotron resonance (ICR) study of ion/molecule reactions of $C_7H_8^{\bullet+}$ isomers[7] demonstrated that non-decomposing $C_7H_8^{\bullet+}$ ions from toluene preserve the toluene structure and do not undergo ring expansion. Gas-phase radiolysis studies of toluene and other alkylbenzenes demonstrated[8] the formation of $C_7H_7^+$ ions, whose reactions are characteristic of the Bz^+ structure. Collisional activation spectra of $C_7H_7^+$ ions, produced from various precursors by electron ionization, established[9,10] in addition to Tr^+ the formation of long-lived Bz^+ as well as tolyl ions in the gas phase. Finally, photodis-

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[†] Dedicated to Dr. S. Meyerson in recognition of his pioneering work on toluene and tropylium.

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sociation of $C_7H_8^{\bullet+}$ from toluene in an ICR established[11,12] the formation of $C_7H_7^+$ ions, whose ion/molecule reaction with the neutral precursor,

$$C_7H_7^+ + C_6H_5CH_3 \rightarrow C_8H_9^+ + C_6H_6 \qquad (2)$$

is characteristic of the Bz^+ structure, since it proceeds by methylene transfer. It was concluded that both Tr^+ and Bz^+ are stable species which can exist for seconds as separate entities in the gas phase. Photodissociation spectroscopy of $C_7H_8^{\bullet+}$ isomers[13] proved the separate existence, on a time scale of seconds, of $TOL^{\bullet+}$ and $CHT^{\bullet+}$, without interconversion.

The Reaction Mechanism

The salient features of a reaction mechanism by which Tr^+ is formed from toluene were established in the early 1970s. Formation of Bz^+ had to be included, in view of the results from ion/molecule reactions and collisional activation studies. $TOL^{\bullet+}$ and $CHT^{\bullet+}$ were obviously two stable species residing in potential energy minima, in view of the photodissociation spectroscopy studies. They had to interconvert below their respective dissociation thresholds, to Bz^+ and Tr^+, for hydrogen scrambling to occur. At higher energies, direct dissociation becomes more favored relative to the isomerization, since the degree of scrambling was observed to decrease with increasing internal energy of the toluene ion.[14] Scrambling observed in $C_7H_7^+$ ions after formation[14,15] clearly indicated that Tr^+ and Bz^+ can interconvert, provided they had enough internal energy to dissociate. The formation of a common $C_7H_8^{\bullet+}$ structure of high symmetry from toluene and other isomers had to be discarded in favor of two parallel routes[14,16] from $TOL^{\bullet+}$ to Tr^+: (1) isomerization to $CHT^{\bullet+}$ followed by $H^\bullet$ loss and (2) C–H cleavage forming Bz^+ followed by isomerization to Tr^+. Details of the $TOL^{\bullet+} \rightarrow CHT^{\bullet+}$ and $Bz^+ \rightarrow Tr^+$ isomerization mechanisms were ironed out experimentally[17,18] and theoretically.[19,20] Two minimum energy reaction paths were suggested,[17-21] for $TOL^{\bullet+} \rightarrow CHT^{\bullet+}$. In the first an α-H atom first migrates to the ipso position of the aromatic ring (1,2 migration), followed by formation of a norcaradiene radical cation, which isomerizes to $CHT^{\bullet+}$, while in the second an α-H atom migrates to the ortho position (1,3 migration).

An Interlude on Energetics

The enthalpies of formation of $TOL^{\bullet+}$, $CHT^{\bullet+}$, and Bz^+ are quite well established. That of Tr^+ is somewhat less certain. What is quite certain[22] is that $TOL^{\bullet+}$ is more stable than $CHT^{\bullet+}$, while Tr^+ is more stable than Bz^+: $\Delta H_f°(TOL^{\bullet+}) < \Delta H_f°(CHT^{\bullet+})$ and $\Delta H_f°(Tr^+) < \Delta H_f°(Bz^+)$. Table 1 summarizes some of the better established and/or more recent thermochemical information. The value quoted for $\Delta H_f°_0(Tr^+)$ is from *ab initio* calculations.[33] There is a previous experimental value from photoelectron photoion coincidence (PEPICO) data,[34] which is closely similar, but the PEPICO results have to be reinterpreted, as will be shown below.

Table 1. Gas-Phase Enthalpies of Formation (kcal/mol) and Ionization Energies (eV)[a]

species	$\Delta H_f°_0$ (neutral)	IE	$\Delta H_f°_0$ (ion)
$C_7H_8^{\bullet+}$ ($TOL^{\bullet+}$)	17.5	8.8276[b]	221
$C_7H_8^{\bullet+}$ ($CHT^{\bullet+}$)	48.7	8.29 ± 0.01[c]	240
$C_7H_7^+$ (Bz^+)	53[a,d]	≤7.27 ± 0.03[e]	219
		7.20 ± 0.02[f]	219.6 ± 1.2[g]
	54.7 ± 1[h]	7.2484 ± 0.0004[i]	221.8 ± 1[i]
$C_7H_7^+$ (Tr^+)		6.236 ± 0.005[j]	208.2[k]

[a] All values are from reference 23 unless otherwise noted. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] Reference 27. [f] Reference 28. [g] Reference 29. [h] Reference 30. [i] Reference 31. [j] Reference 32. [k] Reference 33.

The benzyl–hydrogen bond dissociation energy has been a topic of some discussion[1,35-37] in relation to the appearance energy of $C_7H_7^+$. The value accepted today,[30,31,38] $D°_0(C_6H_5CH_2\text{–}H) = 88.9 \pm 1.0$ kcal/mol, is considerably higher than the accepted value in the early days of the mass spectrometric study of toluene fragmentation.[35-37] Combining this value with $IE(Bz^\bullet) = 7.2484$ eV yields a predicted thermochemical value for the appearance energy of Bz^+: $AE(Bz^+) = 11.1$ eV. Finally, the ionic bond energy is calculated to be[31] $D°_0(C_6H_5CH_2^+\text{–}H) = 52.6 \pm 1.0$ kcal/mol. This value is based on the very accurate adiabatic ionization energy of $Bz^\bullet$ quoted above and on the somewhat less accurately known formation enthalpy of the benzyl radical.[31] PEPICO results on benzyl bromide[29] yielded a somewhat lower value of $D°_0(C_6H_5CH_2^+\text{–}H) = 50.4 \pm 1.2$ kcal/mol = 2.18 eV. Combining this latter value with the very accurate ionization energy,[24] $IE(TOL) = 8.8276$ eV, yields $AE(Bz^+) = 11.0$ eV.

Is the Tropylium Ion (Tr^+) Formed from Toluene at Its Thermochemical Threshold?

An article bearing this name has been published recently.[33] The question was raised indirectly in two prior papers: one was a reinvestigation of the collisional activation mass spectra of $C_7H_7^+$ ion mixtures,[22] and

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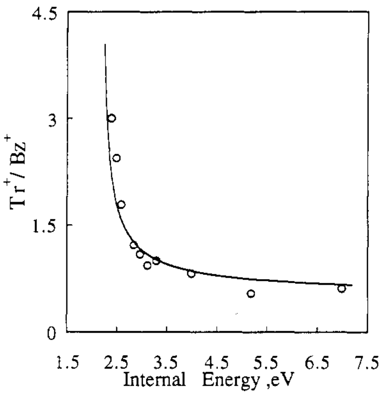

Figure 1. Internal energy dependence of Tr^+/Bz^+ abundance ratio: (—) the RRKM/QET calculation for dissociations of isomerizing ions, $t = 1$ s; (○) results of photodissociation[40] and charge exchange experiments.[41] Reprinted with permission from ref 33. Copyright 1993 Elsevier Science Publishers.

the other was a time-resolved photodissociation study of the toluene ion.[39]

Quantitation of the isomeric ion mixture Tr^+/Br^+ has been achieved in photodissociation and charge exchange experiments[41] using the ion/molecule reaction (2), to "titrate" the Bz^+ ions. Collisional activation has been employed for this purpose in electron ionization experiments.[42,43] The photodissociation and charge exchange results, which are for fairly well defined internal energies, are presented in Figure 1. The Tr^+/Bz^+ abundance ratio is observed to decrease with increasing internal energy of the TOL^+. Under electron ionization, the ratio first declines with increasing electron energy, and then rises again, because of the isomerization[42] of Bz^+ to Tr^+. The reinvestigation of collisional activation mass spectra[22] demonstrated however, unexpectedly, that at the lowest energies attainable the Bz^+ content failed to fall below 50%, and it was concluded that toluene ions do not generate tropylium ions at their dissociation limit. Since Tr^+ is considerably more stable (~11 kcal/mol) than Bz^+, it was expected that an energy range should be found for which nearly pure Tr^+ is formed.

Can experimental determinations of appearance energies help in answering this question? The appearance energy of $C_7H_7^+$ from toluene has been repeatedly measured over the years, and the results are summarized in Table 2. The thermochemicaly expected appearance energy for Tr^+ is ~11 kcal/mol lower than for Bz^+, i.e., ~10.5 eV. The early experimental values[35,44] were all in excess of even the thermochemically calculated value for Bz^+. Even most of the recent values[22,47] are higher than 11.1 eV. However, electron ionization with ion trapping,[45] high-sensitivity photoionization,[25,46] and analysis of PEPICO data[34] gave values in the range of 10.5–10.7 eV, which was ascribed to Tr^+ formation. It has recently[33,48] been demonstrated that the value of 10.7 ± 0.1 eV is appropriate for 298 K and that at 0 K $AE_{0K}(Tr^+) \approx AE_{0K}(Bz^+) = 11.1 \pm 0.1$ eV; in other words, Tr^+ is not formed at its thermochemical threshold. The appearance energies of Tr^+ and Bz^+ are equal within experimental error.

Table 2. Appearance Energy (AE, eV) of $C_7H_7^+$ from Toluene

year	AE	method	ref
1954	11.8 ± 0.1	electron ionization	35
1966	11.7 ± 0.1	photoionization	44a
1968	11.55 ± 0.05	photoionization	44b
1975	10.70	electron ionization and ion trapping	45
1977, 1978	10.71 ± 0.03	photoionization	25, 46
1983	10.52 ± 0.07 (0 K)	PEPICO	34
1988	11.9 ± 0.2	metastable ions	22
1988	11.46 ± 0.05	energy-selected electrons	22
1991	11.25 ± 0.05	photoionization	47
1993	11.5 ± 0.1 (0 K)	photoionization	48
1993	11.1 ± 0.1 (0 K) 10.7 ± 0.1 (298 K)	photoionization and ion trapping	33, 48

Why Are Ion Traps Useful?

Some of the appearance energies quoted in Table 2 were measured in ion traps. The major reason for using ion traps has been the "kinetic shift" which reaction 1 demonstrates. The conventional kinetic shift is defined as the excess energy required to observe detectable (1%) dissociation within 10 μs, appropriate to conventional mass spectrometer appearance energy measurement.[39] Early RRKM/QET calculations[49] have predicted a kinetic shift of 0.6 eV for a rate of $k = 10^5$ s^{-1}. The kinetic shift was investigated experimentally using electron ionization[45] and photoionization.[33,47,48,50] The appearance energies shift to lower values with increasing ion trapping time, as expected, since lower rate constants are being sampled at longer times. Time-resolved photodissociation experiments[39] have predicted a conventional shift of 0.59 eV and a threshold of 2.7 eV, which when combined with the ionization energy of toluene (Table 1) yield a predicted appearance energy of 11.5 eV on the microsecond time scale. This value is in agreement with recent values for energy-selected electrons[22] and photoionization.[48] The intrinsic kinetic shift is taken as the energy needed for 10% fragmentation in competition with radiative relaxation of the excited ion.[39] The latter definition is appropriate to an ion-trap appearance energy experiment unlimited by ion containment time. The predicted value based on time-resolved photodissociation is[39] 0.19 eV, corresponding to a threshold of 2.3 eV and an appearance energy of 11.1 eV, in agreement with the recent 0 K value.[33,48]

An additional reason for using ion traps has been the prediction[51] that the Tr^+/Bz^+ abundance ratio should increase with increasing ion lifetimes at low ionizing

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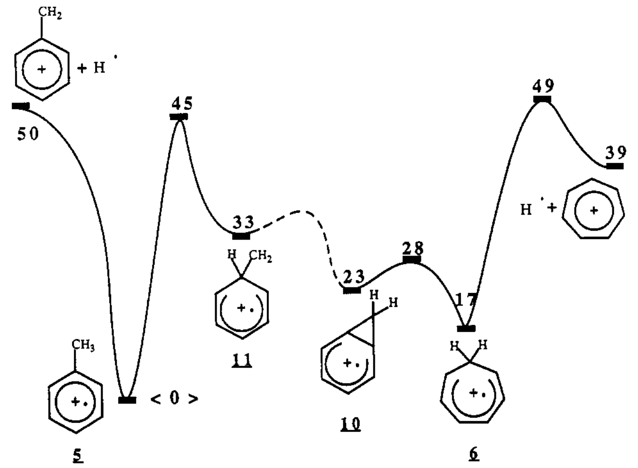

Figure 2. Schematic potential energy diagram. The relative energies (kcal mol^{-1}) are the arithmetic means of values calculated by PMP3, MP4SDTQ, and QCISD(T)//HF/3-21G. Species numbering follows the notation of Dewar and Landman.[20] Reprinted with permission from ref 33. Copyright 1993 Elsevier Science Publishers.

energies (see Figure 6 of ref 51). This point will be discussed further below.

The Potential Energy Profile: *Ab Initio* Calculations

Different potential energy profiles were suggested over the years for the isomerization and dissociation reactions in the $TOL^{•+}/CHT^{•+}$ system.[1,10,20,33,39] MINDO/3 calculations[20] gave incorrect energetics, for example, $\Delta H_f(CHT^{•+}) < \Delta H_f(TOL^{•+})$. The relative position of Tr^+ on the potential energy profile remained unclear until recently. State of the art *ab initio* theory is such that the $TOL^{•+}/CHT^{•+}$ interconversion and H abstraction may now be studied at a fairly high computational level. This has been done recently.[33] Both of the minimum energy reaction paths suggested by MINDO/3 were calculated, but only the first was found significant since there are high barriers along the second. The resultant potential energy profile is given in Figure 2 (the numbering given to the different species is as in the work by Dewar and Landman[20]). Several important results transpired: (a) There is a reverse activation energy for $H^•$ abstraction from $CHT^{•+}$ of ≈10 kcal/mol. Thus, although Tr^+ is 11 kcal/mol more stable than Bz^+, its appearance energy is not lower than that of Bz^+ by this energy (0.48 eV), owing to the barrier which prevents Tr^+ from being formed at its thermochemical limit. Bz^+, however, is formed at its thermochemical limit, since $H^•$ abstraction from $TOL^{•+}$ has no reverse activation energy. The notion of a reverse activation energy for $H^•$ abstraction from $CHT^{•+}$ was first raised in the Rylander, Meyerson, and Grubb paper[1] and has now been proved both experimentally and theoretically to be correct. (b) The critical energies for formation of Bz^+ and Tr^+ from $TOL^{•+}$ are almost equal, within the accuracy of *ab initio* calculations, with that for Tr^+ being perhaps 1.6 kcal/mol (0.07 eV) lower. The actual values calculated, 2.18 eV and 2.11 eV for Bz^+ and Tr^+, respectively, are in excellent agreement with the experimental values of 2.18 eV for Bz^+ [29] and 2.11 eV for $C_7H_7^+$,[39] to be discussed below. (c) The highest isomerization barrier along the reaction coordinate is for the 1,2 migration transition structure (TS 5–11 in Figure 2), yet even this barrier is lower than the transition states for $H^•$ loss from either $TOL^{•+}$ or $CHT^{•+}$, allowing interconversion of $TOL^{•+}$ and $CHT^{•+}$ below their dissociation limits.

Reaction Dynamics. Rate–Energy (*k*(*E*)) Dependences

The rate–energy dependence, i.e., the dependence of the microcanonical rate coefficient $k(E)$ on the internal energy of the ion, is a very basic attribute of a reaction. Bombach *et al.*[51] have determined the breakdown diagram of the toluene cation, i.e., the fractional bundance of ions as a function of energy, by time-resolved fixed wavelength (He I) PEPICO. They have not determined $k(E)$ directly, but by analyzing the data through RRKM calculations they deduced the rate–energy functions of Tr^+ and Bz^+. In their model, the curves for Tr^+ and Bz^+ cross each other (Figure 3 of ref 51). The curve for Tr^+ begins at a photon energy of 10.52 eV but rises slowly with energy, while that for Bz^+ begins at 11.17 eV and rises steeply with energy. This interpretation may be ruled out on several grounds: (a) There has been no energy range found for which pure Tr^+ is formed[22] (see previous sections). (b) The appearance energies for Bz^+ and Tr^+ are equal within experimental error.[33,48] (c) *Ab initio* calculations give nearly equal critical energies for Bz^+ and Tr^+ production from toluene. (d) RRKM/QET calculations cannot simply be carried out for two parallel reactions from a single precursor, $TOL^{•+}$; even a simplified scheme must, at least, include the $TOL^{•+} \rightleftharpoons CHT^{•+}$ isomerization; in fact, reaction 1 in toluene belongs to a well-worked-out example for dissociation of isomerizing ions.[52] This has been pointed out recently.[50] A simplified reaction scheme includes the following[33] (notation is as in the paper by Baer *et al.*[52]):

$$TOL^{•+} \xrightarrow{k_4} Bz^+ + H^• \tag{3}$$

$$TOL^{•+} \underset{k_2}{\overset{k_3}{\rightleftharpoons}} CHT^{•+} \tag{4}$$

$$CHT^{•+} \xrightarrow{k_1} Tr^+ + H^• \tag{5}$$

Rate–energy dependences were calculated[33] for k_1, k_2, k_3, and k_4 by RRKM. The vibrational frequencies and critical energies employed in the calculations were the results of the *ab initio* calculations. The $k(E)$'s are presented in Figure 3. The solution of coupled differential equations for the decay rates gave[33]

$$[Bz^+] = k_4\left[\frac{\beta_-}{\lambda_-}(1 - e^{-\lambda_- t}) - \frac{\beta_+}{\lambda_+}(1 - e^{-\lambda_+ t})\right]$$

$$[Tr^+] = k_1\left[\frac{1}{\lambda_-}(1 - e^{-\lambda_- t}) - \frac{1}{\lambda_+}(1 - e^{-\lambda_+ t})\right]$$

where

$$\lambda_\pm = \frac{a_1 + b_2}{2} \pm {}^1/_2[(a_1 + b_2)^2 - 4a_1b_2 + 4a_2b_1]^{1/2}$$

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(52) Baer, T.; Brand, W. A.; Bunn, T. L.; Butler, J. J. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 45–55.

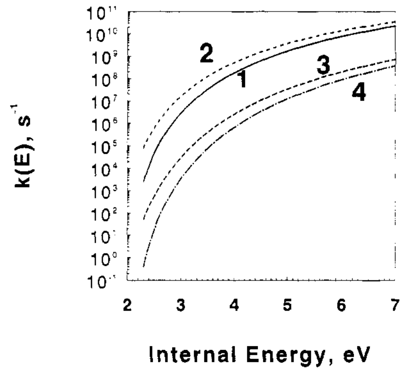

Figure 3. RRKM rate–energy curves based on *ab initio* potential energy and vibrational frequency calculations. Reactions 1 and 2 are the dissociation of $CHT^{\bullet+}$ to $Tr^+ + H$ and the isomerization of $CHT^{\bullet+}$ to $TOL^{\bullet+}$, respectively. Reactions 4 and 3 are the dissociation of $TOL^{\bullet+}$ to $Bz^+ + H$ and the isomerization of $TOL^{\bullet+}$ to $CHT^{\bullet+}$, respectively. $E_0(1) = 31.8$ kcal/mol; $E_0(2) = 28.3$ kcal/mol; $E_0(3) = 45.1$ kcal/mol; $E_0(4) = 50.2$ kcal/mol. Vibrational frequencies are scaled (×0.89) *ab initio* values.

$$\beta_{\pm} = -\frac{a_1 + \lambda_{\pm}}{b_1}$$

$a_1 = -k_1 - k_2 - k_{RAD}$, $a_2 = k_2$, $b_1 = k_3$, $b_2 = -k_3 - k_4 - k_{RAD}$, and k_{RAD} is the IR radiative decay constant.

These expressions allowed the calculation of the Tr^+/Bz^+ ratio as a function of energy. The results are included in Figure 1. The final, infinite-time ratio, is given by

$$[Tr^+]/[Bz^+] = k_1k_3/[k_4(k_1 + k_2)]$$

The calculated results are observed to be in excellent agreement with experimental Tr^+/Bz^+ ratios over a wide energy range. This lends strong support to the quantitative accuracy of the RRKM model calculations.[33] The $k(E)$ for reaction 1 has been determined in an elegant experiment, using time-resolved photodissociation.[39] The results were fitted by RRKM calculations. The striking outcomes were (1) a critical energy $E_0 = 2.11$ eV in excellent agreement with the thermochemistry of Bz^+ and (2) a rather negative activation entropy, $\Delta S^{\ddagger}_{1000K} = -11.7$ eu, characteristic of rearrangement reactions. The time-resolved photodissociation data were in the form of time plots of ion peak heights as a function of delay between a laser pulse and a mass spectral analysis pulse. The observation of $C_7H_7^+$ represented the sum of $[Bz^+] + [Tr^+]$. The experimental rate–energy dependence is the result of the complex interplay between dissociation and isomerization in the $C_7H_8^{\bullet+}$ reaction system. While the time plots could be fitted[39] with a RRKM type $k(E)$ dependence with a single $E_0/\Delta S^{\ddagger}$ pair, they can also be fitted satisfactorily and quantitatively by the more elaborate RRKM model[33] using the assigned values for $k_1(E)$, $k_2(E)$, $k_3(E)$, and $k_4(E)$ (Figure 4).

The theoretical modeling of the photodissociation results demonstrates that the problem has been solved. The energetics of the overall reaction fits that of Bz^+ formation, since the Tr^+ threshold is nearly the same. The overall reaction has a negative activation entropy because of the tight transition states of the isomerization steps.

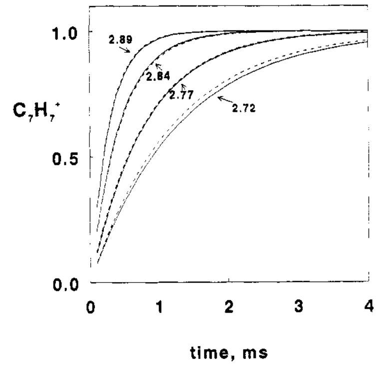

Figure 4. Calculated time-resolved photodissociation time plots for ion energies $E_{ion} = 2.72$, 2.77, 2.84, and 2.89 eV, respectively. The dashed curves are based on single dissociation rate constants of 920, 1400, 2250, and 3600 s^{-1}, respectively (from ref 39); the continuous curves are calculated for the $[Tr^+] + [Bz^+]$ sum (from the model of ref 33).

Do Highly Excited Rydberg States Play a Role?

The question of dissociation from discrete states with discrete ion lifetimes versus a continuum of states and a continuum of ion lifetimes has been raised over the years in connection with the toluene ion fragmentation.[6,53,54] The notion of an autoionizing level leading to slow dissociation under electron ionization was first brought up in 1965.[53] The possibility that autoionizing Rydberg states play a special role in leading to nonstatistical Tr^+/Bz^+ ratios under electron ionization and photoionization has been brought up recently.[48] There is a large "Franck–Condon gap" between the second and third electronic states (corresponding to parts of the first and second photoelectron bands in the spectrum of toluene.[51]) The probability for direct ionization in this gap is very low. It is filled, however, by autoionizing Rydberg states.[25,48] It is in this energy region of the Franck–Condon gap that the onset of $C_7H_7^+$ takes place.[48] It has been demonstrated that the structure due to the autoionizing Rydberg states, observed in the photoionization efficiency curve of $C_7H_8^{\bullet+}$, is reproduced in the Bz^+ (Figure 5) but not in the Tr^+ photoionization efficiency curve. In fact there is a minimum in the Tr^+/Bz^+ ratio under photoionization at the photon energy (~10.95 eV) at which the autoionizing structure is a maximum, indicating a nonstatistical non-RRKM like dissociation forming Bz^+. The conclusion was[48] that there was no energy range under either electron ionization or photoionization under which pure Tr^+ is formed for two major reasons: (a) There is the reverse activation barrier in the exit channel leading from $CHT^{\bullet+}$ to $Tr^+ + H^{\bullet}$ discussed earlier. (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. The Rydberg states presumably dissociate via C–H cleavage, perhaps through interaction with a valence state, 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.

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(53) Meyer, F.; Harrison, A. G. *J. Chem. Phys.* **1965**, *43*, 1778–1782.
(54) Buttrill, S. E., Jr. *Ibid.* **1974**, *61*, 619–624.

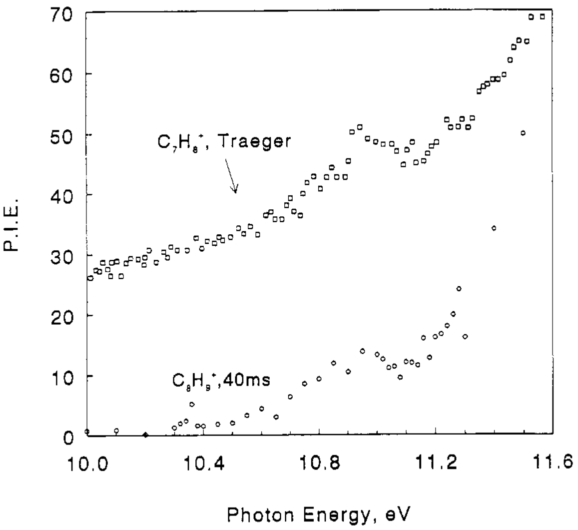

Figure 5. Photoionization efficiency curves for parent $C_7H_8^{\bullet+}$ from toluene[25] and $C_8H_9^+$ at an ion storage time of 40 ms. The ion $C_8H_9^+$ is the product of reaction 2, and its photoionization reflects that of Bz^+ (taken from ref 48).

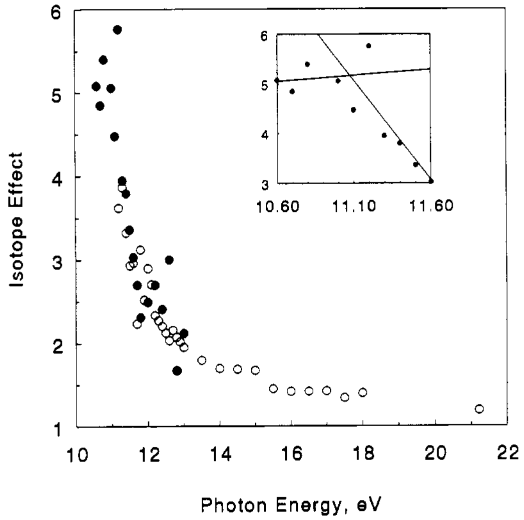

Figure 6. Isotope effect for H$^\bullet$ versus D$^\bullet$ loss from $C_6H_5CD_3$ as a function of photon energy: (○) isotope effect obtained by monitoring $C_7X_7^+$ (X = H or D) without ion storage; (●) isotope effect obtained by monitoring $C_7X_7^+$ (Tr^+, X = H or D) at t = 40 ms (adapted from Figure 7 of ref 48; the H/D loss ratio was multipled by $^3/_5$).

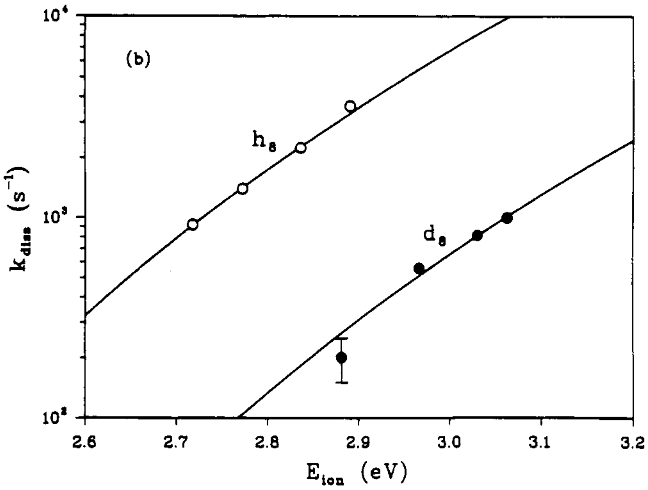

Figure 7. RRKM rate–energy curves for $C_7H_8^{\bullet+}$ and $C_7D_8^{\bullet+}$: (—) calculated; (○, ●) experimental time-resolved photodissociation data reprinted with permission from ref 39. Copyright 1991 Elsevier Science Publishers.

Table 3. Predicted and Observed Kinetic Shifts for $C_7H_7^+$ and $C_7D_7^+$ Appearance Energies (AEs)

ion	type of kinetic shift	kinetic shift,[39] eV	internal energy threshold,[39] eV	AE, eV predicted	AE, eV obsd
$C_7H_7^+$	conventional	0.59	2.7	11.5	11.5[48]
	intrinsic	0.19	2.3	11.11	11.1[33,48]
	true value	0	2.11	10.94	
$C_7D_7^+$	conventional	0.97	3.1	11.9	12.0[50]
	intrinsic	0.47	2.6	11.4	11.4[50]
	true value	0	2.13	10.96	

Isotope Effects

Isotope effects were observed as early as 1964.[55] An isotope effect of 3.6 favoring H$^\bullet$ loss over D$^\bullet$ loss, was observed for the so-called "slow" reaction (microsecond range) in toluene.[53] It was realized[56] that there were two factors affecting H versus D loss in partially deuterated toluenes: (1) A "preference factor", defined as the ratio of the probability of loss of a hydrogen atom from a side-chain position to that for the loss of a hydrogen atom from a ring position, and (2) the "isotope factor", defined as the ratio of the probability of loss of a hydrogen atom from any position to that for the loss of a deuterium atom from the same position. The preference factor was found to be 1.0 for metastable ion decompositions in the microsecond time range while the isotope factor was found to be 3.50. Howe and McLafferty[14] realized that not only was the degree of scrambling, observed through the preference factor, energy dependent but also the isotope effect depended on the internal energy of the toluene ion. This effect was predicted[57] by RRKM/QET calculations. It was observed experimentally under electron ionization,[14] under laser photodissociation,[11] and under photoionization.[48] It is expected that the isotope effect should become infinite at the bond dissociation energy of the C–D bond in the cation.[11] In practice (Figure 6), the isotope effect rises very steeply at low photon energies and levels off. This reflects a broadening effect of the thermal energy distribution. In fact, below the 0 K threshold the average internal energy of the ion no longer varies with the photon energy; as the photon energy is reduced, ions of higher thermal energies contribute and the isotope effect is more or less constant. As expected,[11] this provides additional support for the dissociation onset. Since Tr^+ could be distinguished from Bz^+ in the photoionization experiment,[48] the observed 11.1 ± 0.1 eV photon energy, for which the isotope effect begins to decline with increasing photon energy, is also the Tr^+ onset.

The fully deuterated isotopomer of reaction 1 has been studied, demonstrating the existence of not only intramolecular but also intermolecular isotope effects.[39] The experimental and calculated $k(E)$ dependences for $C_7H_8^{\bullet+}$ and $C_7D_8^{\bullet+}$ are presented in Figure 7. The critical energies E_0 and activation entropies $\Delta S^\ddagger$ are

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(55) Burr, J. G.; Meyer, R. A. *Ibid.* **1964**, *40*, 2046–2047.

(56) Beynon, J. H.; Corn, J. E.; Baitinger, W. E.; Caprioli, R. M.; Benkeser, R. A. *Org. Mass Spectrom.* **1970**, *3*, 1371–1377.

(57) Vestal, M.; Lerner, G. Fundamental Studies Relating to the Radiation Chemistry of Small Organic Molecules. Aerospace Research Laboratory Report 67-0114; U.S. Defense Documentation Center: Alexandria, VA, 1967.

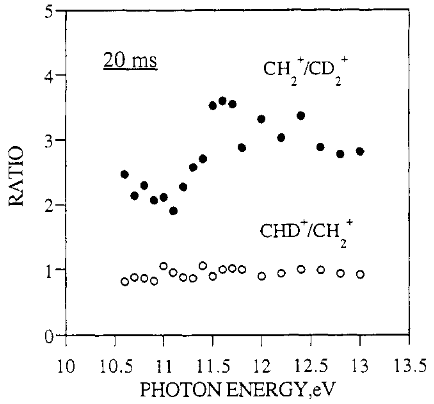

Figure 8. Methylene ion (CX_2^+, X = H or D) transfer ratios as a function of photon energy. The reaction products observed are due to benzyl ion, $C_7H_5D_2^+$ and $C_7H_4D_3^+$, reactions with C_6H_5-CD_5 (from ref 48).

the same for the two isotopomers within experimental error.[39] The predicted kinetic shifts and appearance energies are quite different[39] and are summarized in Table 3. Experimental results[33,47,48,50] (Table 3) are in excellent agreement with the predicted appearance energies.

Partially deuterated benzyl ions can transfer CH_2^+, CHD^+, or CD_2^+ to toluene, and the CX_2^+ group transferred reflects the isotopic CX_2 unit of the reactant ion, since no isotopic scrambling occurs in the isotopomer collision complexes of ion/molecule reaction 2.[41] The preferential, nonstatistical, formation of Bz^+ over Tr^+ below ~11.1 eV was given further proof[48] by the observation of an increased direct CD_2^+ transfer probability from $C_6H_5CD_2^+$ to $C_6H_5CD_3$ (Figure 8).

Summary

In this Account we have described the historical background for the understanding of the unimolecular dissociation of the gas-phase toluene radical cation. It is now clear that both Bz^+ and Tr^+ ions are formed in a fairly complex isomerization/dissociation scheme. Some of the original ideas,[1] e.g., formation of $CHT^{\bullet +}$ and existence of a reverse activation energy in the dissociation of this latter ion, have proved to be correct. The development of powerful experimental techniques, notably those involving ion trapping and time-resolved studies[39,48] have proved to be of great importance. From the point of view of theory, the combination of *ab initio* calculations of the potential energy profile with RRKM/QET calculations has turned out to be invaluable.[33] The overall behavior of the reaction, demonstrated in calculated and experimental $k(E)$'s, kinetic shifts, and isotope effects, is definitely RRKM like. The nonstatistical behavior of autoionizing Rydberg states in Franck–Codon gaps is intriguing. Electric fields were used for ion trapping;[48] since such fields are known to affect the autoionizing and dissociative behavior of highly excited Rydberg states,[58,59] this aspect warrants further study.

The results from our own work reported in this Account are due to the hard work of several members of my research group: Dr. Y. Gotkis, M. Peres, Dr. N. Ohmichi, L. Steens, and J. Laskin. Work on ab initio calculations was done in collaboration with Dr. A. Ioffe and Prof. S. Shaik. Funding has been provided by the Israel Science Foundation and by The James Franck Research Center.

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(58) Chupka, W. A. *J. Chem. Phys.* **1993**, *98*, 4520–4530; **1993**, *99*, 5800–5807.
(59) Bahatt, D.; Even, U.; Levine, R. D. *Ibid* **1993**, *98*, 1744–1747.