Theoretical Investigation of the Formation of the Tropylium Ion From the Toluene Radical Cation

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ABSTRACT: The formation of the tropylium ion, $C_7H_7^+$, in the mass spectrum of toluene is a chemical process that has been extensively studied. There is, however, still debate as to the structure of the moieties and the reaction pathways involved. This work presents the first computationally complete reaction schemes for the formation of tropylium from toluene to be reported. The calculations were performed at the HF/6-31G(d, p) and the DFT/B3LYP/6-311++G(2d) levels of theory using Gaussian 03W. The previously unreported optimized structures and energies for a transition state and an intermediate in one scheme and a transition state in the other have been determined. These results are consistent with the previously reported literature and the available experimental data.   © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 1322–1327, 2009

Key words: tropylium; reaction mechanism; potential energy surface; transition state

Introduction

For several years, the mass spectrum of toluene has been of interest because of the many species produced during the electron impact. The most prominent peak in the spectrum is at m/e = 91 [1]. This peak may be accounted for by hydrogen cleavage from the parent toluene molecular cation (Tol$^{+\bullet}$) resulting in $C_7H_7^+$. Despite numerous pub-

lications from several research groups, there is still debate as to the structure of this moiety and the reaction pathways involved [2–11]. The two most probable structures are the tropylium ion (Tr$^+$) and the benzylium ion (Bz$^+$) (see Fig. 1).

In the early 1930s, Huckel predicted that Tr$^+$ has a stable structure [12]. The first experimental data supporting the existence of Tr$^+$ in the mass spectrum of toluene was obtained by Rylander et al. [2]. They also observed hydrogen scrambling in the deuterated forms of toluene which suggested that the $C_7H_7^+$ species was the highly symmetric Tr$^+$.

In contrast, evidence for Bz$^+$ resulted from techniques developed in the late 1960s and early 1970s that showed that the $C_7H_7^+$ species reacts with the
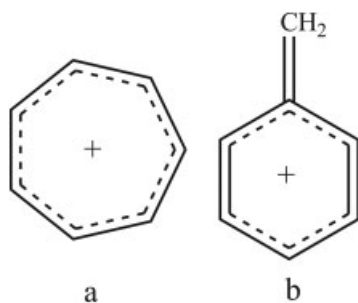
FIGURE 1. Representations of (a) the tropylium ion and (b) the benzylium ion.

neutral precursor [3–5] through methylene transfer [6, 7]. Indeed, several studies on the branching ratio between these two structures have been performed [8, 9].

The appearance energy for $C_7H_7^+$ from toluene has been experimentally determined to be 11.1 eV [10]. Quantum mechanical calculations of the potential energy surface for the production of Tr^+ and Bz^+ have been performed using perturbation theory but are not complete [8, 10].

This work compares energies calculated using density functional theory (DFT) with those calculated with perturbation theory and elaborates on the mechanism. These calculations show that Bz^+ and Tr^+ can interconvert in this system. The proposed mechanism for this isomerization is similar to the mechanism that Dewar and Landman calculated at the MINDO level [11].

Computational Methods

All quantum mechanical calculations were performed using Gaussian 03W [13] on a Microsoft Windows XP equipped Dell Optiplex GX260 PC having a 2.0 GHz Pentium-4 processor and 256 MB of memory. The molecular structures were input into Gaussian 03W via PCMODEL [14]. Hartree–Fock [15] (HF) SCF runs where performed using the 6-31G(d, p) basis set, whereas DFT [16] calculations used the B3LYP [17, 18] hybrid functional and the 6-311++G(2d) basis set.

Results and Discussion

Reaction Scheme 1 (shown in Fig. 2) accounts for the formation of Tr^+. It is similar to the mechanism that was proposed by Dewar and Landman for the

formation of Tr^+ and $H \cdot$ from the $Tol^{+ \cdot}$ [11]. This mechanism begins with a hydrogen migration in the $Tol^{+ \cdot}$, from the methyl group to the ipso position of the six-membered ring to form the first intermediate (Int1). Formation of a bond between the methyl carbon and an alpha carbon produces the second intermediate (Int2). This intermediate is composed of a six-membered ring and a three-membered ring (norcaradienyl ion). Dissociation of the bond common to the rings in a disrotatory fashion produces a cycloheptatriene intermediate (Int3). The last step in the formation of the tropylium ion and atomic hydrogen is a hydrogen cleavage from the former methyl carbon in the cycloheptatriene intermediate. The energies of this proposed scheme at the HF/6-31G(d, p) and B3LYP/6-311++G(2d) levels of theory are given in Table I and are shown graphically in Figure 3. All energy values have been corrected for zero point energies so that these values may be compared with the experimental results. The tabulated values are the energy differences with respect to the $Tol^{+ \cdot}$ ion.

The relative energies of most of the species in this scheme are consistent between the two methods employed. The largest deviation occurs for TS1 where the HF energy is almost 7 kcal/mol higher than the DFT energy. It is not certain why the HF is so much higher than the DFT energy whereas the structural details calculated by both methods are very similar. Conversely, the energies calculated for Int1 and TS2 are similar for the two methods but there are significant differences between bond angles calculated by the two methods. These differences might be accounted for by the addition of electron correlation in density functional theory.
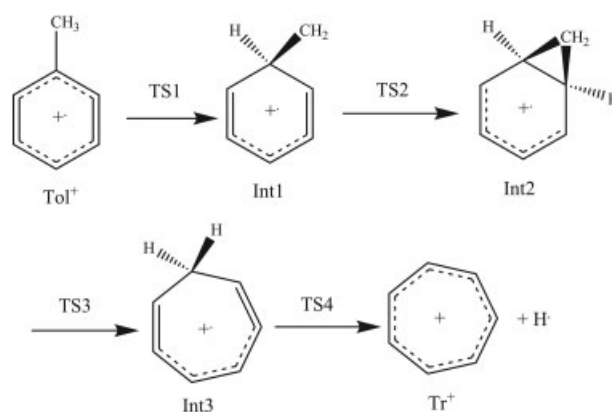
FIGURE 2. Reaction Scheme 1 for the formation of Tr^+ from $Tol^{+ \cdot}$.

TABLE I _____

Energy differences relative to Tol$^{+\cdot}$ for the species comprising Scheme 1.

| Species | This work | | Dewar and Landman [11] | Moon et al. [8] | | Lifshitz |
	HF/6-31G(d,p)	DFT/B3LYP/6-311++G(2d)	MINDO/3	HF/6-31G**	G2(MP2,SVP)	et al. [10, 19]
Tol$^{+\cdot}$	0.0	0.0	0.0	0.0	0.0	0.0
TS1	44.0	37.2	34.2			45.0
Int1	34.9	35.6	26.3			33.0
TS2	36.2	37.4	29.7			
Int2	27.0	22.8	21.2			23.0
TS3	35.1	30.5	17.6			28.0
Int3	18.9	14.8	−5.6	18.9		17.0
TS4	51.9	47.0		52.3	48.2	49.0
Tr^{+} + H$^{\cdot}$	45.3	43.8		45.9	42.0	39.0

Entries are in units of kcal/mol.

The structures of Int2, TS3, Int3, TS4, and Tr$^+$ are similar between the two methods that were employed in this work except that the distances between two atoms that are relevant for a transition state are smaller for the HF calculations. For example, in TS4, the distance between the methylene carbon and the hydrogen that is being ejected is 1.854 Å with HF whereas the distance with DFT/B3LYP is 2.030 Å.

The energies presented here are in reasonable agreement with the values calculated by Dewar and Landman considering the MINDO/3 method that they used. Their mean absolute error for the calculated heat of formation was 11 kcal/mol [11]. Taking this into consideration, all the HF/6-31G(d, p) values are in good agreement with the MINDO/3 results except for the values for TS3 and Int3. The energies are also in excellent agreement with those
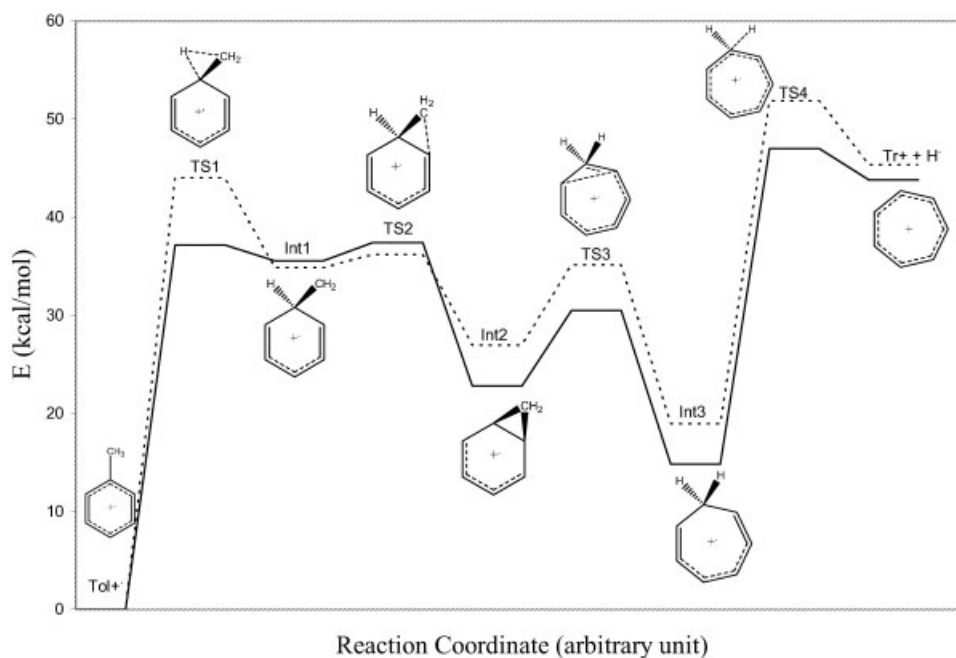
FIGURE 3. HF/6-31G(d, p) (dashed) and DFT/B3LYP/6-311++G(2d) (solid) energies for the formation of the tropylium ion via Scheme 1.
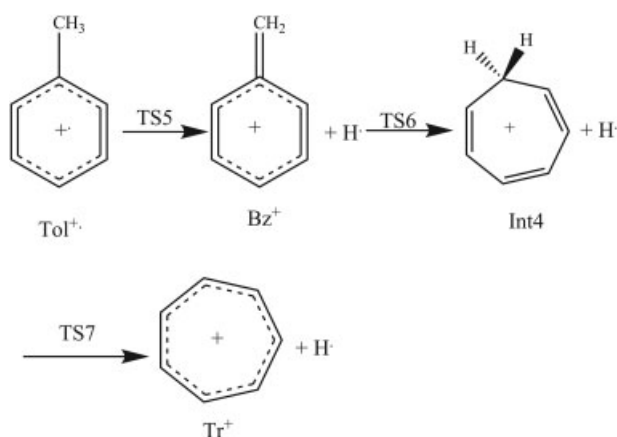
FIGURE 4. Reaction Scheme 2 for the formation of Tr^+ from $Tol^{+\cdot}$.

obtained by Moon et al. [8] at the HF/6-31G** level of theory. The differences may be attributed to the polarization functions. These new results are a completion of the mechanism at this level of theory.

The energies calculated with DFT/B3LYP/6-311++G(2d) are comparable with the values calculated with G2(MP2, SVP) by Moon et al. [8] and those of Lifshitz et al. [19]. The latter are the arithmetic mean of values calculated by PMP3, MP4SDTQ, and QCISD(T)//HF/3-21G. TS2 was not found in the literature. The Article by Lifshitz states that there is some uncertainty about the exact energy of TS2, but it is definitely considerably lower than the energy of TS1 [19]. The energy presented here is contrary to this statement in that the TS2 energy is slightly higher than the energy of TS1 with density functional theory. The largest devia-

tions between these two sets of data are for TS1 and $Tr^+ + H^\cdot$. Scheme 1 has also been completed at the DFT/B3LYP/6-311++G(2d) level of theory.

A less energetically favorable process for the formation of the tropylium ion is shown in Reaction Scheme 2 (see Fig. 4). This scheme begins with cleavage of a hydrogen from the methyl carbon of $Tol^{+\cdot}$ to produce the Bz^+ ion and $H^\cdot$ molecule through TS5. TS5 has not been previously reported in the literature. Even though the barrier is small, a transition state does exist. Formation of a bond between the methyl carbon and the α carbon produces the norcaradienyl cation (Int4). A hydrogen shift from the former methyl carbon to the carbon that was at the ipso position of the six-membered ring produces the Tr^+. The energies of Scheme 2 are provided in Table II and shown graphically in Figure 5. Scheme 1 is clearly a more favorable mechanism than Scheme 2 for the formation of the tropylium ion because the highest energy barrier is 80 kcal/mol lower in the former. The structures involved in Scheme 1 have symmetry properties that maximize the π interactions within the systems. The rings of the structures involved in Scheme 2 are slightly contorted which decreases the stability of the π interactions of the systems. There is a minima (Int*) and transition state (TS*) between Bz^+ and Int4 in a mechanism proposed in the literature [20] that could not be found. Every attempt resulted in minimization to the Bz^+ structure.

The energies and structures are very similar between HF/6-31G(d, p) and DFT/B3LYP/6-311++G(2d) until we get to TS6. The energy for TS6 is about 5 kcal/mol higher for HF than for DFT. This can be explained for by the structure of this transition

TABLE II
Energy differences relative to $Tol^{+\cdot}$ for the species comprising Scheme 2.

	This Work		Cone et al. [20]	Moon et al. [8]		Lifshitz
Species	HF/6-31G(d,p)	DFT/B3LYP/6-311++G(2d)	MINDO/3	HF/6-31G**	G2(MP2,SVP)	et al. [10, 19]
$Tol^{+\cdot}$	0.0	0.0	0.0	0.0	0.0	0.0
TS5	54.9	54.0				
$Bz^+ + H^\cdot$	50.8	52.6	8.2	51.4	48.9	50.0
$TS^* + H^\cdot$			25.8			
$Int^* + H^\cdot$			23.7			
$TS6 + H^\cdot$	120.6	115.0	31.5			
$Int4 + H^\cdot$	115.4	108.2	28.7			
$TS7 + H^\cdot$	131.9	121.0	40.9			
$Tr^+ + H^\cdot$	45.3	43.8	−16.6			

Entries are in units of kcal/mol.
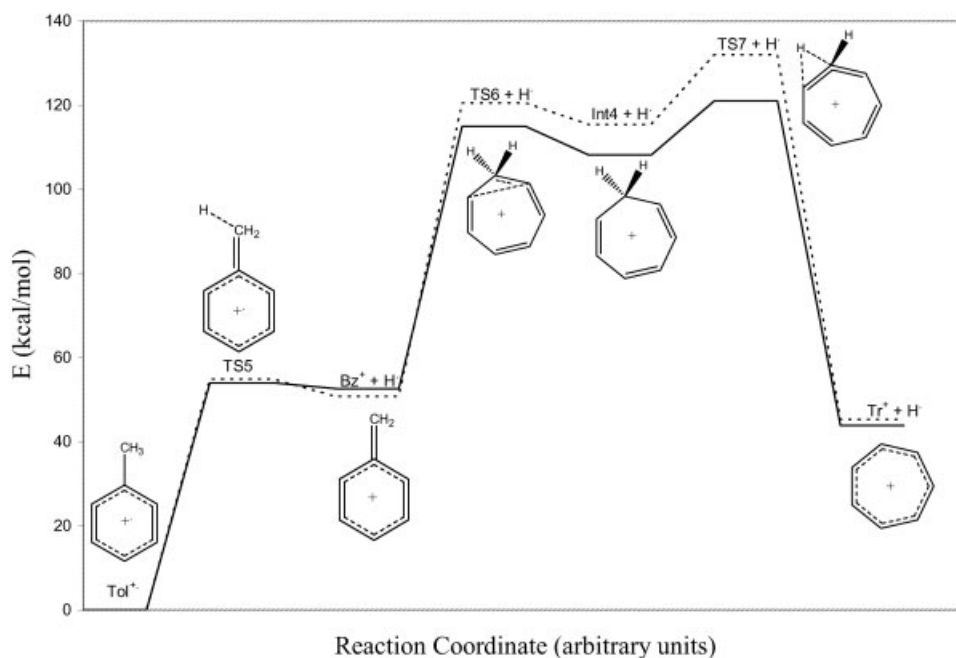
FIGURE 5. HF/6-31G(d, p) (dashed) and DFT/B3LYP/6-311++G(2d) (solid) energies for the formation of the tropylium ion via Scheme 2.

state. The bond lengths are similar, but the DFT calculated species has a planar seven-membered ring that maximizes the π interactions. In contrast, this moiety has a puckered ring under HF. Further, Int4 is approximately 7 kcal/mol higher with HF than with DFT. As the overall structure is very similar between the two methods, it is not certain why this deviation occurs unless it has something to do with electron correlation. The HF energy of TS7 is almost 11 kcal/mol higher. This deviation may be accounted for by the small differences in the structures calculated by the two methods.

There were few comparable results for this mechanism in the literature. The energies are not similar to the MINDO/3 results obtained by Cone et al. [20]. This is probably because their heat of formation data excludes the hydrogen that is lost at the beginning of the reaction. The other data, whereas sparse, are in excellent agreement with the values presented here.

The ionization potential (IP) of toluene to $\text{Tol}^{+\bullet}$ at 0 K is 8.8276 ± 0.0006 eV according to a recent experimental determination [21]. The critical energy ($E_0 = 2.11$ eV) and the intrinsic kinetic shift due to radiative decay in the infrared region (IS = 0.19 eV) have also been reported [22]. For comparison with the available experimental data, the appearance energies (AE) of Tr^+ and Bz^+ may be determined from their highest

energy barriers along the minimum energy reaction path. Thus the appearance energy of C_7H_7^+ may be calculated from $\text{AE} = \text{IP} + E_0 + \text{IS} = 11.13$ eV. After adding the intrinsic kinetic shift, the HF/6-31G(d,p) calculated energies for the IP of toluene, and the AEs of Tr^+ and Bz^+ are 7.1922, 9.63 (i.e., $9.44 + 0.19$), and 9.76 eV, respectively. The percent relative errors of the experimental to the calculated values for these quantities are thus 18.5%, 13.5%, and 13.3%, which is not in good agreement.

The IP of toluene, and the AEs of Tr^+ and Bz^+ calculated at the DFT/B3LYP/6-311G++(2d) level of theory are 8.5869, 10.82, and 11.12 eV, giving percent relative errors of 2.7%, 2.8%, and 0.1%, respectively. Thus, the DFT values are in excellent agreement with the experimentally determined ionization potential as well as the appearance energies of Tr^+ and Bz^+.

Conclusions

Two computationally complete reaction schemes have been presented for the formation of tropylium from the toluene radical cation. These are the first examples of such complete mechanisms. A previously unreported transition state and intermediate for one scheme and an unreported transition state for the other have been determined. The results are

consistent with previously reported partial schemes and the available experimental data.

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