

ON THE C–C COUPLING OF THE NAPHTHYLIUM ION WITH METHANE

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

Unlike other medium-sized hydrocarbon cations $C_mH_n^+$ ($m = 7-11$, $n = 6-12$), the naphthylum ion $C_{10}H_7^+$ undergoes a thermal reaction with methane to form the C–C coupled product $C_{11}H_9^+$ concomitant with dehydrogenation. This reaction, which might be of relevance in the context of the growth of hydrocarbon species under extreme conditions, is suggested to lead to a benzylium-type cation in analogy to the C–C coupling of phenyl cations with methane.

Keywords: Benzotropylium; C–C coupling; Mass spectrometry; Methane activation; Naphthylum ion.

The activation of methane constitutes one of the “holy grails” in chemistry¹ and moreover is part of the challenge for solving the global energy problems faced in the 21st century. In particular, more efficient ways to transform the enormous resources of methane into more useful products such as methanol are of considerable interest², and also the oxidative C–C coupling of methane to C_2 hydrocarbons is economically attractive. Model studies in the gas phase, whether experimental, theoretical, or both, can provide very valuable insights into the elementary processes involved in such transformations³. The activation of methane poses a particular challenge and even in gas-phase model systems usually involves energetic species such as radical cations^{4,5} or transition-metal catalysis^{6,7}, but also main-group metals have been considered in gas-phase models of methane conversion⁸⁻¹⁰. In this context, a related task for chemistry is unraveling the

routes for the generation of larger hydrocarbons (either ionic or neutral) in interstellar environments and, most recently, in the higher atmosphere of Saturn's moon Titan¹¹. The conceptual chemical challenges in such environments are the low temperatures and pressures in conjunction with the absence of putatively catalytically active metal species. While ion chemistry^{12,13} has provided scenarios for the formation of C_mH_n compounds with $m \leq 7$, routes to larger hydrocarbons are less obvious and are usually based on condensation reactions of $C_mH_n^+$ ions with unsaturated precursors such as acetylene¹⁴, whereas methane itself only plays a minor role in these growth processes.

We have recently proposed a scenario for the growth of hydrocarbon species under the extreme conditions of interstellar environments or extraterrestrial atmospheres which involves quasi-barrierless coupling reactions of intermediately formed medium-sized $C_mH_n^{2+}$ dications with hydrocarbons such as acetylene^{15,16} or benzene¹⁷ and most notably also with methane¹⁸. These bond-forming reactions of molecular dications reactions¹⁹ yield doubly charged C-C coupling products via loss of either atomic or molecular hydrogen. In general, the corresponding $C_mH_n^+$ monocations with $m > 6$ are either much less reactive or do not react with methane at all. In contrast, smaller hydrocarbon monocations do indeed undergo C-C coupling reactions with methane, but the rate constants rapidly decrease with size. On the basis of the data available in the literature, reaction (1) involves the largest $C_mH_n^+$ ion reacting with methane under thermal conditions²⁰⁻²³.



EXPERIMENTAL

The experiments were performed with a TSQ Classic mass spectrometer^{17,24} equipped with ion sources for electron ionization (EI), chemical ionization (CI), electrospray ionization (ESI), and atmospheric pressure chemical ionization (APCI); all experiments described here were performed with the EI source. 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 vacuum of the manifold. The kinetic energy of the ions entering the octopole can be varied between 0 and 200 eV, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or collision-induced dissociation (CID) at elevated kinetic energies. The ion/molecule reactions of the $C_mH_n^+$ monocations described below were performed by mass-selecting the ions of interest with the first quadrupole (Q1) at a mass resolution fully sufficient to select the corresponding monocations. Note, however, that the contributions of [¹³C]₁-isotopes of hydrogen-depleted cations can contribute to some extent, but these interferences, though recognized, are of

limited importance in the present context. Note further that within the limits of our instrumentation, we could not further cool the hydrocarbon cations investigated in this work.

The mass-selected cations were then reacted with neutral methane admitted to the octopole at a typical pressure of 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 species reported here, the beam width at half maximum amounts to 1.1 ± 0.1 eV in the laboratory frame. The bimolecular 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 unit mass resolution was adjusted. Ion abundances were determined using a Daley-type detector operated in the counting mode. Typically, about hundred scans were accumulated resulting in an average scan time of 5 min per spectrum.

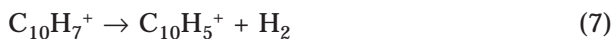
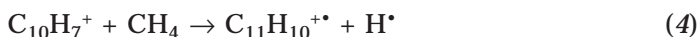
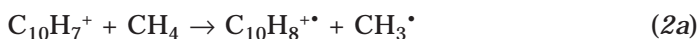
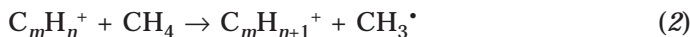
In the case of the EI experiments using toluene as a precursor, a small but notable amount of the toluene diffuses into the octopole reaction region which inter alia leads to the formation of $C_8H_9^+$ (m/z 105) via the well-known reaction of benzylium ion with neutral toluene²². The corresponding products are therefore not due to a C-C coupling involving methane and were identified and corrected by experiments with labeled toluene.

RESULTS AND DISCUSSION

In the context of our recent study of the reactions of hydrocarbon dications with methane¹⁸, the corresponding reactions of several $C_mH_n^+$ monocations were studied as well. Prior to a more detailed consideration of the experimental findings, some general remarks about the experimental methodology are made. At first, the ions examined in this work are generated via electron ionization (EI) which is to be considered as a "hard" ionization method leading to significant excitation of the ions formed including the generation of electronically excited states as well as the induction of isomerizations. As our machinery does not allow further measures for ion thermalization, these "hot" ions may accordingly contribute to the reactivity observed. On the other hand, "hot" species may also be less reactive in thermal ion/molecule reactions which crucially depend on an extended lifetime of the reaction intermediates^{18,25}. Next, multipole set-ups as the one used in the present experiments are in general not ideally suited for the investigation of the kinetics of ion/molecule reactions for several reasons: (i) due to the fixed interaction region in a multipole device, only the reagent pressure rather than the reaction time is available as a variable kinetically relevant parameter^{9,26}, (ii) mass- and kinetic-energy discrimination effects in the product-ion sampling may lead to a systematic under- or overestimation of the product-ion yields^{27,28}, and (iii) the kinetic energy

spread of the incident ion beam can affect the simplified analysis of reactant-ion conversion in terms pseudo-first order reaction kinetics²⁹. Finally, most of the reactions reported below are very slow (i.e. often much less than a per mille of the gas-kinetic collision rate) such that the reaction channels observed may be due to either excited states as well as isomers or due to reactions with trace impurities present in the background of the vacuum system; the latter issue is rather difficult to control when very slow ion/ molecule reactions are studied at extremely low pressures³⁰⁻³². The relative rate constants given in Table I should thus only be considered as a first-order approximation.

Despite the systematic shortcomings of the multipole experiment for the analysis of the kinetic of ion/molecule reactions outlined in the previous paragraph, the results obtained for a series of $C_mH_n^+$ cations ($m = 7-11$, $n = 6-12$) summarized in Table I allow two major and unambiguous conclusions. (i) Most of the ions react rather slowly, and if any significant reactivity is observed, this is associated with formal hydrogen-atom transfer from methane to the hydrocarbon ion according to reaction (2). (ii) The naphthylm ion $C_{10}H_7^+$ is a notable exception: In addition to hydrogen abstraction (reaction (2a)), it also promotes a C-C bond coupling with a reasonable rate, i.e. reaction (3) which is analogous to reaction (1). As further C-C coupling reactions, expulsion of atomic hydrogen (reaction (4)) as well as adduct formation (reaction (5)) are observed as minor pathways (Fig. 1).



The branching ratio between reactions (2a), (3), (4), and (5) is estimated as 92:4:3:1 (Fig. 1a). In addition to the bimolecular reaction products, unimolecular fragmentation via loss of atomic and molecular hydrogen (reactions (6) and (7)) is observed which is attributed to the presence of “hot” $C_{10}H_7^+$ cations formed upon generation of the precursor ions via electron ionization. Fully consistent with this view of reactions (6) and (7) as unimolecular processes, they also occur in the absence of any collision gas and the absolute amount of the fragments ions $C_{10}H_5^+$ and $C_{10}H_6^{2+}$ does not depend on the pressure of methane (Fig. 1).

TABLE I
Relative rate constants^a and branching ratios^b of hydrogen-atom transfer (H_T) and C–C bond coupling (CC)^c in the reactions of mass-selected $C_mH_n^+$ cations with neutral methane

Precursor	Selected ion	k_{rel}^a	H_T	CC	$\phi_{CC}^{d,e}$
Toluene	$C_7H_5^+$	0.04	91	9	0.004
	$C_7H_6^+$	12	99	1	0.12
	$C_7H_7^+$	0.12	92	8	0.01
	$C_7H_8^+$	0.09	96	4	0.006
<i>p</i> -Xylene	$C_8H_7^+$	0.3	40	60	0.18
	$C_8H_8^+$	0.06		100	0.06
	$C_8H_9^+$	0.01		100	0.01
	$C_8H_{10}^+$	0.02		100	0.02
Mesitylene	$C_9H_{11}^+$	0.7	98	2	0.014
	$C_9H_{12}^+$	0.01	80	20	0.002
Naphthalene	$C_{10}H_6^+$	0.9	77	23	0.2
	$C_{10}H_7^+$	100	92	8	8.0
	$C_{10}H_8^+$	1.4	95	5	0.07
1-Methylnaphthalene	$C_{11}H_8^+$	34	99	<1	0.14
	$C_{11}H_9^+$	0.1	97	3	0.004
	$C_{11}H_{10}^{2+}$	0.01	70	30	0.004

^a Formal rate constants derived from the amount of dication conversion in the presence of methane under single collision conditions (ca. 10^{-4} mbar) relative to the fastest reaction of $C_{10}H_7^+$ ($k_{rel} = 100$). ^b Normalized to $\Sigma = 100$. ^c Here, all C–C coupling channels are summed up irrespective whether atomic or molecular hydrogen is lost. ^d Relative efficiency of the C–C coupling expressed as the product of k_{rel} and the branching ratios of the coupling reactions. ^e The absolute overall rate constant for the reaction of $C_{10}H_7^+$ is $(6 \pm 3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; see the text.

In order to achieve an estimate of the absolute rate constant of the reaction of $C_{10}H_7^+$ with methane, the amount of conversion at a given pressure of methane in the octopole collision cell was measured relative to the well-known reaction of N_2^+ with methane ($k = 1.15 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)³³. Using this procedure as a first approximation for the determination of rate constants of ion/molecule reactions in a multipole-based mass spectrometer^{17,26,34}, an overall rate constant of $k(C_{10}H_7^+) = (6 \pm 3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is derived, which corresponds to about 6% of the gas-kinetic collision rate ($1.0 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Moreover, most of the total ion/molecule reactivity is associated with hydrogen-atom abstraction (reaction (2a)), whereas the C–C coupling processes (reactions (3)–(5)) comprise less than a tenth of the total reactivity. Accordingly, only about 1 of 200 collisions of $C_{10}H_7^+$ with methane leads to C–C coupling. Notwithstanding the low efficiency, the signals due to the C–C coupling products can be observed unambiguously and thus do not arise from impurities present in the background of the vacuum system (see blue and red traces in Fig. 1a).

The occurrence of a C–C coupling reaction is further supported by isotopic labeling in that the reaction between $C_{10}H_7^+$ and CD_4 is associated with extensive H/D equilibration. Thus, the major route of C–C coupling leads to the loss of HD to afford a $C_{11}H_6D_3^+$ cation (Fig. 1b) indicating the loss of positional identity of the H and D atoms prior to the occurrence of dehydrogenation. In contrast, hydrogen-atom abstraction occurs with high

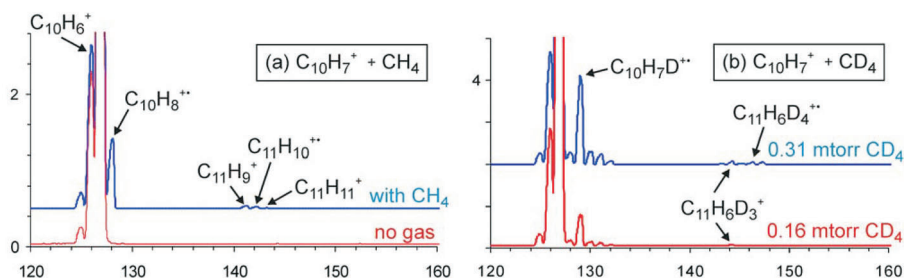


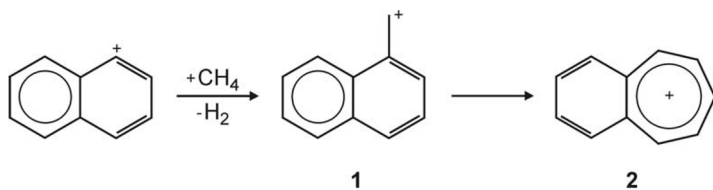
FIG. 1

Relevant regions of the mass spectra illustrating the reaction of mass-selected $C_{10}H_7^+$ cations with neutral methane. Figure 1a shows unimolecular dissociation of “hot” $C_{10}H_7^+$ in the absence of any collision gas (red trace) as well as the new products formed in the presence of methane (blue trace with a vertical offset of 0.5). The vertical axis is given relative to the intensity of the $C_{10}H_7^+$ parent ion (100, off-scale). Figure 1b shows the corresponding results for CD_4 under single collision conditions (red trace) and at elevated pressure of CD_4 in the octopole collision cell (blue trace with a vertical offset of 2)

selectivity, because $C_{10}H_7D^+$ (m/z 129) is formed predominantly, although also notable amounts of further H/D exchange products are observed (e.g. the ions at m/z 130–132 in the blue trace of Fig. 1b); also a trace of degenerate H/D exchange is observed, i.e. formation of $C_{10}H_6D^+$ (m/z 128). In this context, we note that H/D exchange has also been reported for naphthylum ion in the presence of deuterium molecules³⁵. With several other neutral heteroatom molecules, however, only adduct formation has been observed for naphthylum ions^{36,37}. With respect to the chemistry of the ionosphere of Titan these results suggest that naphthylum ions can contribute to the growth of larger hydrocarbons in the presence of methane as a C_1 building block. Note, however, that the competing reaction (2a) limits the steady-state concentration of $C_{10}H_7^+$ which can be reached in a methane-rich atmosphere. Unlike the corresponding dicationic species, however, reactions (3)–(5) are almost a singularity in the series of $C_mH_n^+$ ions (Table I). For example, the coupling product $C_{11}H_9^+$ formed in reaction (3) is several orders of magnitude less reactive towards methane, where it is to be considered additionally that the precursor ion has been generated by EI and may hence not only contain a considerable amount of excess energy, but further may consist of a mixture of isomeric ions.

The exceptional behavior of $C_{10}H_7^+$ is quite intriguing and provokes the question for the underlying reason(s). At the first sight, naphthylum may appear as a simple aryl cation; however, the system is more complicated than expected. Thus, the 1- and 2-naphthylum ions are very close in energy^{35,38,39} and also the separation of the singlet and triplet states is much smaller for naphthylum^{35,40} than in the smaller phenylum ion⁴¹. This situation led Ascenzi et al.³⁵ to the suggestion that dissociative ionization of naphthyl derivatives $C_{10}H_7X$ (here, $X = H$) by means of EI is likely to afford mixtures of 1- and 2-naphthylum in the singlet and triplet electronic states. Considering the use of EI as a non-selective ionization method, we therefore refrain from a more detailed discussion of these aspects; photoionization with reactive monitoring would probably be the most suitable means to address this problem^{18,25,42,43}. Notwithstanding, the mechanism of the addition of methane concomitant with dehydrogenation according to reaction (3) can be understood by reference to the analogous reaction of phenylum ion with methane²². Thus, it has been suggested that the C–C coupling of $C_6H_5^+$ and methane (reaction (1)) proceeds either barrierless or quasi-barrierless towards an adduct corresponding to toluene protonated at the *ipso*-position²². The energy gain associated with this process is not only sufficient for a whole array of hydrogen migrations, but it also suffices for skeletal rearrangements, e.g. ring expansion to the cycloheptadienyl mani-

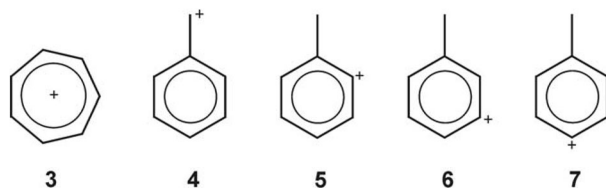
fold. The energy barrier associated with the final dehydrogenation process is also well within the internal energy of the intermediates and the product formed corresponds to the benzylium ion, which can subsequently rearrange to the more stable tropylium ion⁴⁴. By analogy, the reaction of naphthylmethyl cation with methane most probably leads to a benzylium ion, i.e. the naphthylmethyl cation, $C_{10}H_7CH_2^+$ (**1**), which may subsequently rearrange to the putatively more stable benzotropylium structure^{45–48} **2** (Scheme 1).



SCHEME 1

Suggested dehydrogenative C–C coupling of 1-naphthylmethyl cation with methane to the 1-naphthylmethyl cation **1**⁺ and the subsequent skeletal rearrangement to benzotropylium **2**⁺; an analogous route to **2**⁺ evolves for the reaction of 2-naphthylmethyl cation

Ascribing the C–C coupling reaction to a genuine aryl cation provides an explanation, why most of the other $C_mH_n^+$ ions do not react in the same way (or much less efficiently, Table I). As an example, let us consider the $C_7H_7^+$ cation as the next higher homologue of phenylium. The most stable isomer of $C_7H_7^+$ is the tropylium ion (**3**; Scheme 2, $\Delta_f H = 896$ kJ mol⁻¹) with the benzylium ion (**4**; $\Delta_f H = 919$ kJ mol⁻¹) only somewhat higher in energy, whereas the tolyl cations **5–7** are considerably less stable ($\Delta_f H = 1087$, 1093, and 1101 kJ mol⁻¹ for the *o*-, *m*-, and *p*-tolyl cations, respectively)^{49,50}. Dissociative ionization of a neutral C_7H_7-X compound (here, X = H, Table I) is hence likely to afford either **3** or **4**, but only traces of **5–7**. As only the latter are genuine aryl cations which could react with methane in analogy to reaction (1), it is understandable why the efficiency of C–C coupling with



SCHEME 2

Structures of the $C_7H_7^+$ isomers **3–7**; for further details, see refs^{49,50}

mass-selected $C_7H_7^+$ is very low and in fact close to the detection limit of the experiment. Similar considerations apply for most of the other $C_mH_n^+$ ions studied here. In particular, the large difference in the efficiencies of C–C coupling for $C_{10}H_7^+$ and the higher homologue $C_{11}H_9^+$ derived from 1-methylnaphthalene finds a rationale and further supports the suggestion that reaction (3) is likely to afford the naphthylmethyl cation **1** or benzotropylium **2** via subsequent rearrangement, rather than methylnaphthyl-ium ions.

CONCLUSIONS

Mass spectrometric experiments using a multipole instrument demonstrate that most of the hydrocarbon monocations $C_mH_n^+$ ($m = 7-11$, $n = 6-12$) generated by (dissociative) ionization of arenes are unreactive towards methane. Only genuine arenium ions, i.e. phenylium $C_6H_5^+$ and naphthylum $C_{10}H_7^+$, are notable exceptions in this respect. The alkylated homologues do not undergo similar C–C coupling reactions with comparable rate constants, because isomeric structures such derived from benzylium or tropylium ions are more stable, less reactive, and easily accessible via hydrogen migrations or skeletal rearrangements. Within the specific context of the ionosphere of Titan, the data suggest that genuine arenium ions can indeed contribute to the growth of hydrocarbons ions in a methane-rich atmosphere^{12,13,51,52}, but the reactivity of $C_6H_5^+$ and $C_{10}H_7^+$ with methane appears to be an exceptional, and $C_mH_n^+$ monocations with $m \geq 7$ thus cannot provide a general growth scenario for the formation of larger hydrocarbon compounds on Titan.

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