Reactivity of $C_9H_n^{2+}$ dications with methane

Jana Vachelová, Jana Roithová *

Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, 12843 Prague 2, Czech Republic

ABSTRACT

The reactivities of $C_9H_x^{2+}$ dications ($x = 6$–8) generated by electron ionization (EI) of indene, 1-phenylpropyne, and 3-phenylpropyne, respectively, were studied in thermal collisions with methane. The most reactive dications correspond to dehydrogenated $C_9H_6^{2+}$, which show about 65% yield of C–C coupling products. The yield of coupling products in the reactions of radical dications $C_9H_7^{2+}$ drop to about 15% and the reactivity is dominated by electron transfer and charge-separation processes. The reaction between $C_9H_8^{2+}$ and methane leads mostly to proton transfer. There are differences between reactivities of analogous dications generated from different neutral precursors and therefore it can be stated that even dications generated by EI retain a partial memory of the structure of the neutral precursor.

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1. Introduction

Doubly charged ions are extremely reactive species [1–5]. The large reactivity results from their high potential energy which is a consequence of the large charge density that they accommodate [6]. For most of the small dications with only few atoms the second ionization energies are rather large and therefore these dications show a large tendency for electron transfer in the collisions with neutral species [2]. The second ionization energies of medium-sized dications as, e.g., $C_7H_8^{2+}$ [7,8] are already on the order of the first ionization energies of atoms or small molecules and therefore electron transfer is often suppressed and other reactivity channels can be observed [9]. For hydrocarbon dications, frequently proton transfer represents the dominant channel [10].

Medium-sized $C_nH_m^{2+}$ dications can undergo also reaction with methane, which results in a growing of the hydrocarbon chain [6,9,10]. This reaction is of particular interest for explaining the formation of larger hydrocarbons in the interstellar space or in planetary atmospheres [11]. The yield of the chain-growth reactions can be dependent of the structure of dicationic reactants. Laboratory studies of these reactions are, however, often performed with dications generated from the neutral precursors by electron ionization. The dications can therefore be formed with large internal energy and study of reactivities of various isomers may be impossible, because the isomeric dications could rapidly interconvert into each other and always a similar mixture of isomeric

dications would be formed. Here, we will address the reactivity differences between dications generated by electron ionization from different neutral precursors with the sum formula C_9H_8.

2. Experimental

The experiments were performed with a TSQ mass spectrometer (triple stage quadrupole from Thermo Finnigan) equipped with an ion source for electron ionization (EI) and chemical ionization; all experiments described here were performed with the EI source [12]. The analyzer region of the TSQ bears a QOQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The ion/molecule reactions of the $C_9H_8^{2+}$ dications described below were performed by mass-selecting the ions of interest with the first quadrupole (Q1) at a mass resolution fully sufficient to select dicationic species, i.e., half masses were well-resolved from each other. The mass-selected dications were then reacted with perdeuterated methane admitted to the octopole at pressures on the order of 1×10^{-4} mbar. The abundances of different reaction channels depend on the pressure of methane. In order to show the differences, we list results at different pressures in Electronic Supporting Information (ESI). The temperature of the manifold was set to $40\,^{\circ}$C. 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 [13]; 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

* Corresponding author. Tel.: +420 221951322; fax: +420 221951326.
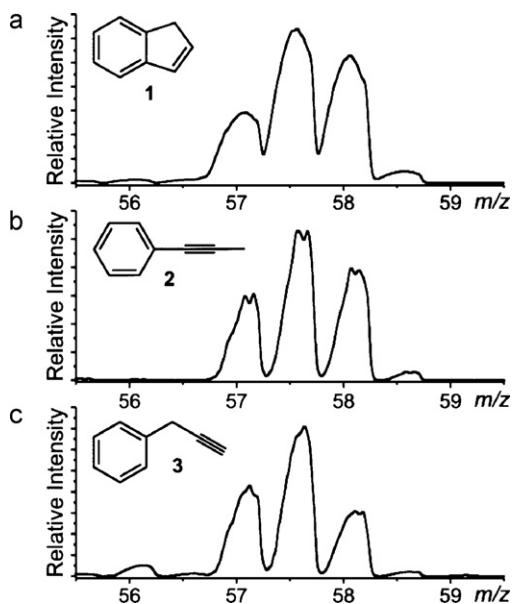*E-mail address:* roithova@natur.cuni.cz (J. Roithová).

Fig. 1. Relative abundances of dications generated from indene (a), 1-phenylpropyne (b), and 3-phenylpropyne (c).

reactions reported below were recorded at an ion kinetic energy which corresponds to the point of inflection of the curve obtained by retarding-potential analysis. 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. Usually, several hundreds of scans were accumulated per spectrum and the reported results are averages of at least three spectra. In the tables, the integrated intensities of the corresponding peaks are listed. For the charge-separation channels, abundances of only heavier fragments are summed; otherwise one channel would be counted two times. Further, the abundances of lighter ions coming from the charge separation are discriminated in our instrument, most probably because of their large kinetic energy [14], therefore we prefer to consider the heavier fragment ions.
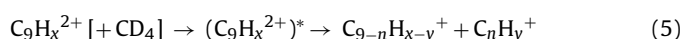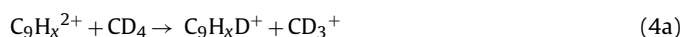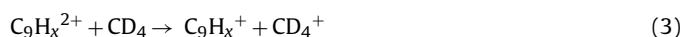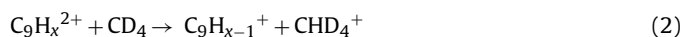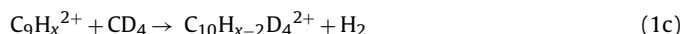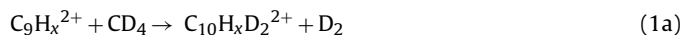
3. Results and discussion

For the investigation of the reactivity of dications generated from different isomers of C_9H_8, we have chosen indene (**1**), 1-phenylpropyne (**2**), and 3-phenylpropyne (**3**), respectively, as neutral precursors. These particular compounds were chosen on purpose, because they could give a hint, whether the interaction of methane with the dication is preferred at the aromatic site, or whether the terminal or internal triple bond serves as the preferred interaction site. Hence, we can expect some differences between indene on one hand and phenylpropynes on the other.

Double ionization of medium hydrocarbons leads usually to the formation of mixtures of dications with different number of hydrogen atoms. In the case of the neutral C_9H_8 molecules, the dications $C_9H_8^{2+}$ (m/z 58), $C_9H_7^{2+}$ (m/z 57.5), and $C_9H_6^{2+}$ (m/z 57) are generated. Fig. 1 shows the relative yields of these dications for different neutral precursors and it reveals that their abundances are very similar for all precursors. It is to be noted that, for example, the ions with nominal mass-to-charge ratio 58 are not purely $C_9H_8^{2+}$ dications, but there are also $^{13}CC_8H_7^{2+}$ dications present and we also cannot exclude singly charged ions with the mass 58, which could be formed from impurities present in the inlet system. Nevertheless, the abundances of the studied dications are very similar and the ions were generated under the same conditions, so we will neglect the minor differences caused by isobaric impurities and only look for the major differences in the reactivities of

dications generated from different neutral precursors. As to the possible structures of the generated dications, we refer to the paper with detailed theoretical calculations on the $C_9H_8^{2+}$ potential-energy surface [15].

Fig. 2 shows mass spectra of the daughter ions formed from the reaction between mass selected dications generated from indene and perdeuterated methane at nominally zero collision energy. The product ions can be sorted to several categories, which can be classified as bond-forming reactions leading to C_{10}-dications (Eqs. (1a)–(1c)), proton transfer (Eq. (2)), electron transfer (Eq. (3)), hydride transfer (Eqs. (4a)–(4d)), and finally dications can simply undergo charge separation reactions upon collision (Eq. (5)).

$$C_9H_x^{2+} + CD_4 \rightarrow C_{10}H_xD_2^{2+} + D_2 \tag{1a}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_{10}H_{x-1}D_3^{2+} + HD \tag{1b}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_{10}H_{x-2}D_4^{2+} + H_2 \tag{1c}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_9H_{x-1}^+ + CHD_4^+ \tag{2}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_9H_x^+ + CD_4^+ \tag{3}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_9H_xD^+ + CD_3^+ \tag{4a}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_9H_{x-1}D_2^+ + CHD_2^+ \tag{4b}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_9H_{x-2}D_3^+ + CH_2D^+ \tag{4c}$$

$$C_9H_x^{2+} + CD_4 \rightarrow C_9H_{x-3}D_4^+ + CH_3^+ \tag{4d}$$

$$C_9H_x^{2+} [+ CD_4] \rightarrow (C_9H_x^{2+})^* \rightarrow C_{9-n}H_{x-y}^+ + C_nH_y^+ \tag{5}$$

At the first sight, the dehydrogenated dications $C_9H_6^{2+}$ are the most reactive ones. The abundance of the C_{10} coupling products amounts to 67% of the total yield of all product ions (Eqs. (1a)–(1c)). From the pronounced scrambling of the H and D atoms, we can deduce that the reaction proceeds via a long-lived intermediate, which undergoes elimination of a hydrogen molecule (either H_2, HD, or D_2) to yield the final product. The second most abundant channel (17%) corresponds to a hydride transfer (Eqs. (4a)–(4d)). Even in this channel, we can observe a pronounced scrambling of H and D atoms. A similar effect was already observed for the reaction between $C_7H_6^{2+}$ and CD_4 [16]. Theoretical calculations made for this smaller system showed that both reactions, i.e., bond-forming reaction and hydride transfer, proceed via a common intermediate. The lifetime of this intermediate and the branching ratio between these two channels is strongly influenced by the collision energy of the reactants. At small collision energies as investigated here, the bond-forming channel prevails.

In contrast, the abundance of proton transfer channel (Eq. (2)) is 5% and that of electron transfer only 0.3% (Eq. (3)). All charge-separation channels (here dominantly $C_7H_3^+ + C_2H_3^+$) represent 11% of the product ions.

As to the structure of the reaction intermediate: For the reaction between $C_7H_6^{2+}$ and CH_4 it has been theoretically shown that methane is most probably transformed to an exo-methylene group introduced to the ring of $C_7H_6^{2+}$, which is concomitant with elimination of the H_2 molecule. Hence, according to this rationale we would expect the elimination of D_2 in the labeled reaction $C_9H_6^{2+}$ and CD_4 investigated here. However, it has also been shown that the energy barriers for the proton ring-walk in the intermediates are very low and therefore a rapid hydrogen scrambling is expected [15,16]. The statistical distribution of D_2:HD:H_2 losses from the $C_{10}H_6D_4^{2+}$ intermediate corresponds to 5:8:2, which roughly corresponds to the experimental findings (see Fig. 2a). We thus conclude that the C–C coupling reaction proceeds via a long-lived intermediate. On the other hand, in the hydride transfer channel, the statistical distribution of the $C_9H_xD_y^+$ products would correspond to $C_9H_6D^+$:$C_9H_5D_2^+$:$C_9H_4D_3^+$:$C_9H_3D_4^+ = 5:15:9:1$. The formation of $C_9H_6D^+$ is, however, preferred in the experiment. This
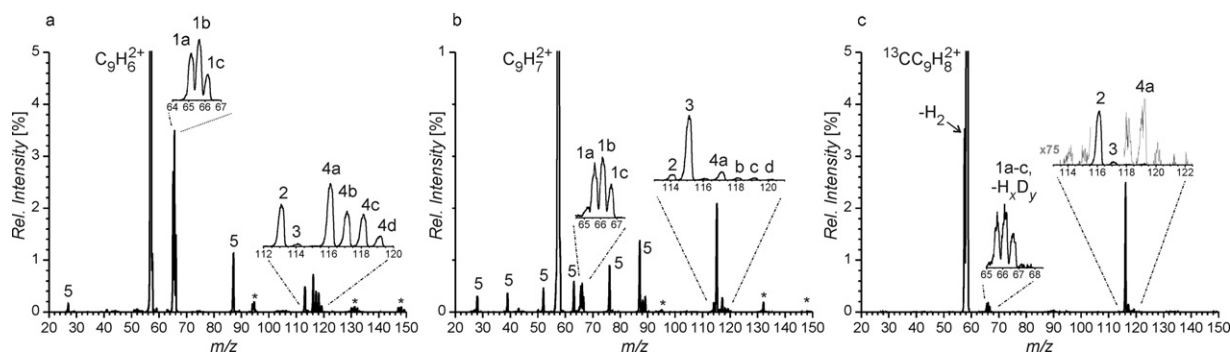
Fig. 2. Spectra of the ionic products from the reactions of methane with $C_9H_6^{2+}$ (a), $C_9H_7^{2+}$ (b), and $^{13}CC_8H_8^{2+}$ (c). The ions were generated from indene. The abundances of parent ion peaks were normalized to 100. The star-symbols denote secondary reactions and reactions with traces of benzene present in the collision cell. The numbers (and letters) denote products from the reactions listed above. The spectrum of $C_9H_8^{2+}$ is almost identical to that of $^{13}CC_8H_8^{2+}$, hence it is not shown.

is again in agreement with the results found for the $C_7H_6^{2+}/CD_4$ system: the hydride transfer occurs for the intermediates with a higher internal energy and hence with a shorter life time.

The spectrum of the product of the reaction between $C_9H_7^{2+}$ and CD_4 (Fig. 2b) contains at the first sight much more peaks corresponding to the charge-separation channels (Eq. (5)). In fact, charge-separation channels dominate the reactivity of the $C_9H_7^{2+}$ dications and represent 42% of the total yield of the products. The reduced reactivity in comparison with the other dications can be associated with the fact that the $C_9H_7^{2+}$ dication is an open-shell species. The second most abundant channel is electron transfer (30%). The bond-forming products represent here only 18% and the related hydride transfer 6%. Finally, the relative yield of the proton-transfer products amounts to 3%.

The last investigated dication, $C_9H_8^{2+}$, is derived directly by double ionization from the parent compound. Here, we evaluate results obtained for the $^{13}C_1$-containing dications ($^{13}CC_8H_8^{2+}$, m/z 58.5), because the parent ions do not contain isobaric impurities. However, the differences between the product spectra obtained for the reactions of ions with m/z 58 and those with m/z 58.5 are small (see Tables 3 and 4 and ESI). The generated $C_9H_8^{2+}$ dications undergo dehydrogenation [17–19] either already in the ion source (Fig. 1) or in the collision cell (Fig. 2c). This dehydrogenation product is more abundant (52%) than the product ions originating from the reaction with methane. It is to be noted that no hydrogen-atom loss is detected for metastable dications $C_9H_8^{2+}$. The dominant channel in the reaction of $C_9H_8^{2+}$ and CD_4 corresponds to proton transfer (38%). This is most probably associated with the fact that the parent dications have more hydrogen atoms than the other two ($C_9H_6^{2+}$ and $C_9H_7^{2+}$). For the same reason the hydride-transfer channel is almost completely suppressed (below 1%). The second most abundant channel corresponds to the bond-forming reactions (6%). Note that the bond-forming reaction between $C_9H_8^{2+}$ and methane is associated with twofold elimination of a hydrogen molecule or elimination of molecular and atomic hydrogen. The abundances of the electron transfer and charge-separation channels amount to 2.1% and 1.7%, respectively.

As shown above, the dehydrogenation product $C_9H_6^{2+}$ is much more reactive toward methane than the parent ions $C_9H_8^{2+}$. Hence, we cannot exclude that the products of the bond-forming channel originate from the reaction of the $^{13}CC_8H_6^{2+}$ dications formed by the H_2 loss. In order to estimate their possible contribution, the insert in Fig. 2c shows the region of C_9 monocations in the same relative zoom (gray line, the ion abundance is multiplied by a factor of 75) with respect to the insert with bond-forming products as it is in Fig. 2a. The ion with m/z 114 can represent the products of proton transfer from the $^{13}CC_8H_6^{2+}$ dications. The relative abundance of

the ions with m/z 114 with respect to the intensity of the bond-forming products (m/z 65–68) suggests that the reactivity of the dehydrogenated $^{13}CC_8H_6^{2+}$ dications could contribute by about one third to the overall yield of the bond-forming products (compare with relative abundance of m/z 113 with respect to the ions with m/z 65–67 in Fig. 2a) (Table 1).

The reactivities of dications generated from isomeric neutral precursors are very similar as it was expected (all spectra can be found in ESI). Notwithstanding these similarities, we can deduce several small, but significant differences. For the most reactive $C_9H_6^{2+}$ dications, the bond-forming reactions represent the far most abundant channels. Dications $C_9H_6^{2+}$ generated from indene show the largest ratio between C–C coupling reaction and hydride transfer (67.0:16.5, i.e., 4.1), hence between the reaction channels, which both presumably lead via the same reaction complex. This finding points to the possibility that the isomers of $C_9H_6^{2+}$ dominantly generated from indene have lowest energy barrier for the C–C coupling. On the other hand, the $C_9H_6^{2+}$ dications generated from 1-phenylpropyne, the ratio between the C–C coupling reaction and hydride transfer amounts to 64.2:21.9 = 2.9. Hence, for the dicationic isomers preferentially generated from 1-phenylpropyne, the largest energy barrier for C–C coupling is expected. At the same time, these dications show a larger abundance of the proton transfer channel and a lower abundance of charge separation channels in comparison with other $C_9H_6^{2+}$ dications.

Note that the ratio between C–C coupling and hydride transfer is very sensitive to the collision energy of the reactants. We have carefully calibrated the collision energy scale before each experiment. Further, if the differences between various dications would be caused by different collision energy, then we would have to expect that for dications generated from 1-phenylpropyne, a larger collision energy was used. This would be reflected in a larger abundance of the charge-separation products. Exactly opposite is, however, observed.

The reaction was further studied at a smaller pressure (transmission of the parent ions was set to 92–93%, Table S1 in ESI). The overall interpretation stays the same, only the abundance of the charge-separation reactions relatively increases (to about 20%) and the abundance of hydride transfer decreases. The ratio between the bond-forming channels and hydride transfer stays the largest for the dications generated from indene and the smallest for dications generated from 1-phenylpropyne (Table 2).

The reactivity of dications generated by double-ionization followed by a hydrogen-atom loss shows a large dependence on the pressure of the methane reactant. Especially, the ratio between the abundances of electron transfer and the charge-separation channels changes dramatically, which is evident from the reactivity measurements at different pressures (Table S2 in ESI). While it

Table 1
Relative abundances of products coming from the reaction between $C_9H_6^{2+} + CD_4$.

Neutral precursor	Bond-forming reactions 1a–1c	Hydride transfer 4a–4d	Proton transfer 2	Electron transfer 3	Charge-separations 5
Indene	67.0 ± 0.4	16.5 ± 0.2	4.8 ± 0.1	0.3 ± 0.1	11.2 ± 0.4
1-Phenylpropyne	64.2 ± 0.2	21.9 ± 0.1	6.7 ± 0.1	0.3 ± 0.1	6.8 ± 0.1
3-Phenylpropyne	65.4 ± 0.1	17.4 ± 0.1	5.9 ± 0.1	0.2 ± 0.1	11.0 ± 0.1

Table 2
Relative abundances of products coming from the reaction between $C_9H_7^{2+} + CD_4$.

Neutral precursor	Bond-forming reactions 1a–1c	Hydride transfer 4a–4d	Proton transfer 2	Electron transfer 3	Charge-separations 5
Indene	18.4 ± 0.4	6.4 ± 0.1	2.6 ± 0.1	30.2 ± 1.7	42.3 ± 1.4
1-Phenylpropyne	13.3 ± 1.0	5.9 ± 0.2	6.6 ± 0.3	39.4 ± 0.5	34.8 ± 1.0
3-Phenylpropyne	16.2 ± 1.0	5.9 ± 0.6	5.7 ± 0.2	37.3 ± 0.3	34.9 ± 0.9

Table 3
Relative abundances of products coming from the reaction between $^{13}CC_8H_8^{2+} + CD_4$.

Neutral precursor	Bond-forming reactions 1a–1c	Hydride transfer 4a–4d	Proton transfer 2	Electron transfer 3	Charge-separations 5
Indene	12.2 ± 0.3	1.7 ± 0.1	78.4 ± 0.6	4.4 ± 0.5	3.5 ± 0.1
1-Phenylpropyne	13.7 ± 0.2	1.2 ± 0.1	77.4 ± 0.2	3.1 ± 0.1	4.5 ± 0.1
3-Phenylpropyne	19.4 ± 0.5	2.2 ± 0.3	68.3 ± 0.5	5.1 ± 0.4	4.9 ± 0.2

Table 4
Relative abundances of products coming from the reaction between $C_9H_8^{2+} + CD_4$.

Neutral precursor	Bond-forming reactions 1a–1c	Hydride transfer 4a–4d	Proton transfer 2	Electron transfer 3	Charge-separations 5
Indene	11.4 ± 1.1	1.9 ± 0.1	76.5 ± 0.1	6.4 ± 1.8	3.8 ± 0.4
1-Phenylpropyne	14.6 ± 0.6	1.7 ± 0.1	72.2 ± 1.3	4.6 ± 0.1	6.9 ± 0.7
3-Phenylpropyne	18.4 ± 0.1	3.1 ± 0.1	63.3 ± 0.1	8.6 ± 0.2	6.7 ± 0.2

is difficult to quantitatively analyze the differences in reactivities, we can conclude that for dications generated from indene again the largest ratio between the bond-forming reactions and hydride transfer is observed, whereas for 1-phenylpropyne the ratio tends to be the smallest.

Finally, we have compared the $C_9H_8^{2+}$ dications (Tables 3 and 4 for $^{13}CC_8H_8^{2+}$ with m/z 58.5 and $C_9H_8^{2+}$ with m/z 58, respectively). Elimination of molecular hydrogen is the dominant channel for the dications generated from all these precursors. This channel is present also in the metastable ion spectrum and therefore its relative abundance depends strongly on the pressure of the collision gas. We have therefore excluded this channel from the calculations of the branching ratios (tables with this channel included can be found in ESI). The reactivities can be again best compared by the ratio between the various channels. Here, the ratio between the bond-forming reactions and the dominant proton transfer is evaluated. At the first sight, the smallest ratio is obtained for indene, whereas the bond-forming reactions are most preferred for 3-phenylpropyne. The results found for $^{13}CC_8H_8^{2+}$ (m/z 58.5) and for the more abundant $C_9H_8^{2+}$ dications (m/z 58) are consistent, but the latter are burdened with a larger experimental errors and show more charge-separation and electron-transfer reactions, which might be due to the contributions of the $^{13}CC_8H_7^{2+}$ radical dications.

In summary, we can conclude that we have detected some differences between reactivities of analogous dications generated from isomeric hydrocarbon precursors. This suggests that although electron ionization is a very energetic process, the generated dications retain a partial memory of the structure of the neutral precursor. We have reproducibly detected differences in branching between the C–C coupling channel and other channels. For the

$C_9H_6^{2+}$ and $C_9H_7^{2+}$ dications, the ratio between the C–C coupling and hydride-transfer channels can be evaluated. This ratio suggests that the dications generated from indene have relatively the lowest energy barriers for the C–C coupling reaction in comparison to the hydride transfer. An alternative explanation could also be that the dications generated from indene bear the lowest internal energy and therefore the C–C coupling is more preferred. As to the parent $C_9H_8^{2+}$ dications, the dications generated from indene show the largest abundance of proton transfer.

4. Conclusions

Hydrocarbon dications are extremely reactive species with large potential energy and therefore they are prone to many rearrangements. Here, we have shown that various $C_9H_x^{2+}$ dications generated from the closely related precursors indene, 1-phenylpropyne, and 3-phenylpropyne, respectively, show very similar reactivities with methane. The most reactive dications correspond to $C_9H_6^{2+}$ in that they reveal about 65% yield of C_{10}-products and about 20% yield of hydride transfer to methane. The radical dications $C_9H_7^{2+}$ undergo mostly charge-separation reactions and electron transfer. Finally, the $C_9H_8^{2+}$ dications show mostly proton transfer reaction (about 36% yield) and dehydrogenation (about 50% yield). Complete scrambling of hydrogen atoms, which occurs during the C–C coupling processes, suggests that these reactions proceed via long-lived intermediates. Further, also the hydride transfer proceeds via an intermediate, but its life time is shorter so that we observe only partial hydrogen scrambling in this channel. Comparison of reactivities of dications generated from different neutral precursors reveals that the reactivities are

very similar. There are small differences, which however do not allow a generalization of the reactivity patterns based on the structures of isomeric dications.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.12.002.

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