International Journal of Mass Spectrometry 280 (2009) 32–37

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Reactions of the dications $C_7H_6^{2+}$, $C_7H_7^{2+}$, and $C_7H_8^{2+}$ with methane: Predominance of doubly charged intermediates

Jana Roithová [a,b,*], Claire L. Ricketts [b], Detlef Schröder [b]

[a] Charles University in Prague, Faculty of Science, Department of Organic Chemistry, Hlavova 8, 12843 Prague 2, Czech Republic
[b] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague, Czech Republic

ARTICLE INFO

Article history:
Received 12 May 2008
Received in revised form 11 July 2008
Accepted 18 July 2008
Available online 30 July 2008

☆ Dedicated to Prof. Zdenek Herman on the occasion of his 75th birthday.

Keywords:
Bond-forming reactions
Dications
DFT calculations
Hydride transfer
Mass spectrometry

ABSTRACT

The reactions of methane with the dications $C_7H_6^{2+}$, $C_7H_7^{2+}$, and $C_7H_8^{2+}$ generated by electron ionization of toluene are studied using mass-spectrometry tools. It is shown that the reactivity is dominated by the formation of doubly charged intermediates, which can either eliminate molecular hydrogen to yield doubly charged products or undergo charge-separation reactions leading to the formation of a methyl cation and the corresponding $C_7H_{n+1}^+$ monocation. Typical processes observed for dications, like electron transfer or proton transfer, are largely suppressed. The theoretically derived mechanism of the reaction between $C_7H_6^{2+}$ and CH_4 indicates that the formation of the doubly charged intermediate is kinetically preferred at low internal energies of the reactants. In agreement, the experimental results show a pronounced hydrogen scrambling and dominant formation of the doubly charged products at low collision energies, whereas direct hydride transfer prevails at larger collision energies.

1. Introduction

Ions generated from toluene have attracted unceasing interest already for several years. The reason for this interest stems from their relatively simple structure and well-defined reactivity [1–3]. For example, the time-honored rearrangement of the benzyl cation to the tropylium ion can be used as a thermometer of the internal energy of the generated ions [4]. The profound knowledge about the chemistry of the C_7-ions was the reason why a whole series of singly and doubly charged ions generated from toluene was chosen for systematic studies of the interactions of ions with surfaces covered by a hydrocarbon layer. These comprehensive studies not only provide a rationale of the observed reactivities of the C_7-ions with surfaces, but also explain the dependencies of the reactivities on the incident energies and the incident angles [5–7]. The central motif of the reactivity of the dications generated from toluene with the surface was charge transfer and subsequently either direct fragmentation or reactions with hydrocarbons deposited on the surface and further fragmentations. In this work, we would like to contribute to the knowledge about possible surface reactions of C_7-dications with hydrocarbons by a gas-phase model study of the reactions of $C_7H_6^{2+}$, $C_7H_7^{2+}$, and $C_7H_8^{2+}$ with methane. The experimental work includes labeling studies and is complemented by theoretical studies employing density functional theory.

2. Experimental and computational details

The experiments were performed with a TSQ Classic mass spectrometer [8,9] equipped with an ion source for electron ionization (EI). The analyzer region of the TSQ Classic bears a QOQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The octopole serving as a collision cell has a separate housing which limits the penetration of gases admitted to the octopole to the ultrahigh vacuum of the manifold. The kinetic energy of the ions entering the octopole can be varied, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or at elevated kinetic energies. The $C_7H_m^{2+}$ dications were mass-selected by means of the first quadrupole (Q1) at a mass resolution fully sufficient to select the corresponding dicationic species. Note, however, that the contribution of isobaric $[^{13}C_1]$-isotopes of hydrogen-depleted dications cannot be avoided. The mass-selected dications were then reacted with neutral methane admitted to the octopole at pres-

---

* Corresponding author at: Charles University in Prague, Faculty of Science, Department of Organic Chemistry, Hlavova 8, 12843 Prague 2, Czech Republic. Tel.: +420 221 951322; fax: +420 221 951326.
E-mail address: roithova@natur.cuni.cz (J. Roithová).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.07.017

sures of typically 10^{-4} mbar. The collision energy was adjusted by changing the offset between the first quadrupole and the octopole, while the offset of Q2 was locked to the sum of the offsets of Q1 and O. The zero-point of the kinetic energy scale as well as the width of the kinetic energy distribution were determined by means of retarding-potential analysis; for the dicationic species reported here, the beam width at half maximum amounts to 2.2 ± 0.2 eV in the laboratory frame. The bimolecular reactions reported below were recorded at nominally "zero" collision energy (the reactant ions are slowed down by the octopole potential, which corresponds to the point of inflection of the curve obtained by retarding-potential analysis of the reactant) [10]; the corresponding kinetic energy of reactant ions ranges from 0 eV to roughly 2 eV as implied by the kinetic energy distribution. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2, for which again a mass resolution fully sufficient to analyze dicationic species was adjusted. Ion abundances were determined using a Daley-type detector operated in the counting mode. Usually, several tens of scans were accumulated to achieve a good signal-to-noise ratio in the resulting spectra. The abundances of light products of charge-separation reactions are lower as compared to the heavier fragments, which is due to the large kinetic energy deposited in the fragments upon charge separation. Doubly charged ions dissociate isotropically with respect to the collision cell, which means that fragments gain a large momentum in all directions with respect to the original forward direction of the parent ion. The lighter ions gain larger velocity, which most probably leads to a large defocusing of the beam and these ions are therefore discriminated.

The complementary calculations of the $C_7H_m^{2+} + CH_4$ reaction were performed using the density functional theory method B3LYP [11–13] in conjunction with 6–311 + G(2d,p) triple-zeta basis set as implemented in the Gaussian 03 suite [14]. For all optimized structures, frequency analysis at the same level of theory was performed in order to assign them as genuine minima or transition structures on the potential-energy surface as well as to calculate zero-point vibrational energies (ZPVEs). All transition structures were further characterized by an intrinsic reaction coordinate calculation [15,16]. Relative energies (E_{rel}) are given at 0 K and are anchored to the energy of reactants $E_{rel}(C_7H_6^{2+} + CH_4) = 0.00$ eV. Total energies and geometries of all calculated structures can be found in the Supplementary material.

3. Results and discussion

3.1. Experimental results

The reactions of dications with neutral molecules are usually dominated by electron transfer or dissociative electron transfer [10]. For hydrogen-containing dications, proton transfer becomes an effectively competing channel, which largely prevails, if electron transfer is disfavored [17]. All these processes are usually direct without formation of intermediates, which can be nicely illustrated by the scattering diagrams of product ions obtained from crossed-beam experiments [18,19]. The formation of two singly charged products is associated – due to the electrostatic repulsion – with a large kinetic energy release as shown by energy-resolved experiments [20].

Similar reactivity patterns are also expected for dications derived from small hydrocarbons [21]. However, the second ionization energies of larger hydrocarbons drop to values of about 14 eV [22,23], which are comparable to the first ionization energies of many atoms and small molecules. As a consequence, the electron-transfer reactions are not thermodynamically favored anymore and are hence suppressed. Instead, proton-transfer reactions [17] and bond-forming reactions [25,26] are expected to prevail. The bond-forming reactions proceed via doubly charged intermediates with lifetimes usually long enough to undergo a series of rearrangements. The reaction sequence is finished either by a charge-separation process and formation of two singly charged products [24] or by elimination of a neutral molecule and formation of doubly charged products [25,26].

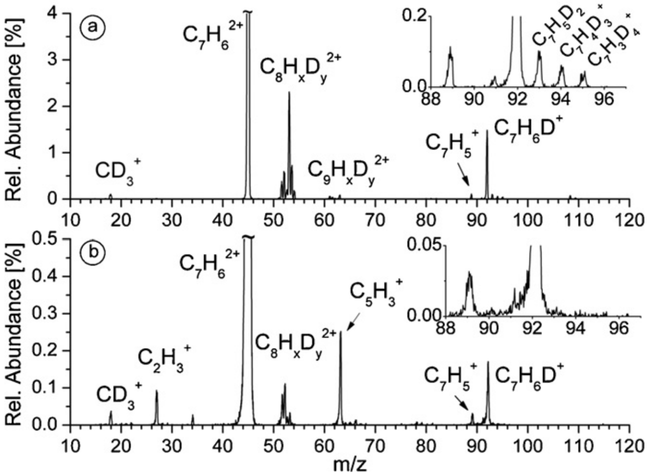


Fig. 1. Q2-mass spectra of products of the reaction of mass-selected $C_7H_6^{2+}$ with CD_4 at collision energies $E_{CM} = 0.0$ eV (a) and $E_{CM} = 1.4$ eV (b). The insets in (a) and (b) show the expanded mass region of the $C_7H_mD_n^+$ monocations amplified by a factor of 20 and 10, respectively. Note that the signal corresponding to $C_2D_5^+$ (m/z 34) in (b) is due to a secondary reaction of CD_3^+ with CD_4.

Recently, we have shown that the reaction of acetylene with the $C_7H_6^{2+}$ dication generated from toluene does not only lead to the expected proton- and electron-transfers, but also yields larger $C_9H_6^{2+}$ and $C_9H_7^{2+}$ dications as products [27]. The reaction proceeds via a long-lived intermediate $C_9H_8^{2+}$, which undergoes a series of complex rearrangements to form a stable indene skeleton [28]. The reaction sequence is finished by elimination of either atomic or molecular hydrogen. This bond-forming channel appears a general route in the reaction of medium-sized hydrocarbon dications with acetylene and the yield of doubly charged products even increases for larger dications [27].

Inspired by these condensation reactions, we decided to probe reactions of hydrocarbon dications with the simplest hydrocarbon, methane. The reaction of methane with the most reactive dication derived from toluene, $C_7H_6^{2+}$, brings several surprising results (Fig. 1). Firstly, if the reaction is conducted at nominally zero collision energy, the dominant products correspond to a doubly charged hydrocarbon ions with eight carbon atoms (reaction (1)).

$$C_7H_m^{2+} + CH_4 \rightarrow [C_8H_{m+4}]^{2+} \rightarrow C_8H_{m+2}^{2+} + H_2 \rightarrow C_8H_m^{2+} + 2H_2 \tag{1}$$

$$C_7H_m^{2+} + CH_4 \rightarrow [C_8H_{m+4}]^{2+} \rightarrow C_7H_{m+1}^{+} + CH_3^{+} \tag{2}$$

This reaction and also its kinetics has been already described in detail in the context of the chemistry of Titan [29] and is thus not pursued here any further. Secondly, proton transfer is almost absent and instead the second most-abundant channel corresponds to a hydride transfer from methane to the dication (reaction (2)). Even more surprisingly, a significant amount of H/D scrambling [30,31] is observed for the products of the hydride-transfer reaction (see the inset in Fig. 1a), which strongly suggests that this reaction proceeds via a long-lived intermediate. Thus, it can be concluded that the reactivity of the $C_7H_6^{2+}$ dication with methane at nominally

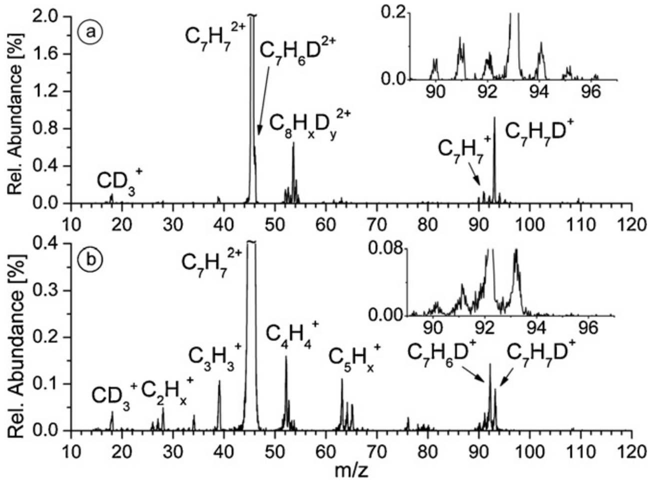


Fig. 2. Q2-mass spectra of products of the reaction of mass-selected $C_7H_7^{2+}$ with CD_4 at collision energies $E_{CM} = 0.0$ eV (a) and $E_{CM} = 1.4$ eV (b). The insets in (a) and (b) show the expanded mass region of the $C_7H_mD_n^+$ monocations amplified by a factor of 10 and 5, respectively. Note that the signal corresponding to $C_2D_5^+$ (m/z 34) in (b) is due to a secondary reaction of CD_3^+ with CD_4.

zero collision energy is determined by the formation of a long-lived intermediate complex, which can either eliminate molecular hydrogen or a methyl cation.

At elevated collision energies, collision-induced processes become more important in that the major channel observed corresponds to fragmentation of $C_7H_6^{2+}$ to yield $C_5H_3^+$ and $C_2H_3^+$ (Fig. 1b); note the mass-discrimination of the lighter $C_2H_3^+$ fragment compared to $C_5H_3^+$ (ca. 1:2) which is typical for Coulomb explosions of multiply charged ions to fragments of largely different masses (see also Section 2) [32–34]. The products of the bond-forming reaction (1) can be still observed, but the larger collision energy leads to a larger degree of dehydrogenation of the products [23,26,27,35–38]. Further, the product of formal hydride transfer does not show such pronounced H/D scrambling, which witnesses a shorter lifetime of the collision complex or even suppression of its formation. Note further that the absolute conversion at elevated collision energy is approximately one order of magnitude lower than at $E_{CM} = 0$ eV, which is perfectly consistent with the description of reactions (1) and (2) as exothermic ion/molecule reactions.

The reaction of the radical dication $C_7H_7^{2+}$ with perdeuterated methane has a very similar result (Fig. 2). At zero collision energy, the spectrum of products is dominated by signals of $C_8H_mD_n^{2+}$ dications, products of bond-forming reactions according to (1). The formal hydride transfer is again associated with the partial H/D scrambling to yield either $C_7H_7D^+$ (m/z 93), $C_7H_6D_2^+$ (m/z 94), $C_7H_5D_3^+$ (m/z 95), and even traces of $C_7H_4D_4^+$ (m/z 96). The products can subsequently lose one H- or D-atom, e.g., $C_7H_7D^+ \rightarrow C_7H_6D^+ + H$, to yield the stable tropylium or benzylium ion as witnessed by a signal of $C_7H_6D^+$ (m/z 92). Further, small peaks corresponding to electron- and proton-transfers can be observed as well. Interestingly, scrambling of hydrogen atoms can be observed also for the parent dication itself, which indicates that in addition to a hydrogen molecule or a methyl cation, the doubly charged intermediate can also lose a methane molecule. Such a degenerate channel was not observed in the reaction of $C_7H_6^{2+}$ with methane, which suggests that the more unsaturated dication yields a more stable doubly charged intermediate, which subsequently fragments via relatively lower barriers to yield products according to reactions (1) or (2) and does not dissociate back to the reactants.

Elevated collision energies in the reaction of $C_7H_7^{2+}$ with methane lead to a more pronounced dissociation of the parent dication in comparison with the closed-shell dication $C_7H_6^{2+}$; the major channels are $C_7H_7^{2+} \rightarrow C_4H_4^+ + C_3H_3^+$, and $C_7H_7^{2+} \rightarrow C_5H_3^+ + C_2H_4^+$. The bond-forming processes are largely suppressed and the formal hydride transfer is mostly followed by the loss of atomic hydrogen. The efficiency of the coupling reaction is largely reduced compared to the quasi-thermal conditions. All these findings are in accord with the intuitive suggestion that the lifetime of the doubly charged intermediate is suppressed at elevated collision energies of reactants (Fig. 3).

The largest dication studied, $C_7H_8^{2+}$, is least reactive. About 2% of the parent dications lose molecular hydrogen to yield $C_7H_6^{2+}$, which of course can contribute as a reactant to the spectrum of products. However, the abundance of the products coming from the reaction of $C_7H_6^{2+}$ with methane is small as evidenced by the absence of a signal at m/z 89, which corresponds to the proton transfer from $C_7H_6^{2+}$ to methane (Fig. 1). Accordingly, the data for $C_7H_8^{2+}$ are not further corrected for contributions of $C_7H_6^{2+}$. Similar to the dications discussed above, also the dication $C_7H_8^{2+}$ appears to form a long-lived intermediate with methane, which can subsequently dissociate to products in three principal pathways. First, the degenerate addition and loss of methane is evidenced by a signal of $C_7H_7D^{2+}$ and the relative yield of this reaction is larger than for the $C_7H_7^{2+}$ reactant. Thus, the yield of the dissociation of the intermediates backward to the reactants is increasing for the reactants in the row $C_7H_6^{2+} < C_7H_7^{2+} < C_7H_8^{2+}$. Second, the formal hydride transfer (m/z 94–96) is associated with less pronounced hydrogen scrambling than it was found for the reactant $C_7H_7^{2+}$ and for $C_7H_6^{2+}$, which again indicates a shorter lifetime of the reaction intermediate. Finally, a series of products coming from the bond-forming reaction (1) is detected (m/z 52–55) in that the reaction sequence is mostly ended by sequential loss of two hydrogen molecules instead of one, which is a consequence of the larger number of the hydrogen atoms in $C_7H_8^{2+}$ compared to the reactants discussed above [39]. These channels proceeding via long-lived intermediates are accompanied by a pronounced proton-transfer channel leading to $C_7H_7^+$ and CD_4H^+, of which the former product ion most probably corresponds to the tropylium/benzylium manifold. Elevated collision energies have analogous consequences as observed for the

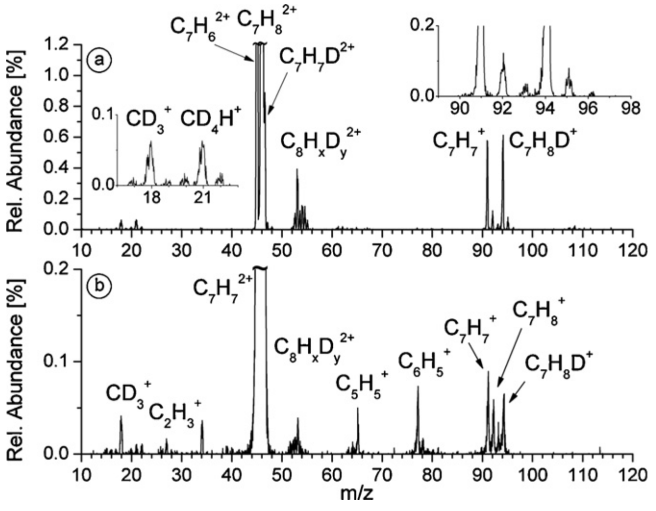
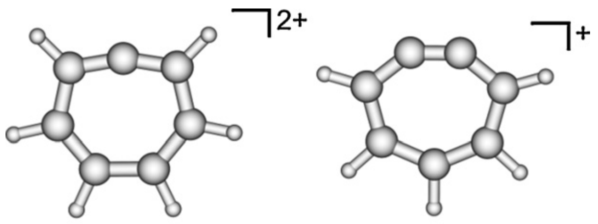


Fig. 3. Q2-mass spectra of products of the reaction of mass-selected $C_7H_8^{2+}$ with CD_4 at collision energies $E_{CM} = 0.0$ eV (a) and $E_{CM} = 1.4$ eV (b). The insets in Fig. 2a show the expanded mass region of the $CH_mD_n^+$ and $C_7H_mD_n^+$ monocations amplified by a factor of 12 and 6, respectively. Note that the signal corresponding to $C_2D_5^+$ (m/z 34) is due to a secondary reaction of CD_3^+ with CD_4.



1^{2+} **2**$^{+}$

Scheme 1. Cycloheptatrienylidene dication (**1**$^{2+}$) and cyclohepta-4,6-dien-2-yn-1-yl cation (**2**$^{+}$).

other reactants. Thus, the reaction processes leading via doubly charged intermediates are largely suppressed and instead a rather pronounced fragmentation is observed.

In summary, the ion/molecule reactions of the $C_7H_m{}^{2+}$ dications with methane at zero collision energy proceed through a formation of a doubly charged intermediate. The experimental findings suggest that the lifetimes of these intermediates are sufficient for a series of rearrangements, which lead to the scrambling of hydrogen atoms and the formation of stable doubly charged products with eight carbon atoms. The alternative pathways proceed via Coulomb explosion of the intermediates to form products of formal hydride transfer. This channel is also associated with H/D scrambling proving the formation of a long-lived intermediate; however, the scrambling is less pronounced than in the channel leading to the doubly charged product. Hence, it is concluded that the intermediates with larger internal energy and thus shorter lifetime will more easily decompose through Coulomb explosion. Further, a degenerate reaction with perdeuterated methane evidenced by scrambling of hydrogen atoms in the parent ion is observed for $C_7H_7{}^{2+}$ and even more so for $C_7H_8{}^{2+}$. This finding indicates that the energy barriers leading to the C_8-products become closer in energy to the entrance channel for the more saturated dications and therefore forward and backward reactions compete more effectively. As a consequence, lower yields of C_8-products are obtained in comparison with the reaction of the more unsaturated dication $C_7H_6{}^{2+}$.

3.2. Computational results

In order to support and rationalize the experimental results, the reaction mechanism for the most reactive dication $C_7H_6{}^{2+}$ is investigated by means of density functional calculations. The most stable geometry of $C_7H_6{}^{2+}$ corresponds to the cycloheptatrienylidene dication (**1**$^{2+}$, Scheme 1), which is considered as the reacting ion [38]. According to the computations, electron transfer is associated with an exothermicity of 1.17 eV (the calculated ionization energy of methane amounts to 12.47 eV, which is very close to the experimental value 12.61 ± 0.01 eV [40]). In accordance with the "reaction window" theory [41–44], electron transfer is kinetically disfavored and the corresponding products are not observed in the experiment. Proton transfer from the $C_7H_6{}^{2+}$ dication to methane leads to the formation the cyclohepta-4,6-dien-2-yn-1-yl cation (**2**$^{+}$) and $CH_5{}^{+}$ (the calculated proton affinity of methane amounts to 5.61 eV, which is in excellent agreement with the experimental value of 5.63 eV [40]). Proton transfer is exothermic by 2.44 eV, but it is most probably hindered by a Coulomb barrier and therefore it cannot efficiently compete with the other processes observed in the experiment.

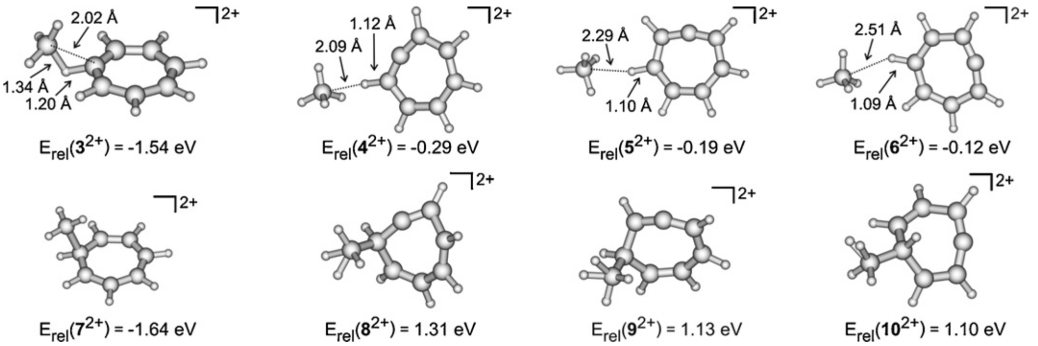
The formation of a complex between methane and the $C_7H_6{}^{2+}$ dication can proceed either through the formation of a carbon-carbon bond between methane and the carbenoid carbon atom of the dication or the complex formation can be mediated by hydrogen atoms of the dication (Scheme 2), where the former brings the largest stabilization of as much as 1.54 eV (structure **3**$^{2+}$). The alternative complexes **4**$^{2+}$–**6**$^{2+}$ bring only small energy gains, which are not sufficient for a subsequent formation of a carbon–carbon bond between both reactants. The corresponding covalently bound intermediates **8**$^{2+}$–**10**$^{2+}$ lie considerably higher in energy than the reactants and therefore these reaction pathways can be safely excluded. Interestingly, this result is the opposite of what was found for the interaction of $C_7H_6{}^{2+}$ with neutral acetylene [27,28], for which the most stable complexes were formed by the bonding of a hydrogen atom of the dication with the π electrons of acetylene.

The further reactivity of the complex **3**$^{2+}$ is determined by an extremely small energy barrier (TS**3**/**7**$^{2+}$) for the formation of the dication **7**$^{2+}$ with covalent bonds between all carbon atoms. This reaction step is most probably responsible for the efficient competition between the bond-forming reactions and the simple hydride transfer. Once the covalently bound intermediate is formed, many possible rearrangements can be suggested [45,46]. Scheme 3 shows simple hydrogen rearrangements and demonstrates that the dicationic intermediate formed has enough internal energy for hydrogen scrambling as is observed in the experiments. These results already account for all experimental observations; hence the rearrangements on the $C_8H_{10}{}^{2+}$ PES are not explored any further. However, rearrangements leading to ring expansions or contractions could well be conceived and are therefore likely to occur in the long-lived intermediates [47–50].

The competition between the elimination of molecular hydrogen from the intermediate and the charge-separation channel leading to the tropylium ion (**14**$^{+}$) and a methyl cation is shown in Scheme 4. The most straightforward reaction pathway for the loss of molecular hydrogen leads to the intermediate **15**$^{2+}$, which corresponds to the methyltropylium ion protonated at the methyl group. Two possible pathways to the key intermediate **15**$^{2+}$ were found. The first one involves a rearrangement from the intermediate **11**$^{2+}$, where a hydrogen atom is transferred from a carbon atom next to the carbon atom bearing the methyl group. The barrier for this 1,3-hydrogen migration is 0.64 eV below the energy of the reactants. The second possibility represents a 1,2-hydrogen migration within the structure **7**$^{2+}$. The corresponding energy barrier lies −1.38 eV below the energy of reactants. However, the associated intrinsic reaction coordinate does not lead directly to the intermediate **15**$^{2+}$, but to the degenerate transition structure TS**15**$^{2+}$/**15**$^{2+}$, where the imaginary frequency represents a rotation of the pre-dissociated H_2 molecule; TS**15**$^{2+}$/**15**$^{2+}$ lies 0.15 eV in energy above the minimum **15**$^{2+}$.

The elimination of H_2 from **15**$^{2+}$ leads to a product with a structure corresponding to doubly charged *exo*-methylene-2,4,6-cycloheptatriene (**16**$^{2+}$). The reaction has an overall exothermicity of 1.34 eV. All attempts to localize a transition structure for dehydrogenation at the B3LYP/6–311 + G(2d,p) level led to the direct elimination of H_2 molecule. The transition structure could have been, however, found using a small basis set 6–31G. The corresponding single-point energy of this structure using the triple-ζ basis set amounts to −1.39 eV, which is lower than the dissociation limit for dehydrogenation (E_{rel}(**16**$^{2+}$ + H_2) = −1.34 eV). It means that the spurious transition structure found at a lower level of theory represents only a point on the dissociation curve at a higher level of theory. Accordingly, we assume that the elimination of H_2 is a continuously endothermic process without any apparent energy barrier in excess of the reaction endothermicity with respect to **15**$^{2+}$.

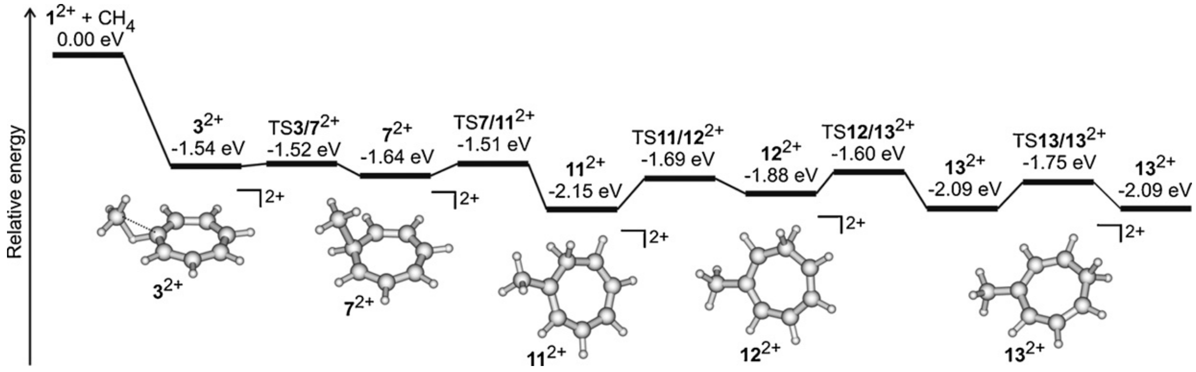
The competing Coulomb explosion of the intermediate to the stable tropylium ion and a methyl cation is much more thermodynamically favored; the computed exothermicity amounts to 3.97 eV. However, the process is hindered kinetically by a Coulomb



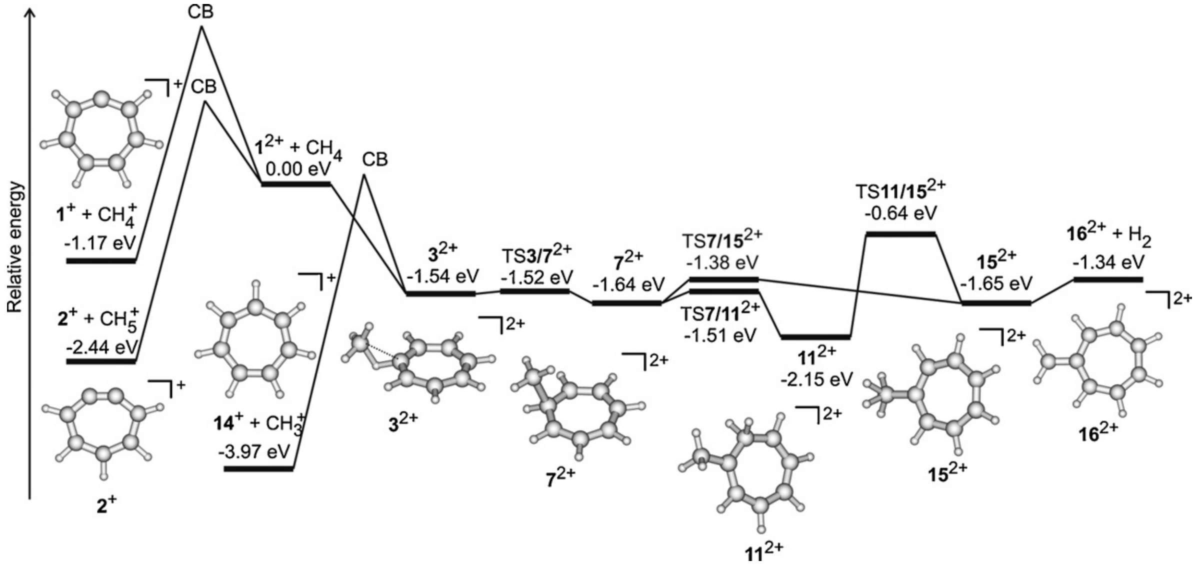
Scheme 2. Complexes between the $C_7H_6^{2+}$ dication and methane and the corresponding covalently bound $C_8H_{10}^{2+}$ isomers. Energies are given relative to $E_{rel}(C_7H_6^{2+} + CH_4) = 0.00$ eV.

barrier, thereby allowing occurrence of the bond-forming reactions. The suggested mechanism is further supported by the fact that increase of the collision energy of the reactants leads to a suppression of the bond-forming processes, whereas the hydride transfer prevails. Further more, the calculations show that reaction (2) corresponds to a hydride transfer only in a formal, stoichiometric sense. Instead, reaction (2) proceeds via the intimate addition complex **3**$^{2+}$ from which the loss of CH_3^+ occurs in a charge-separation process—a genuine step of H^- transfer is not involved, however.

Finally, let us address the parallels between the ion/molecule study presented here and the ion/surface reactions investigated by Herman and coworkers [5]. The reactivities of hydrocarbon dications observed at the surface are interpreted by a sequence, in which electron transfer takes place first and the observed products correspond to either fragmentations or surface reactions of the so-formed singly charged ions. This scenario was deduced from the rather similar pattern of products for the surface reactions of the analogous singly and doubly charged reactants. Interestingly, it was proved by labeling experiments that some products came



Scheme 3. Potential-energy surface for the hydrogen migration in the $C_8H_{10}^{2+}$ dication.



Scheme 4. Potential-energy surface for product formation from the $C_8H_{10}^{2+}$ intermediate (CB stands for Coulomb barrier).

from fragmentation of intermediates originating from hydrogen transfer from the surface hydrocarbons to the incident ion. For example, abundant formation of $C_6HD_4^+$ was observed in the reactions of $C_7D_8^+/C_7D_8^{2+}$ with the surface hydrocarbons, which evidences formation of a $C_7HD_8^+$ intermediate, which subsequently loses methane [51,52]. This channel was considerably more pronounced for the dicationic reactant than for the monocation. Based on the results presented here, it is suggested that the larger abundance of hydride transfer in the surface reaction of the dication generated from toluene could be due to the unique direct bimolecular reaction of $C_7H_8^{2+}$ ($C_7D_8^{2+}$) with surface hydrocarbons without preceding electron transfer.

4. Conclusions

The reactions of dications $C_7H_6^{2+}$, $C_7H_7^{2+}$, and $C_7H_8^{2+}$ with methane at thermal collision energies are dominated by bond-forming reactions leading to doubly charged products and hydride-transfer processes. The classical impulsive reactions of dications, such as electron- and proton-transfer, are largely suppressed. Both observed channels are associated with hydrogen scrambling, which witnesses the formation of a long-lived intermediates. The theoretical calculations for the reaction of $C_7H_6^{2+}$ with methane show that the reactants form a covalently bound intermediate $C_8H_{10}^{2+}$, which can undergo a series of rearrangements within the range of available internal energy. The energy barrier for the formation of the intermediate is extremely low; therefore this process is kinetically favored at thermal energy. In the end of the reaction sequence, the intermediate dissociates either to the doubly charged product $C_8H_8^{2+}$ and neutral H_2 or to the singly charged products $C_7H_7^+$ and CH_3^+. The elevated collision energy of the reactants leads to a preference for the thermodynamically favored process leading the methyl cation and the tropylium ion, which is also observed in the experiment. Similar reaction mechanisms are expected also for the remaining reactions, because the experimental observations are analogous: Products of bond-forming reactions and hydride transfer are observed; both processes are associated with hydrogen scrambling. In general, the yields of the products are decreasing with the increasing saturation of the reactant dication.

Acknowledgements

JR particularly thanks Zdenek Herman for introducing her into the exciting field of ions chemistry and physics. This work was supported by the Czech Academy of Sciences (Z40550506) and the Ministry of Education of the Czech Republic (MSM0021620857). JR thanks for a L'Oreal 'For Women in Science' stipend.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2008.07.017.

References

[1] H. Hippler, C. Reihs, J. Troe, Z. Phys. Chem. 167 (1990) 1.
[2] L.D. Brouwer, W. Mueller-Markgraf, J. Troe, J. Phys. Chem. 92 (1988) 4905.
[3] C. Lifshitz, Acc. Chem. Res. 27 (1994) 138.
[4] C. Lifshitz, Y. Gotkis, A. Ioffe, J. Laskin, S. Shaik, Int. J. Mass Spectrom. Ion Process. 125 (1993) R7.
[5] J. Jašík, J. Roithová, J. Žabka, A. Pysanenko, L. Feketeová, I. Ipolyi, T.D. Märk, Z. Herman, Int. J. Mass Spectrom. 249–250 (2006) 162.
[6] L. Feketeová, T. Tepnual, V. Grill, P. Scheier, J. Roithová, Z. Herman, T.D. Märk, Int. J. Mass Spectrom. 265 (2007) 337.
[7] Z. Herman, J. Am. Chem. Soc., Mass Spectrom. 14 (2003) 1360.
[8] J. Roithová, D. Schröder, Phys. Chem. Chem. Phys. 9 (2007) 713.
[9] J. Roithová, D. Schröder, J. Míšek, I.G. Stará, I. Starý, Int. J. Mass Spectrom., J. Mass Spectrom. 42 (2007) 1233.
[10] Z. Herman, Int. Rev. Phys. Chem. 15 (1996) 299.
[11] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
[12] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[13] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200.
[14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
[15] C. Gonzalez, H.B. Schlegel, J. Chem. Phys. 90 (1989) 2154.
[16] C. Gonzalez, H.B. Schlegel, J. Phys. Chem. 94 (1990) 5523.
[17] J. Roithová, Z. Herman, D. Schröder, H. Schwarz, Chem. Eur. J. 12 (2006) 2465.
[18] Z. Herman, Int. J. Mass Spectrom. 212 (2001) 413.
[19] S.D. Price, Phys. Chem. Chem. Phys. 5 (2003) 1717.
[20] Z. Herman, Phys. Essays 13 (2000) 480.
[21] J. Jašík, J. Roithová, J. Žabka, R. Thissen, I. Ipolyi, Z. Herman, Int. J. Mass Spectrom. 255 (2006) 150.
[22] J. Roithová, D. Schröder, Int. J. Mass Spectrom. 267 (2007) 134.
[23] J. Roithová, J. Žabka, D. Ascenzi, P. Francezschi, C.L. Ricketts, D. Schröder, Chem. Phys. Lett. 423 (2006) 254.
[24] J. Roithová, J. Žabka, Z. Herman, R. Thissen, D. Schröder, H. Schwarz, J. Phys. Chem. A 110 (2006) 6447.
[25] S.D. Price, Int. J. Mass Spectrom. 260 (2007) 1.
[26] J. Roithová, D. Schröder, Phys. Chem. Chem. Phys. 9 (2007) 2341.
[27] J. Roithová, D. Schröder, J. Am. Chem. Soc. 128 (2006) 4208.
[28] J. Roithová, D. Schröder, Chem. Eur. J. 13 (2007) 2893.
[29] C.L. Ricketts, D. Schröder, C. Alcaraz, J. Roithová, Chem. Eur. J. 14 (2008) 4779.
[30] H. Schwarz, Top. Curr. Chem. 73 (1978) 231.
[31] D. Kuck, Int. J. Mass Spectrom. 213 (2002) 101.
[32] N.G. Tsierkezos, D. Schröder, H. Schwarz, J. Phys. Chem. A 107 (2003) 9575.
[33] N. Tsierkezos, M. Diefenbach, J. Roithová, D. Schröder, H. Schwarz, Inorg. Chem. 44 (2005) 4969.
[34] J. Roithová, P. Milko, Cl.L. Ricketts, D. Schröder, V. Dekoj, M. Bělohradský, J. Am. Chem. Soc. 129 (2007) 10141.
[35] P.G. Sim, W.D. Jamieson, R.K. Boyd, Org. Mass Spectrom. 24 (1989) 327.
[36] H. Perreault, L. Ramaley, F.M. Benoit, P.G. Sim, R.K. Boyd, J. Phys. Chem. A 95 (1991) 4989.
[37] S. Leach, J.H.D. Eland, S.D. Price, J. Phys. Chem. 93 (1989) 7583.
[38] J. Roithová, D. Schröder, P. Gruene, T. Weiske, H. Schwarz, J. Phys. Chem. A 110 (2006) 2970.
[39] P. Milko, D. Schröder, H. Schwarz, J. Roithová, Int. J. Mass Spectrom 277 (2008) 107–112.
[40] Taken from the NIST Chemistry Webbook Database, see: http://webbook.nist.gov/chemistry/.
[41] L. Landau, Phys. Z. Sowjetunion 2 (1932) 46.
[42] C. Zener, Proc. Roy. Soc., Lond. A 137 (1932) 696.
[43] R.E. Olson, F.T. Smith, E. Bauer, Appl. Opt. 10 (1971) 1848.
[44] A. Salop, R.E. Olson, Phys. Chem. 13 (1976) 1312.
[45] P.K. Freeman, J.K. Pugh, J. Am. Chem. Soc. 121 (1999) 2269.
[46] T. Bally, L. Truttmann, F. Williams, J. Mol. Struct. (Theochem) 398–399 (1997) 255.
[47] D. Kuck, Mass Spectrom. Rev. 9 (1990) 187.
[48] D. Kuck, Mass Spectrom. Rev. 9 (1990) 583.
[49] D. Schröder, J. Loos, H. Schwarz, R. Thissen, O. Dutuit, J. Phys. Chem. A 108 (2004) 9931.
[50] T.D. Jaeger, M.A. Duncan, J. Phys. Chem. A 109 (2005) 3311.
[51] M. Mormann, J.Y. Salpin, D. Kuck, Int. J. Mass Spectrom. 249 (2006) 340.
[52] D. Schröder, H. Schwarz, P. Milko, J. Roithová, J. Phys. Chem. A 110 (2006) 8346.