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The involvement of ion–neutral complexes in ethylene loss from $[PhC(CH_3)_2]^+$ and its isomers

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Abstract

High-level ab initio calculations at the G2(MP2,SVP) level have been used to characterize the potential energy surface for ethylene loss from various $[C_9H_{11}]^+$ ions. There is good agreement between the theoretical predictions and available experimental thermochemical data. We have characterized an alternative pathway to the phenylated cyclopropane mechanism originally proposed to explain the results of ^{13}C-labeling studies of ethylene elimination from $[PhC(CH_3)_2]^+$. This alternative mechanism is found to be consistent with experimental results of both ^{13}C- and deuterium-labeling experiments. We also examine the mechanism for ethylene loss and label exchange for several other isomeric $[C_9H_{11}]^+$ ions. It is found that the ^{13}C-label exchange observed in protonated allylbenzene and some of the deuterium-labeling results for other ions can be explained by the intervention of intermediate ion–neutral complexes. Comparisons are made with previous theoretical work on related $[C_3H_6X]^+$ ions (X = Ph, OH, SH and NH_2). (Int J Mass Spectrom 199 (2000) 29–40) © 2000 Elsevier Science B.V.

Keywords: $[C_9H_{11}]^+$; Ethylene elimination; Label exchange; Heats of formation; Ion–neutral complex; G2(MP2,SVP)

1. Introduction

In 1956 Rylander and Meyerson suggested that the apparent equivalence of the side-chain carbons during ethylene elimination from the metastable ion $[PhC(CH_3)_2]^+$ formed from ionized *t*-butylbenzene, could be explained by the participation of phenylated cyclopropane (Scheme 1) [1]. This was a landmark article because it was the first time an ion–neutral complex had been proposed as an intermediate for an ionic reaction. Since that time, ion–neutral complexes have been found to play an important role in numerous gas-phase ion reactions [2].

More recent studies of ethylene elimination from $[PhC(CH_3)_2]^+$ (**1**), employing both ^{13}C- and deuterium-labeled analogues, have been carried out [3–5], leading to the proposition of alternative mechanisms for ethylene elimination from **1** [3–5]. Studies of the mechanism for ethylene elimination from other labeled $[C_9H_{11}]^+$ isomers have also been performed [5–7]. The only relevant theoretical study of $[PhC(CH_3)_2]^+$ of which we are aware examines some aspects of its dissociation using semiempirical calculations [8].

The present work seeks, with the aid of high-level quantum chemical calculations, to examine the process of ethylene loss from $[PhC(CH_3)_2]^+$ (**1**), and to

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Dedicated to Professor Henri Audier on the occasion of his 60th birthday.

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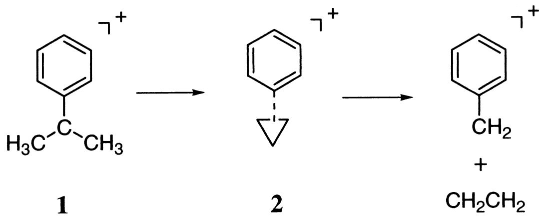


Scheme 1.

determine the mechanism for both carbon- and hydrogen-label exchange. We also investigate mechanisms for ethylene loss and label exchange for other isomeric $[C_9H_{11}]^+$ ions. Heats of formation of the relevant ions are also calculated and compared with available experimental values. Finally, we compare our findings concerning the involvement of ion–neutral complexes in the rearrangement/fragmentation behavior of related $[C_3H_6X]^+$ ions with X = OH [9], SH [10], or NH_2 [10], with those of the present study (X = Ph).

2. Methods and results

Standard ab initio molecular orbital calculations [11] at the G2(MP2,SVP) level [12] have been performed using the Gaussian 94 [13] and MOLPRO [14] packages. The G2(MP2,SVP) method corresponds effectively to QCISD(T)/6-311+G(3df,2p) single-point energies on MP2/6-31G(d) optimized geometries with the inclusion of scaled HF/6-31G(d) zero-point vibrational energies (ZPVE) and a so-called higher level correction (HLC). The G2 family of methods has been shown to generally perform within chemical accuracy ($\pm$ 10 kJ mol^{-1}) for a range of thermochemical quantities [15]. The G2(MP2,SVP) method in particular has been found to perform very well in the calculation of the heats of formation of neutral hydrocarbons [16]. We refer to G2(MP2,SVP) in this article simply as G2 for the sake of brevity. All MP2 calculations in this study, including the geometry optimizations, have been performed with the core electrons frozen (fc).

Heats of formation at 298 K have been calculated using the atomization method, as described by Nicolaides et al. [17], using scaled (by 0.8905) [18] HF/6-31G(d) frequencies for the temperature correction.

MP2/6-31G(d) optimized geometries, including selected bond lengths, are displayed in Figs. 1 and 2. Schematic potential energy profiles are shown in Figs. 3, 4 and 5. All bond lengths (Å) refer to MP2(fc)/6-31G(d) optimized values and all energies (kJ mol^{-1}) refer to G2 values at 0 K, unless otherwise stated.

3. Discussion

In the following discussion, all energies are quoted relative to that for $[PhC(CH_3)_2]^+$ (**1**). For species in which the phenyl ring is protonated, the position of protonation is indicated by the prefix *n*-H^+ [19], where *n* is the location of the proton on the ring relative to the side chain at position 1.

3.1. The potential surface for ethylene elimination from $[PhC(CH_3)_2]^+$ *(**1**)*

The metastable ion **1**, formed by radical loss from a suitable ionized neutral precursor (e.g. *t*-butylbenzene) [1,5], shows a number of metastable fragmentation pathways, including loss of benzene, propyne, and methane [5]. However, by far the dominant pathway (>90%) is that corresponding to ethylene loss [5], and we have examined this in detail with our calculations.

We find two energetically close pathways for ethylene loss from $[PhC(CH_3)_2]^+$ (**1**) (Fig. 3). The first, slightly higher energy pathway, proceeds initially via the transition structure **TS:1 → 3** (Fig. 1), at a relative energy of 190 kJ mol^{-1}, and involves concerted methyl-cation and 1,2-hydrogen shifts. The $[PhCHCH_2CH_3]^+$ (**3**) ion that is produced lies at a relative energy of 30 kJ mol^{-1}.

The second pathway involves initial concerted phenyl-cation and 1,2-hydrogen shifts, proceeding via **TS:1 → 4** with a relative energy of 179 kJ mol^{-1} to give $[\overline{PhCH_2C}HCH_3]^+$ (**4**). This isomer lies at 53 kJ mol^{-1} and has a phenonium ion structure, with

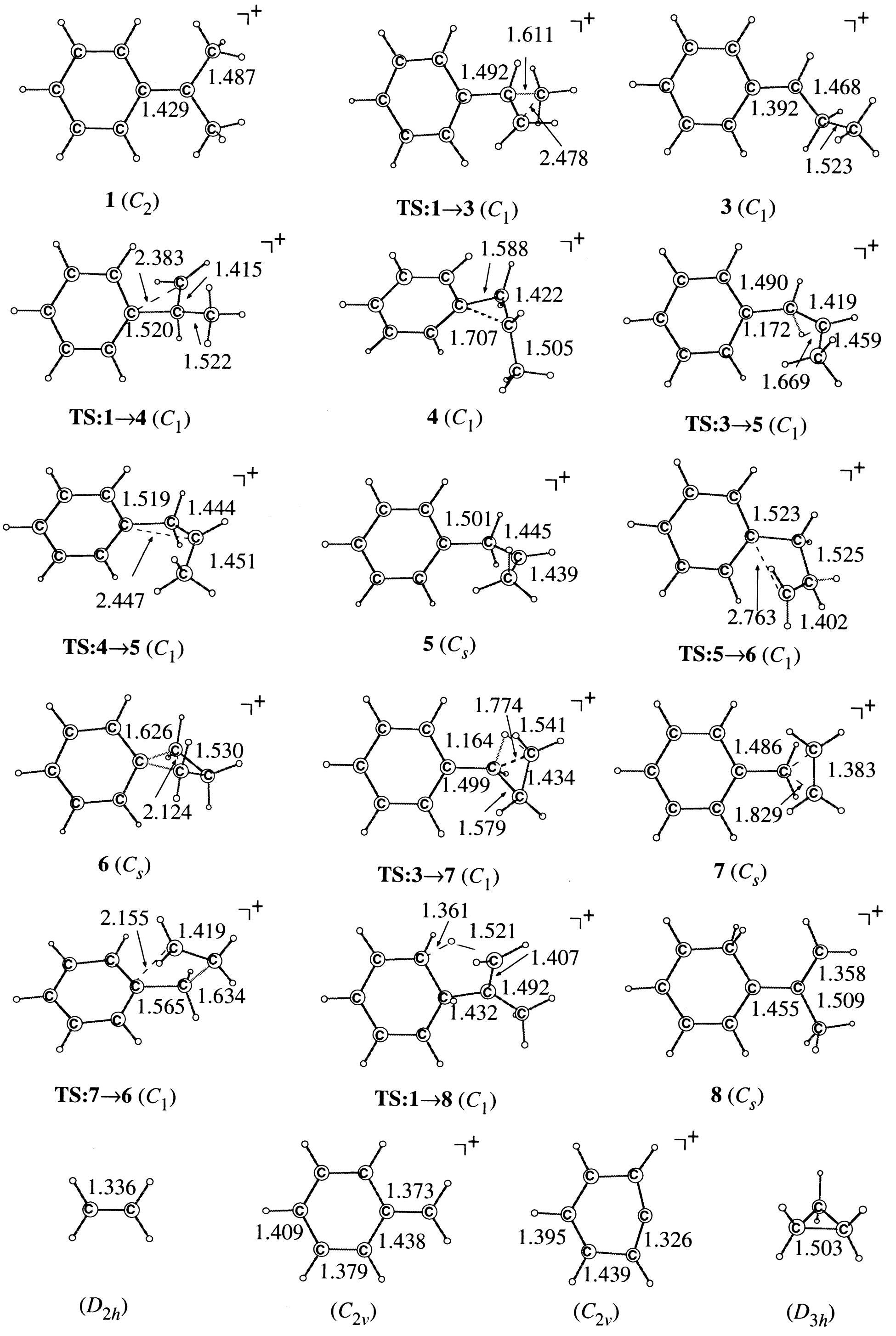


Fig. 1. Selected MP2/6-31G(d) bond lengths (Å) of species relevant to ethylene elimination from $[PhC(CH_3)_2]^+$ (**1**).

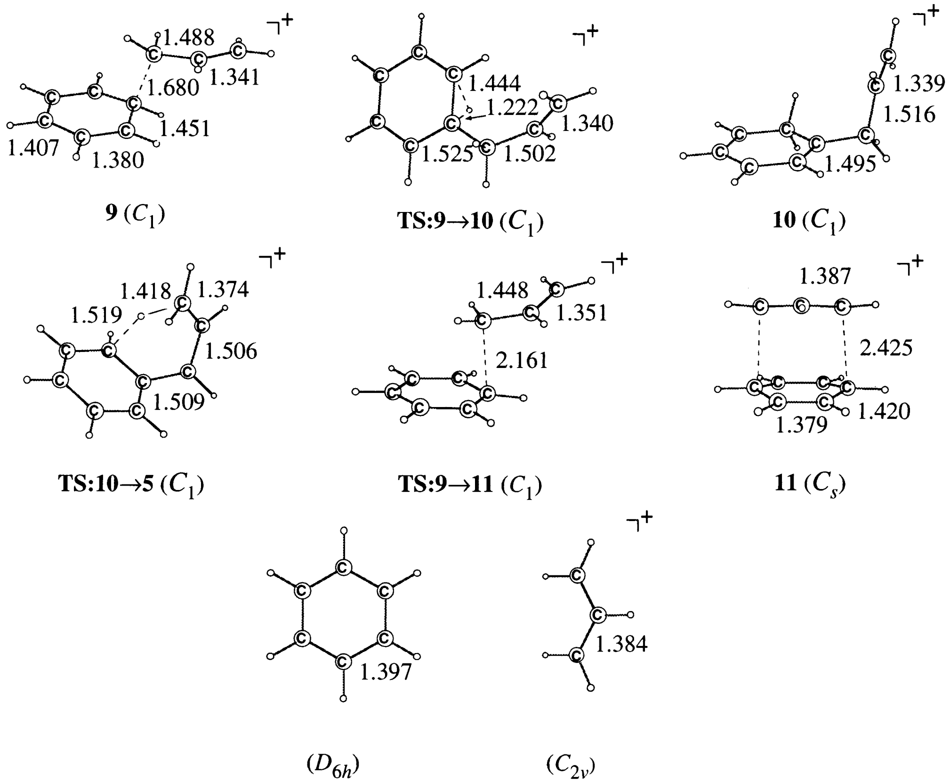


Fig. 2. Selected MP2/6-31G(d) bond lengths (Å) of species relevant to ethylene elimination from protonated allylbenzene (**5**, **9**, or **10**).

bridging C–C bond lengths of 1.588 and 1.707 Å (Fig. 1).

Interconversion of the ions $[\text{PhCHCH}_2\text{CH}_3]^+$ (**3**) and $[\overline{\text{PhCH}_2\text{C}}\text{HCH}_3]^+$ (**4**) can occur via $[\text{PhCH}_2\text{CHCH}_3]^+$ (**5**), which lies at an energy of 113 kJ mol^{-1}. Ion **3** can rearrange to **5** via a 1,2-hydrogen shift (**TS:3** → **5**) at 114 kJ mol^{-1} while **4** can isomerize to **5** via a simple ring opening (**TS:4** → **5**) at 119 kJ mol^{-1}. Thus, ion **5** lies in a very shallow potential energy well, the barriers for its rearrangement to **3** and **4** being only 1 and 6 kJ mol^{-1}, respectively.

The ion $[\text{PhCHCH}_2\text{CH}_3]^+$ (**3**) can rearrange to form the ion–neutral complex $[\text{PhCH}_2\cdots\text{CH}_2\text{CH}_2]^+$ (**7**) via **TS:3** → **7** with a relative energy of 145 kJ mol^{-1}. The ion–neutral complex **7** contains an ethylene moiety linked to a benzyl cation with long bridging C–C bonds (1.829 Å). The ethylenic C=C bond is only slightly elongated compared with its value in ethylene itself while the Ph–CH_2 bond is lengthened by 0.113 Å from its value in the isolated benzyl cation. Dissociation of the complex **7** produces ethylene plus the benzyl cation at 173 kJ mol^{-1}, corresponding to a binding energy of 38 kJ mol^{-1}. An alternative pair of products, cyclopropane plus phenyl cation, is found to lie at the significantly higher energy of 405 kJ mol^{-1}.

It is observed experimentally that ethylene loss from $[\text{PhC(CH}_3)_2]^+$ (**1**) is accompanied by a significantly larger kinetic energy release than from $[\text{PhCHCH}_2\text{CH}_3]^+$ (**3**) [7]. This may be attributed to the large barrier and likely kinetic shift associated with the isomerization of **1** to **3**, producing ethylene with the greater amount of translational energy.

Other pathways that could potentially be important in label exchange during ethylene elimination have also been characterized. One such process is rearrangement via $[\overline{\text{PhCH}_2\text{CH}_2\text{C}}\text{H}_2]^+$ (**6**) (Fig. 4). This

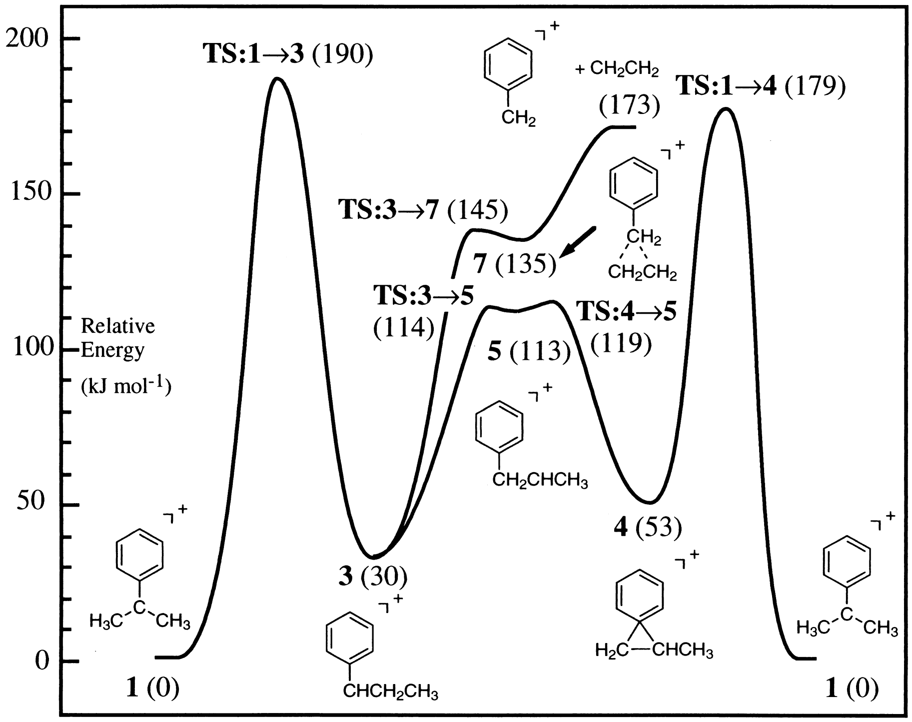


Fig. 3. Schematic G2 potential energy profile for ethylene loss from $[PhC(CH_3)_2]^+$ (**1**). Energies relative to **1** (kJ mol^{-1}) are given in parentheses.

can occur by isomerization of $[PhCH_2CHCH_3]^+$ (**5**) to **6** via **TS:5 → 6** at 185 kJ mol^{-1}, or isomerization of $[PhCH_2 \cdots CH_2CH_2]^+$ (**7**) to **6** via **TS:7 → 6** at 177 kJ mol^{-1}. Ion **6** lies at 122 kJ mol^{-1} and in some respects could be described as a complex between the phenyl cation and cyclopropane (**2**), since the C–C bond lengths linking the two components are quite long (1.626 Å). However, the three carbon atoms in **6** are by no means equivalent, as suggested for the hypothetical structure **2**, with our calculations indicating considerable lengthening of one bond in the cyclopropane moiety (2.124 Å compared with 1.503 Å in isolated cyclopropane).

Another potentially important label-exchange pathway is rearrangement of $[PhC(CH_3)_2]^+$ (**1**) via a hydrogen transfer to the ring, resulting in $[2\text{-}H^+\text{–}PhC(CH_3)CH_2]^+$ (**8**) at 77 kJ mol^{-1}. This occurs via **TS:1 → 8** at a relative energy of 185 kJ mol^{-1} (Fig. 1).

A semiempirical study examining parts of this surface has recently been reported [8]. There is generally reasonable qualitative agreement between the present results and the previous work. However, several species, most notably the ion–neutral complex **7**, were not included in the previous study. In addition, we find that several minima located in shallow wells in the previous study turn out to be transition structures with the present higher level theoretical treatment.

3.2. The potential surface for ethylene loss from $[1\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (9) or $[2\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (10)

As with **1**, the ions produced by protonation of allylbenzene ($PhCH_2CHCH_2$) are found to eliminate ethylene, and interesting results are obtained when ^{13}C-labeled allylbenzenes are examined [7].

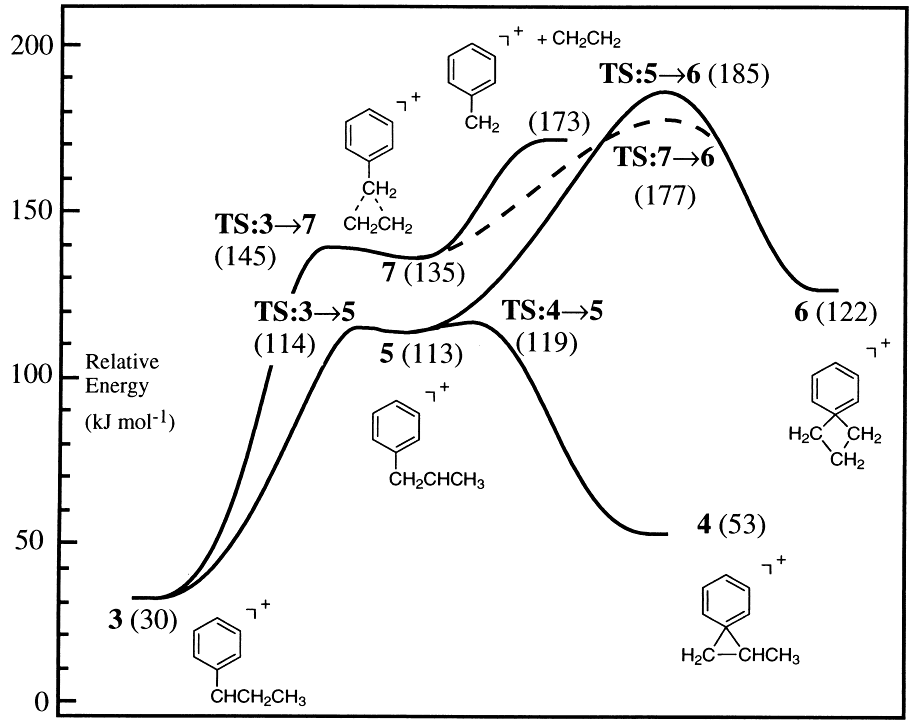


Fig. 4. Schematic G2 potential energy profile for ethylene loss and ^{13}C exchange within $[PhCHCH_2CH_3]^+$ (**3**). Energies relative to $[PhC(CH_3)_2]^+$ (**1**) (kJ mol^{-1}) are given in parentheses.

One of the possible products of the protonation of allylbenzene is $[1\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**9**), which lies at an energy of 130 kJ mol^{-1} (Fig. 5). In some respects, this species resembles a complex between the allyl cation and benzene, with a long C–C bond between these two components (1.680 Å). However, significant distortion of the C–C bonds in both the benzene and allyl cation moieties of **9** is observed (Fig. 2).

Another possible protonation product is $[2\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**10**) which is more stable than **9**, lying at 102 kJ mol^{-1}. Interconversion of **9** and **10** can take place via **TS:9** → **10** at 145 kJ mol^{-1}. Alternatively, a 1,5-hydrogen shift via **TS:10** → **5** at 187 kJ mol^{-1} leads to $[PhCH_2CHCH_3]^+$ (**5**). Ethylene loss from **5** can then occur, as discussed above (see Fig. 3).

Cleavage of a C–C bond in $[1\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**9**) leads to the ion–neutral complex $[C_6H_6\cdots CH_2CHCH_2]^+$ (**11**), which lies at 138 kJ mol^{-1}. The transition structure for this process, **TS:9** → **11**, lies at 162 kJ mol^{-1}. The ion–neutral complex **11** is characterized by long C–C bonds (2.425 Å) between the allyl cation and benzene moieties. The C–C bond lengths in the allyl cation moiety are virtually unchanged from their value in the isolated species, but there is significant bond alternation in the benzene ring of **11** (Fig. 2). The strong interaction between the components of **11** is also manifested in the large stabilization energy calculated for this complex: 115 kJ mol^{-1} relative to the isolated allyl cation plus benzene pair. Dissociation of **11** can give allyl cation plus benzene at an energy of 253 kJ mol^{-1}, but this is a significantly higher energy process than loss of ethylene via **TS:10** → **5**. Rearrangement of **9** or **10** to the ion–neutral complex **11** is a potentially important ^{13}C-label exchange process, as discussed further below.

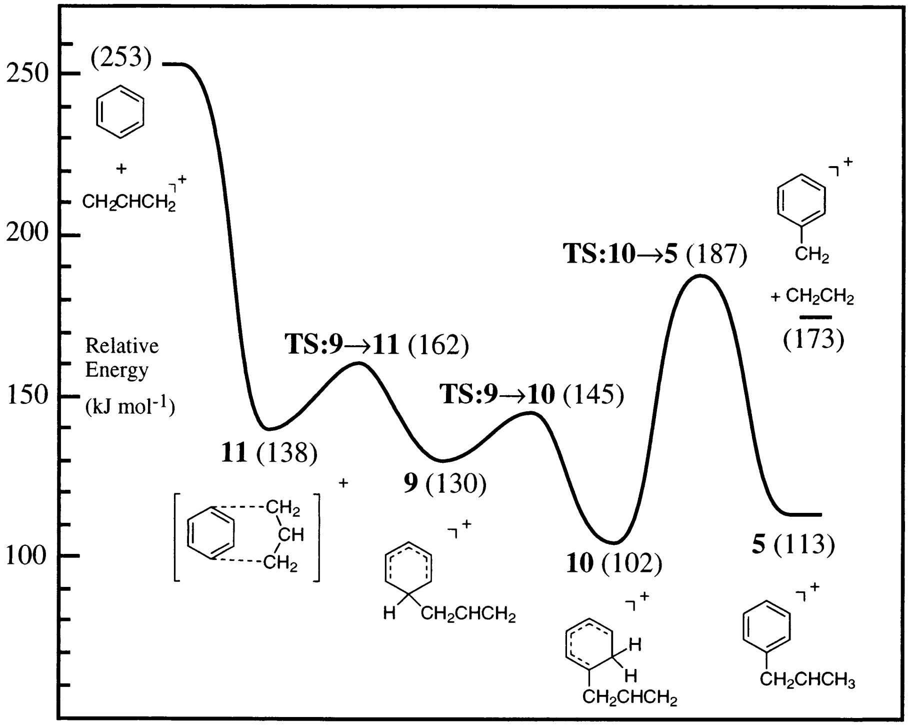


Fig. 5. Schematic G2 potential energy profile for ethylene loss and ^{13}C exchange within [1-H$^+$–PhCH$_2$CHCH$_2$]$^+$ (**9**). Energies relative to [PhC(CH$_3$)$_2$]$^+$ (**1**) (kJ mol^{-1}) are given in parentheses.

3.3. Comparison with experimental thermochemical data

Our calculated heats of formation for the [C$_9$H$_{11}$]$^+$ isomers and possible fragmentation products are compared with available experimental data [20–22] in Table 1. It can be seen that agreement between theory and experiment is very good, the differences being well within the G2 target accuracy (± 10 kJ mol^{-1}) for all cases except [PhCH$_2$CHCH$_3$]$^+$ (**5**) and the CH$_2$CH$_2$ plus [PhCH$_2$]$^+$ pair, where the discrepancies are slightly greater (12 kJ mol^{-1} in each case). As mentioned earlier, the G2(MP2,SVP) method has been found to perform particularly well in the calculation of the heats of formation for neutral hydrocarbons [16]. The present results suggest that this may be equally true for cationic hydrocarbons [24]. The good agreement between theory and experiment lends confidence to our predictions in the cases where experimental thermochemical data are not yet available.

3.4. Rationalization of ^{13}C-labeling experiments

^{13}C-labeling experiments have been previously performed on a number of [C$_9$H$_{11}$]$^+$ isomers [1,3,6,7]. We now attempt to rationalize these results in terms of our calculated potential energy surfaces.

3.4.1. [PhC(CH$_3$)$_2$]$^+$ (1)

Experiments examining ethylene loss from the labeled ion [Ph^{13}C(CH$_3$)$_2$]$^+$ (**1a**) have yielded abundances for the isotopomers of ethylene that are close to those expected (33% CH$_2$CH$_2$ and 67% ^{13}CH$_2$CH$_2$) if complete exchange of all the side-chain carbons was occurring [1,3,7]. The ion–neutral complex **2** was initially proposed to explain this result (Scheme 1) [1]. However, we find that the relative energy of the separated phenyl cation and cyclopropane is 405 kJ mol^{-1} and it therefore seems unlikely that a loosely bound complex between these two species, in which

Table 1
Theoretical and experimental heats of formation (ΔH_{f298}, kJ mol^{-1})

Species	G2	Experiment[a]
$[\mathrm{PhC(CH_3)_2}]^+$ (**1**)	774	770
$[\mathrm{PhCHCH_2CH_3}]^+$ (**3**)	803	811[b]
$[\overline{\mathrm{PhCH_2C}}\mathrm{HCH_3}]^+$ (**4**)	825	
$[\mathrm{PhCH_2CHCH_3}]^+$ (**5**)	887	(899)[c]
$[\overline{\mathrm{PhCH_2CH_2CH_2}}]^+$ (**6**)	893	
$[\mathrm{PhCH_2 \cdots CH_2CH_2}]^+$ (**7**)	909	
$[2\text{-}\mathrm{H^+}\text{–}\mathrm{PhC(CH_2)CH_3}]^+$ (**8**)	850	
$[1\text{-}\mathrm{H^+}\text{–}\mathrm{PhCH_2CHCH_2}]^+$ (**9**)	905	
$[2\text{-}\mathrm{H^+}\text{–}\mathrm{PhCH_2CHCH_2}]^+$ (**10**)	876	
$[\mathrm{C_6H_6 \cdots CH_2CHCH_2}]^+$ (**11**)	913	
$\mathrm{CH_2CH_2} + [\mathrm{PhCH_2}]^+$	950	951, 962[d]
$\mathrm{C_6H_6} + [\mathrm{CH_2CHCH_2}]^+$	1028	1028
$\mathrm{C_3H_6} + [\mathrm{C_6H_5}]^+$	1180	1179

[a] All experimental values are taken from Lias et al. [20] unless otherwise noted.
[b] From Attinà et al. [21].
[c] Estimated in Bowen and Williams [22].
[d] The heat of formation of $[\mathrm{PhCH_2}]^+$ was calculated using recent values of the ionization energy [23a] and heat of formation [23b] of the benzyl radical.

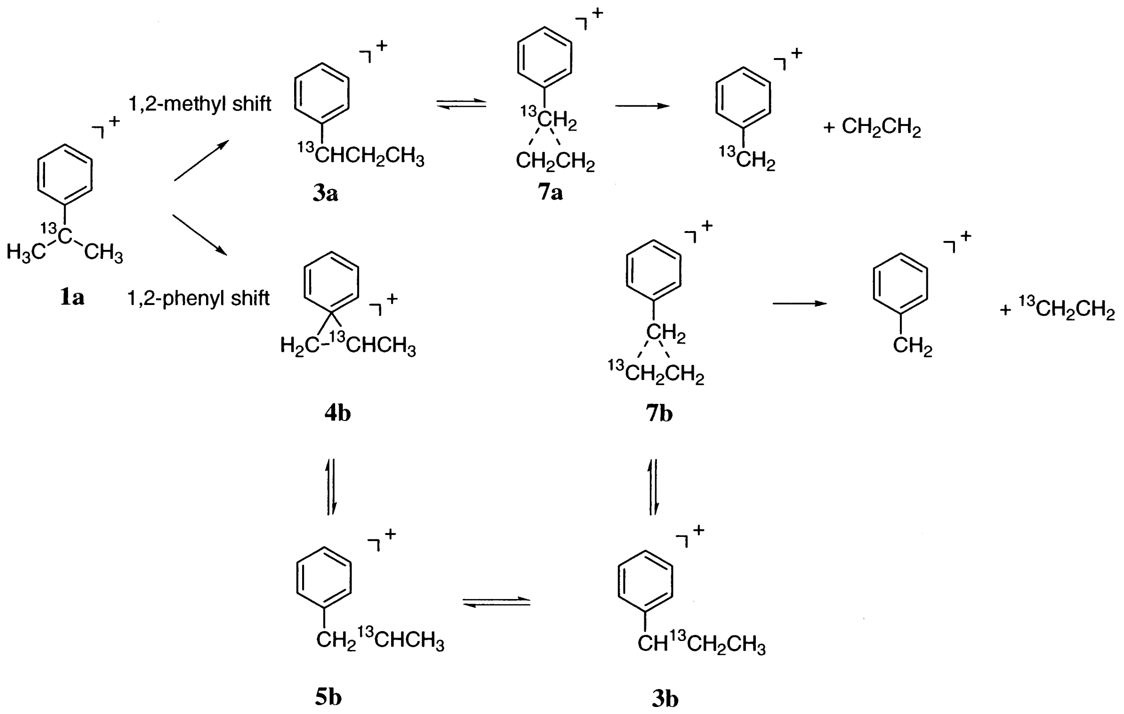
the cyclopropane group is free to rotate as suggested in Scheme 1, could play an important role.

Previously we noted the similarities between $[\overline{\mathrm{PhCH_2CH_2CH_2}}]^+$ (**6**) and the proposed phenylated cyclopropane **2**. It is possible that the observed near-statistical label distribution could result from reversible isomerization of **6** and $[\mathrm{PhCH_2 \cdots CH_2CH_2}]^+$ (**7**). Although the energy required for this rearrangement (177 kJ mol^{-1}) is slightly above the dissociation threshold, the difference is well within the uncertainty of our calculations. On the other hand, a high frequency factor process, such as dissociation, will dominate a lower frequency factor process of comparable energy, such as ring closure to form **6**. This suggests that isomerization via **6**, although not totally precluded, is unlikely to be responsible for the observed near-statistical carbon-label distribution.

A second mechanism has been proposed [3,5] whereby there is a competition between a methyl- or phenyl-cation shift in the initial isomerization of $[\mathrm{PhC(CH_3)_2}]^+$ (**1**), subsequent to the formation, via a 1,2-hydrogen shift of the intermediate primary cation $[\mathrm{PhCH(CH_3)CH_2}]^+$. We find that these methyl-cation (via **TS:1** → **3**) and phenyl-cation (via **TS:1** → **4**) shifts can occur without the intermediacy of $[\mathrm{PhCH(CH_3)CH_2}]^+$, although we note that the transition structures **TS:1** → **3** and **TS:1** → **4** bear a strong resemblance to such a species. The dominance of $^{13}\mathrm{CH_2CH_2}$ loss from **1a** can be explained by this mechanism if the phenyl-cation shift, which will result in exchange of the carbon bonded to the ring, is preferred over the methyl-cation shift, resulting in no such exchange (Scheme 2). This is consistent with the slightly lower calculated barrier for the phenyl-cation shift (**TS:1** → **4**) (Fig. 3). Furthermore, it is found experimentally for **1a** that greater abundances of $^{13}\mathrm{CH_2CH_2}$ (i.e. greater than statistical) are observed when the internal energy of **1a** is decreased by going from the first to the second field-free region [3,7]. These results are most simply rationalized by Scheme 2. A lower-energy process such as **TS:1** → **4** will become increasingly preferred as the internal energy is decreased, with the consequence that an increased proportion of $^{13}\mathrm{CH_2CH_2}$ loss will be observed at lower internal energies.

3.4.2. *$[\mathrm{PhCHCH_2CH_3}]^+$ (**3**)*

Experiments on ethylene loss from ^{13}C-labeled $[\mathrm{PhCHCH_2CH_3}]^+$ (**3**) have also been performed [6]. These experiments find that a relatively small



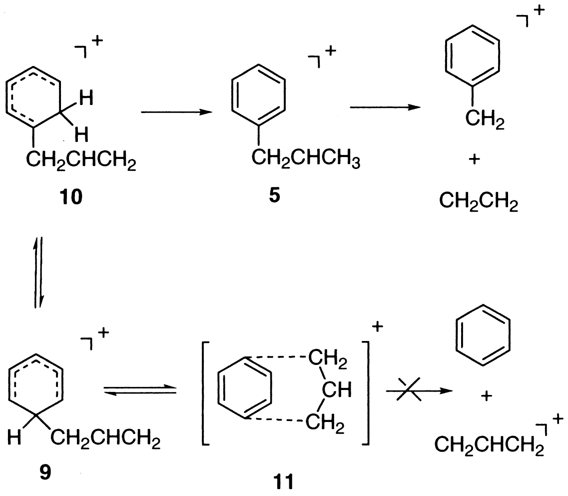
Scheme 2.

amount of exchange of the side-chain carbons occurs prior to ethylene loss. One process that could account for such exchange is reversible isomerization to $[\overline{\mathrm{PhCH_2CH_2CH_2}}]^+$ (**6**) (Fig. 4). The small extent of this exchange supports our suggestion that the dissociation of $[\mathrm{PhCH_2{\cdots}CH_2CH_2}]^+$ (**7**) is favored over isomerization to **6**.

3.4.3. Protonated allylbenzene

^{13}C-label exchange accompanying ethylene loss has also been found in the dissociation of protonated allylbenzene [7]. It was concluded that around 70% of the dissociating ions rearrange by a pathway involving the exchange of α and γ carbons, while the β carbon was found to retain its identity [7]. The $[\overline{\mathrm{PhCH_2CH_2CH_2}}]^+$ ion (**6**) has been suggested as a possible intermediate involved in ^{13}C-label exchange in this system [7]. However, given the earlier discussion concerning the intermediacy of **6**, and the fact that reversible isomerization of **6** and **7** would result in exchange of all side-chain carbon atoms, it is unlikely that **6** is an important intermediate in this case.

We propose an alternative mechanism involving reversible isomerization of $[1\text{-H}^+\text{–PhCH_2CHCH_2}]^+$ (**9**) and $[2\text{-H}^+\text{–PhCH_2CHCH_2}]^+$ (**10**) to the intermediate ion–neutral complex $[\mathrm{C_6H_6{\cdots}CH_2CHCH_2}]^+$ (**11**) to explain the occurrence of α- and γ-carbon exchange (Scheme 3). Due to the symmetrical nature of **11**, it is possible for either end of the allyl cation to attack the ring, resulting in exchange of the α and γ carbons. In order for this to be a viable mechanism, two criteria must be satisfied. Firstly, this process must be able to compete effectively with ethylene elimination. It can be seen from Fig. 5 that this is indeed the case, the energy required for the rearrangement of **10** or **9** to **11** being significantly lower than that for the rate-limiting step (**TS:10** → **5**) for ethylene elimination. Secondly, ethylene loss from **11** via **TS:10** → **5** must occur in preference to its dissociation to benzene plus the allyl cation. The



Scheme 3.

relative energies in Fig. 5 clearly show this condition to be satisfied.

Our mechanism is consistent with the experimental observation that only the α and γ carbons are exchanged [7]. However, our calculations suggest that complete, rather than partial, exchange of these carbons will occur within $[1\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**9**) or $[2\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**10**). The barrier for rearrangement to $[C_6H_6\cdots CH_2CHCH_2]^+$ (**11**) is significantly lower than that for the rate-limiting step for ethylene elimination (**TS:10** → **5**), and we would therefore expect the former process and the accompanying exchange to occur prior to dissociation via **TS:10** → **5**.

One possible explanation for this apparent discrepancy is that a mixture of isomers might be formed during the initial protonation of allylbenzene. On energetic grounds, ring protonation at the 2 position, resulting in $[2\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**10**), is favored over protonation at the 1 position, resulting in $[1\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**9**) (Fig. 5, Table 1). However, it is also possible that protonation will occur on the side chain, resulting in $[PhCH_2CHCH_3]^+$ (**5**). This species is only slightly higher in energy than **10** (by 11 kJ mol^{-1}), making it likely that a mixture of **5** and the ring-protonated species (primarily **10**) is formed. If this is the case, the fraction formed as **10** will undergo complete exchange of the α and γ carbon atoms, while the fraction resulting in $[PhCH_2CHCH_3]^+$ (**5**), followed by isomerization to $[PhCHCH_2CH_3]^+$ (**3**), will undergo only a small proportion of exchange, as discussed for **3** above. This would be consistent with the observed incomplete exchange [7].

3.5. Deuterium exchange

Deuterium-labeling studies have been performed on several $[C_9H_{11}]^+$ isomers [3–5], and we now attempt also to rationalize these results.

3.5.1. $[PhC(CH_3)_2]^+$ (1)

Studies of deuterium-labeled analogues of $[PhC(CH_3)_2]^+$ (**1**) have observed that extensive exchange of the six side-chain hydrogens occurs during ethylene elimination [3–5]. This exchange of side-chain hydrogens is simply explained via reversible isomerization of $[PhCHCH_2CH_3]^+$ (**3**) with $[PhCH_2CHCH_3]^+$ (**5**), and of **3** with the ion–neutral complex $[PhCH_2\cdots CH_2CH_2]^+$ (**7**). Since the energies of **TS:3** → **5** and **TS:3** → **7** are significantly lower than that required for elimination of ethylene, we would expect these processes to result in rapid exchange of all the side-chain hydrogens, prior to dissociation.

Experiment has also found that exchange of the methyl hydrogens with up to two ring hydrogens can occur [3]. These experiments have been interpreted by a mechanism involving exchange of the side-group hydrogens with ring hydrogens at the ortho positions [3]. We find that $[PhC(CH_3)_2]^+$ (**1**) can indeed undergo a 1,4-hydrogen shift from a methyl group to the ortho position of the ring (via **TS:1** → **8**), resulting in $[2\text{-}H^+\text{–}PhC(CH_3)CH_2]^+$ (**8**). The barrier to this process (185 kJ mol^{-1}) is only slightly higher than that for isomerization of **1** to $[PhCH_2CHCH_3]^+$ (**4**) (179 kJ mol^{-1}), so we might expect that some rearrangement via this route could occur. However, since this exchange process is higher in energy than the rate-limiting step for ethylene loss from **1** (i.e. **TS:1** → **4**), we would not expect complete exchange with the ring, consistent with experimental observations [3].

*3.5.2. $[PhCHCH_2CH_3]^+$ (**3**) and $[PhCH_2CHCH_3]^+$ (**5**)*

When the ions $[PhCHCH_2CH_3]^+$ (**3**) and $[PhCH_2CHCH_3]^+$ (**5**) are formed directly, they are likely to have less internal energy than those formed by isomerization from $[PhC(CH_3)_2]^+$ (**1**). It would therefore not be surprising if fragmentation behavior differing from **1** was observed. There is some disagreement concerning deuterium-label exchange in **3** and **5**. One study did not observe any deuterium-label exchange with the ring in the 2,4,6-trideuterated analogue of **5** [5], while another study found that a reasonable amount of exchange with the ring occurs in both the 2- and 4-deuterated analogues of **3** [6]. Since **3** and **5** can rapidly interconvert at the energies relevant to ethylene loss (Figs. 3 and 4), we would expect similar behavior from these isomers. A pathway that could possibly allow exchange with the ring to occur is isomerization of **5** to $[2\text{-}H^+\text{–}PhCH_2CHCH_2]^+$ (**10**). However, the energy of the transition structure for this process (187 kJ mol^{-1}) is above the dissociation threshold for ethylene loss (Fig. 5) so we would not expect this to occur at a significant rate for metastable ions. Although it is possible that there are lower-energy pathways for this exchange, the present results are consistent with the occurrence of little or no deuterium exchange with the ring. Significant deuterium exchange within the side chain was observed in both studies [5,6], the mechanism for this being exactly analogous to that discussed for $[PhC(CH_3)_2]^+$ (**1**) above.

3.6. Comparisons with other $[C_3H_6X]^+$ ions

The $[C_9H_{11}]^+$ ions examined here can be considered as members of the group of $[C_3H_6X]^+$ ions, where in this case $X = C_6H_5$. We have recently carried out analogous studies of the loss of ethylene and HX from other ions of this type ($X = OH$, SH, and NH_2) and identified some general trends concerning the involvement of ion–neutral complexes [9,10]. We now examine the involvement of the ion–neutral complex $[PhCH_2\cdots CH_2CH_2]^+$ (**7**), and other species, in the light of the previous studies.

Some of the factors determining the barrier to rearrangement of $[XCH_2\cdots CH_2CH_2]^+$ to $[XCHCH_2CH_3]^+$ have been previously noted [10]. It was found that in cases where the C–C bonds from ethylene to the bridging carbon are relatively short, a low barrier generally results [10]. In contrast, high barriers are present when these bonds are long. We find that the complex $[PhCH_2\cdots CH_2CH_2]^+$ (**7**) has relatively short bridging C–C bond lengths, comparable to those observed for the cases $X = OH$ [9] and SH [10]. Accordingly [10], we find that the barrier for isomerization of **7** to $[PhCHCH_2CH_3]^+$ (**3**) is also relatively low (10 kJ mol^{-1}). The low value for this barrier allows reversible isomerization between **3** and **7** to occur below the dissociation threshold, making this rearrangement an important process for hydrogen-label exchange in metastable ions.

It is also of interest to compare the involvement of the $[HX\cdots CH_2CHCH_2]^+$ complexes in the various systems. In the present work, we find that the reason for the importance of $[C_6H_6\cdots CH_2CHCH_2]^+$ (**11**) in label exchange is, in part, because loss of ethylene from **9**, **10**, and **11** is favored over the dissociation of **11**, yielding the allyl cation plus benzene. In contrast, dissociation of the complex $[HX\cdots CH_2CHCH_2]^+$ to give the allyl cation plus HX, for $X = OH$, SH, and NH_2, is preferred to the isomerization that would be necessary for ethylene loss [9,10]. Although ethylene loss from $[HX\cdots CH_2CHCH_2]^+$ is not the favored decomposition pathway in these cases, any isomerization via $[HX\cdots CH_2CHCH_2]^+$ that occurs prior to ethylene elimination could contribute to ^{13}C-label exchange.

The involvement of ions of the type $\overline{XCH_2CH_2CH}{}_2^+$ as intermediates in ^{13}C-label exchange was also examined in the cases where $X = OH$, SH, and NH_2 [9,10]. It was concluded that rearrangement via $\overline{XCH_2CH_2CH}{}_2^+$ is unlikely to occur to any great extent in metastable ions, similar to the conclusion that has also been reached in the present case ($X = Ph$).

4. Concluding remarks

The potential energy surfaces associated with ethylene elimination from $[PhC(CH_3)_2]^+$ (**1**) and other $[C_9H_{11}]^+$ isomers have been characterized and the importance of ion–neutral complexes in such eliminations has been examined. Based on these results, we propose mechanisms for ethylene loss from the various ions that are found to satisfactorily account for the observed behavior of deuterium- and ^{13}C-labeled species.

We find that the ^{13}C-labeling results for ethylene elimination from $[PhC(CH_3)_2]^+$ (**1**) are more consistent with a combination of two pathways that involves a phenyl-cation shift (leading to carbon exchange) and a methyl-cation shift (leading to no carbon exchange) (Scheme 2, Fig. 3), with the former being favored, than with the originally proposed phenylated cyclopropane mechanism (Scheme 1). However, we cannot totally discount the operation of the latter.

A number of processes in which ion–neutral complexes are important intermediates are found. The ion–neutral complex $[C_6H_6 \cdots CH_2CHCH_2]^+$ (**11**) is likely to play a role in ^{13}C-label exchange accompanying ethylene elimination from protonated allylbenzene (Scheme 3). Deuterium-label exchange in the side chains of $[PhC(CH_3)_2]^+$ (**1**), $[PhCHCH_2CH_3]^+$ (**3**), and $[PhCH_2CHCH_3]^+$ (**5**) can be explained by a combination of reversible isomerization of **3** to **5** and rearrangement of **3** to the ion–neutral complex $[PhCH_2 \cdots CH_2CH_2]^+$ (**7**). In both cases, reversible rearrangement to the ion–neutral complex can occur below the threshold for dissociation, allowing isomerization to occur in preference to dissociation.

We find good agreement between experimental and calculated thermochemical data.

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