

Rapid Communication

Is the tropylium ion (Tr^+) formed from toluene at its thermochemical threshold?

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Abstract

The role of tropylium ion (Tr^+) versus benzylium ion (Bz^+) formation by H loss from toluene radical cation ($\text{TOL}^{\cdot+}$) was studied by time-resolved photoionization mass spectrometry, by ab initio calculations and by RRKM-QET. Tr^+ is not formed at its thermochemical threshold owing to the presence of a reverse activation energy for the reaction leading from the cycloheptatriene radical cation ($\text{CHT}^{\cdot+}$) to $\text{Tr}^+ + \text{H}$. The critical energies required to form Bz^+ and Tr^+ from $\text{TOL}^{\cdot+}$ are very close, being 2.18 and 2.11 eV, respectively. The computational results are in excellent agreement with experiments regarding appearance energies, heats of formation and Tr^+/Bz^+ abundance ratios as a function of energy.

Key words: Time-resolved photoionization mass spectrometry; Ab initio calculations; RRKM-QET; Toluene; Tropylium; Benzylium.

Introduction

There has been the general belief, since the early work of Rylander et al. [1], that interconversion of the toluene ($\text{TOL}^{\cdot+}$) and cycloheptatriene ($\text{CHT}^{\cdot+}$) radical cations is rapid at the threshold for hydrogen atom loss from toluene:



Since the tropylium ion (Tr^+) is more stable than the benzylium ion (Bz^+) [2], this should lead to preferential formation of Tr^+ over Bz^+ ions at threshold. However, collisional activation experiments [3] led to the conclusion that toluene mol-

ecular ions do not generate Tr^+ at their dissociation limit, since there was no evidence for the generation of pure Tr^+ from $\text{TOL}^{\cdot+}$ at low energies. Furthermore, the kinetics of the reaction have been studied recently [4] by time-resolved photodissociation. Rate-energy curves were obtained and RRKM fitting of the curves gave a critical energy of activation $E_0 = 2.11$ eV which is quite close to the thermochemical energy required [5,6] to give $\text{Bz}^+ + \text{H} \cdot$. The role of Tr^+ versus Bz^+ formation remains therefore unclear, and this is the focus of the present Communication.

State of the art ab initio theory is such that the $\text{TOL}^{\cdot+}/\text{CHT}^{\cdot+}$ interconversion and H-abstraction may now be studied at a fairly high computational level. Furthermore, RRKM-QET calculations can be performed on ab initio potential energy surfaces, thus minimizing the number of free parameters [7]. We have combined a time-resolved photoionization mass spectrometry (TPIMS) experimental

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study of Tr^+ and Bz^+ appearance energies (AEs) with *ab initio* and RRKM calculations of the toluene system.

Experimental

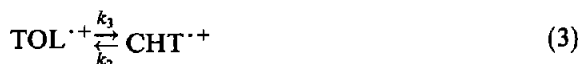
The experimental technique of TPIMS has been described in detail recently [8]. Photoionization is induced by a pulsed vacuum UV light source, in the present case a Hinteregger discharge in hydrogen producing the many-line spectrum. Photoions are trapped in a cylindrical ion trap. They are ejected into a quadrupole mass filter by a drawout pulse, following a variable delay time. In this study ions were stored for up to 40 ms.

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).

Computational details

(a) The *ab initio* MO calculations were performed using the GAUSSIAN 90 and GAUSSIAN 92 suite of programs [9,10] on an IBM/RS6000 (model 550) Workstation. The geometries of C_7H_8^+ isomers and of transition structures for their interconversions, as well as the structures of Bz^+ and Tr^+ were optimized by gradient methods and checked by frequency calculations using the 3-21G basis set at the unrestricted Hartree–Fock (UHF) and restricted Hartree–Fock optimization levels. For stationary points, single point calculations have been performed on post-SCF levels [MP 2–4 and QCISD(T)]. These types of calculations are critical for spin contaminated wavefunctions of open-shell structures. We were unable to extend the basis set further, since even the present single point calculations needed about 20–30 CPU hours per point. Furthermore, enlargement of the basis set at the UHF level did not improve the effect of spin contamination, as judged from the expectation values for the S^2 operator, which should be 0.75 for the pure doublet spin state. As the best energy estimates we used the highest unprojected post-

SCF energies — MP4SDTQ and QCISD(T) — and the highest available projected MP n energy — PMP3 — and took the arithmetic mean of the three energy values for which the difference does not exceed 2–3 kcal mol $^{-1}$ (for the meaning of the notation used, see ref. 11). (b) The calculations of microcanonical rate coefficients $k(E)$ as a function of energy were performed by an RRKM program [12]. Ohmichi et al. noticed earlier [13] that reaction (1) in toluene belongs to a well-worked-out example for dissociation of isomerizing ions [14]. Rate constants were calculated for the following set of reactions (notation is as in the paper by Baer et al. [14]):



The vibrational frequencies and critical energies employed in the calculations were the results of the *ab initio* calculations. (Vibrational frequencies were scaled by a factor 0.89 to account for their systematic overestimation at the Hartree–Fock level [11,15]). The isomerization rate constants k_2 and k_3 were calculated for the highest isomerization barrier along the energy profile discussed below. The solution of coupled differential equations for the decay rates [14] gives

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

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

where

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

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

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

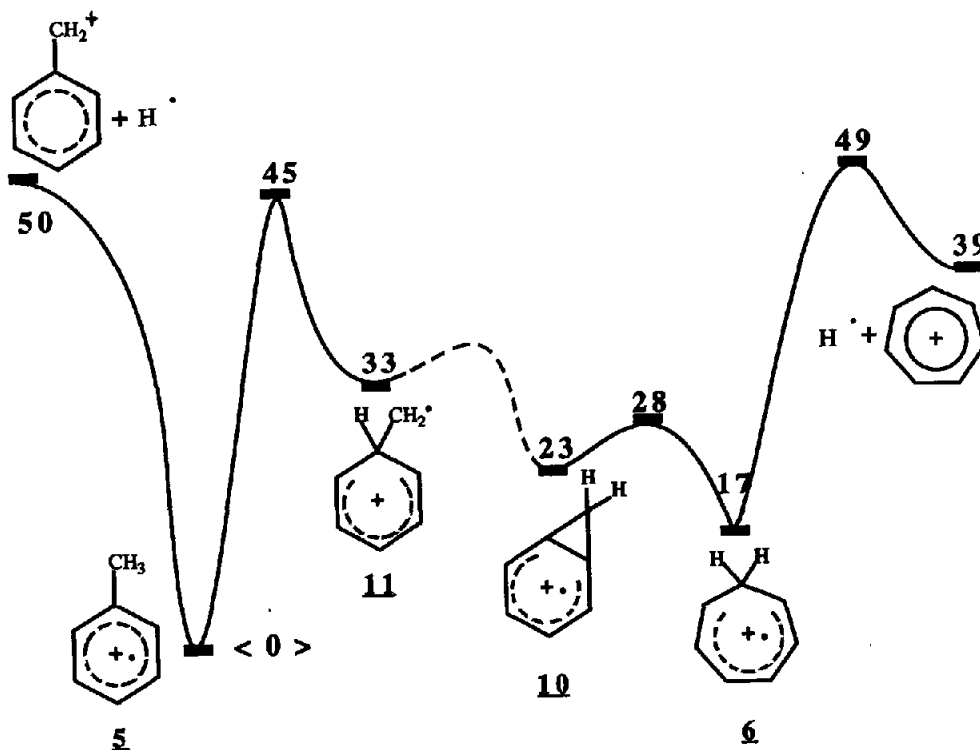


Fig. 1. Schematic potential energy diagram. The relative energies (kcal mol^{-1}) are the arithmetic means of values calculated by PMP3, MP4SDTQ and QCISD(T)//HF/3-21G (see text). Species numbering follows the notation of Dewar and Landman [22]. There is some uncertainty concerning the exact energy of TS 10–11 (— — —), but it is definitely considerably lower than TS 5–11.

decay constant. These expressions allow the calculation of the $[\text{Tr}^+]/[\text{Bz}^+]$ ratio as a function of energy.

Results and discussion

The AEs for Tr^+ and Bz^+ , at $t = 40$ ms storage time, were determined separately, by converting the Bz^+ ion to C_8H_9^+ via the following reaction [13,16–19]:



Tr^+ ions do not undergo reaction (10), while Bz^+ ions are fully converted (“titrated”) to C_8H_9^+ . Within experimental error, the AEs are equal, namely at 298 K, $\text{AE}_{298\text{K}}(\text{Tr}^+) \approx \text{AE}_{298\text{K}}(\text{Bz}^+) = 10.7 \pm 0.1 \text{ eV}$. These AEs translate to 0 K values,

$\text{AE}_{0\text{K}}(\text{Tr}^+) \approx \text{AE}_{0\text{K}}(\text{Bz}^+) = 11.1 \pm 0.1 \text{ eV}$, which agree with the critical energy $E_0 = 2.11 \text{ eV}$ [4] since

$$\begin{aligned} \text{AE}_{0\text{K}} &= \text{IE} + E_0 + \text{IS} \\ &= 8.8276 + 2.11 + 0.19 = 11.13 \text{ eV} \end{aligned} \quad (6)$$

where IE is the accurately known ionization energy of toluene [20] and IS is the intrinsic kinetic shift [4] due to radiative decay in the IR region. The present AEs are in excellent agreement with the high sensitivity value for C_7H_7^+ from toluene [21], which did not distinguish between Tr^+ and Bz^+ . If Tr^+ were formed at its thermochemical threshold, its AE would have been lower than that of Bz^+ , since Tr^+ is believed to be more stable than Bz^+ . The AEs of Tr^+ and Bz^+ coincide closely with the onset of the third electronic state of toluene $^+$. The role of Rydberg states conveying to this ionic

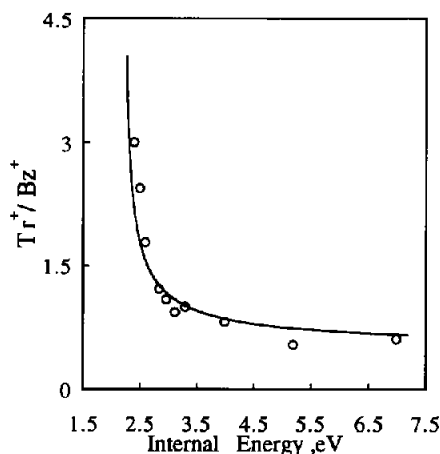


Fig. 2. Internal energy dependence of Tr^+/Bz^+ abundance ratio. —, The RRKM-QET calculation for dissociations of isomerizing ions [14] (see text); \circ , results of photodissociation [17] and charge exchange [19] experiments, which have thermal energy contributions.

state will be discussed separately (C. Lifshitz et al., in preparation).

Previous calculations of the potential energy profile for the interconversion of TOL^+ and CHT^+ were carried out by MINDO/3 [22]. Two minimum energy reaction paths (MERPs) were found. In MERPA an α -H atom first migrates to the ipso position of the aromatic ring (1,2 migration) while in MERPB it migrates to the ortho position (1,3 migration). Both MERPs were calculated in the present study by ab initio methods, but only MERPA was found to be significant since there are high barriers along MERPB. The resultant potential energy profile for MERPA is given in Fig. 1 (the numbering given to the different species is as in the work by Dewar and Landman [22]).

Several important results transpire. (a) There is a reverse activation energy for reaction (4) of $\approx 10 \text{ kcal mol}^{-1}$. Thus, although Tr^+ is 11 kcal mol^{-1} more stable than Bz^+ , its AE is not lower than that of Bz^+ by this energy (0.48 eV), owing to the barrier which prevents Tr^+ being formed at its thermochemical limit. Bz^+ , however, is formed at its thermochemical limit, since reaction (2) has no reverse activation energy. (b) The critical energies for formation of Bz^+ and Tr^+ from TOL^+ are almost equal, within the accuracy of the ab initio

calculations, with that for Tr^+ being perhaps $1.6 \text{ kcal mol}^{-1}$ (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^+ [5] and 2.11 eV for C_7H_7^+ [4]. (c) Since the heat of formation of the Bz^+ cation is rather accurately known, $\Delta H_{f0}^\circ(\text{Bz}^+) = 219.6 \text{ kcal mol}^{-1}$ [2,5], the present ab initio calculations can give the heat of formation of Tr^+ , $\Delta H_{f0}^\circ = 208.2 \text{ kcal mol}^{-1}$. (d) The highest isomerization barrier along the reaction coordinate is for the 1,2 migration transition structure (TS 5–11 in Fig. 1). Yet even this barrier is lower than the transition states for H^+ loss from either TOL^+ or CHT^+ , which agrees with the general belief so far, allowing interconversion of TOL^+ and CHT^+ below their dissociation limits.

The isomerization barrier TS 5–11 was chosen as the rate determining point along the $\text{TOL}^+ \rightleftharpoons \text{CHT}^+$ interconversion (reaction (3)) in RRKM calculations. The Tr^+/Bz^+ ratios were calculated as a function of energy and the results were found to be in very good agreement with experimental data from photodissociation [17] and charge exchange [19] experiments (Fig. 2).

Conclusion

Experimental time-resolved appearance energies, and ab initio calculations are in perfect agreement that Tr^+ is not formed from toluene at its thermochemical threshold, owing to a barrier which exists for the dissociation of CHT^+ to $\text{Tr}^+ + \text{H}^+$.

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References

- 1 P.N. Rylander, S. Meyerson and H.M. Grubb, *J. Am. Chem. Soc.*, **79** (1957) 842.

- 2 S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, *J. Phys. Chem. Ref. Data*, 17 (suppl. 1) (1988).
- 3 J.M. Buschek, J.J. Ridal and J.L. Holmes, *Org. Mass Spectrom.*, 23 (1988) 543.
- 4 F.S. Huang and R.C. Dunbar, *Int. J. Mass Spectrom. Ion Processes*, 109 (1991) 151.
- 5 T. Baer, J.C. Morrow, J.D. Shao and S. Olesik, *J. Am. Chem. Soc.*, 110 (1988) 5633.
- 6 G.-C. Eiden and J.C. Weisshaar, *J. Phys. Chem.*, 95 (1991) 6194.
- 7 N. Heinrich, F. Louage, C. Lifshitz and H. Schwarz, *J. Am. Chem. Soc.*, 110 (1988) 8183.
- 8 C. Lifshitz, *Int. J. Mass Spectrom. Ion Processes*, 106 (1991) 159.
- 9 M.J. Frisch, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M. Robb, J.S. Binkley, C. Gonzalez, D.J. DeFrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol and J.A. Pople, *GAUSSIAN 90*, Revision J, Gaussian Inc., Pittsburgh, PA, 1990.
- 10 M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. DeFrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN 92*, Revision B, Gaussian Inc., Pittsburgh, PA, 1992.
- 11 W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley–Interscience, New York, 1986.
- 12 W.L. Hase and D.L. Bunker, *A General RRKM Program*, QCPE No. 234, Chemistry Department, Indiana University, Bloomington, IN.
- 13 N. Ohmichi, I. Gotkis, L. Steens and C. Lifshitz, *Org. Mass. Spectrom.*, 27 (1992) 383.
- 14 T. Baer, W.A. Brand, T.L. Bunn and J.J. Butler, *Faraday Discuss. Chem. Soc.*, 75 (1983) 45.
- 15 J.A. Pople, H.R. Schlegel, R. Krishnan, D.J. DeFrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout and W.J. Hehre, *Int. J. Quantum. Chem. Symp.*, 15 (1981) 269.
- 16 J. Shen, R.C. Dunbar and G.A. Olah, *J. Am. Chem. Soc.*, 96 (1974) 6227.
- 17 R.C. Dunbar, *J. Am. Chem. Soc.*, 97 (1975) 1382.
- 18 P. Ausloos, J.-A.A. Jackson and S.G. Lias, *Int. J. Mass Spectrom. Ion Phys.*, 33 (1980) 269.
- 19 J.-A.A. Jackson, S.G. Lias and P. Ausloos, *J. Am. Chem. Soc.*, 99 (1977) 7515.
- 20 P. Ausloos, *J. Am. Chem. Soc.*, 104 (1982) 5259.
- 21 K.-T. Lu, G.C. Eiden and J.W. Weisshaar, *J. Phys. Chem.*, 96 (1992) 9742.
- 22 J.C. Traeger and R.C. McLoughlin, *J. Am. Soc.*, 99 (1977) 7351; *Int. J. Mass Spectrom. Ion Phys.*, 27 (1978) 319.
- 23 M.J.S. Dewar and D. Landman, *J. Am. Chem. Soc.*, 99 (1977) 2446.