

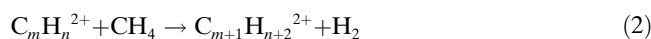
Growth of Larger Hydrocarbons in the Ionosphere of Titan

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Among the many fascinating results of the Cassini–Huygens mission, the mass spectrum of the ionosphere of Titan has attracted considerable attention.^[1] In brief, the ionosphere was found to be surprisingly complex, consisting of hydrocarbon ions $C_mH_n^+$ as well as nitrogen-containing ions $C_nH_nN_o^+$ with mass-to-charge ratios up to the probe's limit of m/z 100;^[2] even much heavier components have been proposed.^[1b,3] While the formation of C_mH_n compounds with $m \leq 7$ is reasonably well understood,^[3–5] routes to larger hydrocarbons are less obvious. Moreover, most of the present models rely on condensation reactions of $C_mH_n^+$ ions with unsaturated precursors such as acetylene,^[6] whereas methane, as the major hydrocarbon in the atmosphere of Titan, only plays a minor role in the subsequent growth processes. Here, we report carbon–carbon (C–C) coupling reactions of methane with medium-sized $C_mH_n^{2+}$ dications leading to larger hydrocarbon molecules. Despite low steady-state concentrations of the dicationic intermediates, kinetic modeling allows predictions about the larger hydrocarbon species present in the ionosphere of Titan, thereby rationalizing the results from the Cassini–Huygens mission which consideration of monocations only cannot explain.

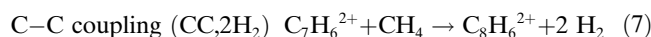
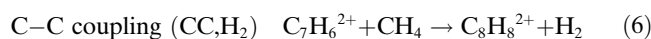
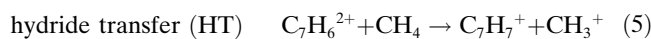
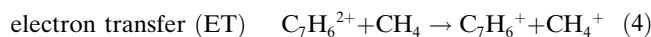
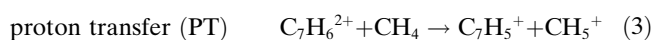
The activation of methane poses a particular challenge and usually involves energetic conditions or metal catalysis.^[7] Under the conditions of the Titan atmosphere (low temperatures and pressures), small hydrocarbon ions can

indeed react with methane, but the rate constants decrease with size, and so far reaction 1 involves the largest $C_mH_n^+$ ion reacting with methane under thermal conditions.^[8,9]



Recently, we proposed double ionization as a feasible route for C–C bond formation under extreme conditions.^[10] In our laboratory experiments (see Supporting Information), $C_mH_n^+$ mono- and $C_mH_n^{2+}$ dications ($m=7–11$, $n=6–12$) were generated by electron ionization (EI) of aromatic precursors, mass-selected, and allowed to interact with methane.^[11] Whereas most $C_mH_n^+$ monocations studied do not show a significant reactivity with methane under these conditions, many $C_mH_n^{2+}$ dications undergo dehydrogenative C–C coupling according to reaction (2); we note in passing that none of these $C_mH_n^{2+}$ dications reacts with nitrogen as the major component in the atmosphere of Titan.

As an example (Figure 1), we refer to the reaction of methane with the $C_7H_6^{2+}$ dication generated upon EI of toluene.^[13] The observed reactions (3)–(7) can be classified as follows.



ET and HT [reactions (4) and (5)] are common processes in the bimolecular chemistry of multiply charged ions,^[14,15] and PT [reaction (3)] is a particularity of hydrogen-containing dications.^[16,17] While reactions (3)–(5), driven by the energy gain upon formation of two singly charged product ions, dominate the reactivity of $C_7H_6^{2+}$ under the experi-

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mental conditions, the bond-forming reactions (6) and (7) associated with C–C coupling can compete to a considerable extent.^[18] In addition to the ionic products given in reactions (3)–(7), Figure 1 shows the fragments $C_2H_3^+ + C_5H_3^+$ due to

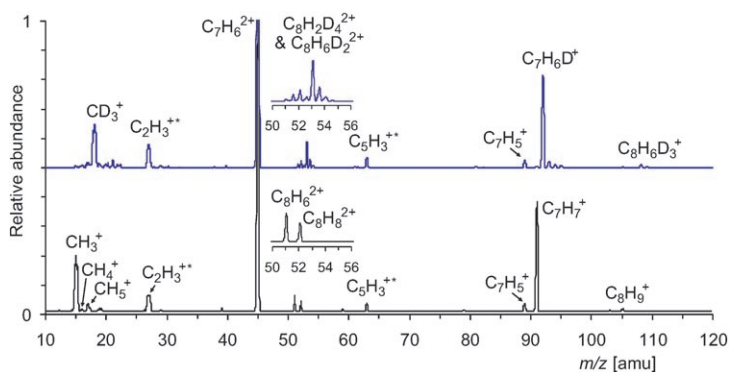


Figure 1. Ion/molecule reaction of mass-selected $C_7H_6^{2+}$ generated by EI of toluene with neutral methane (lower trace) and $[D_4]$ methane (upper trace). The vertical axis refers to an intensity of 1 for the parent ion (shifted upwards by 0.5 for the reaction with CD_4), the mass-region from m/z 10–40 is amplified by a factor of 50, and the mass-region from m/z 50–120 is amplified by a factor of 10; the application of different factors in low- and high-mass regions is due to the discrimination of light fragment ions in detection.^[11,12] Two expanded insets show the isotope patterns of the dicationic C–C coupling products in the mass range m/z 50–56. The monocations $C_2H_3^+$ and $C_5H_3^+$ due to unimolecular dissociation of metastable $C_7H_6^{2+}$ are denoted with an asterisk.

unimolecular Coulomb explosion of the parent dication and a weak signal for the monocationic $C_8H_9^+$ species (with notable deuterium incorporation when using CD_4) which can be assigned to a secondary reaction of methane with the initially formed $C_8H_8^{2+}$ dication via hydride transfer in analogy to reaction (5). Further, the C–C coupling products of $C_7H_6^{2+}$ and CD_4 show substantial H/D equilibration and thereby imply a significant lifetime of the dicationic collision complex $C_8H_6D_4^{2+}$.^[10,11]

The results obtained for a series of $C_mH_n^{2+}$ dications ($m = 7–11$, $n = 6–12$) are summarized in Table 1 using the classification in terms of reactions (3)–(7). The data demonstrate that C–C coupling with methane according to reaction (2) is a general feature of medium-sized $C_mH_n^{2+}$ dications. The corresponding monocations have been studied also, but almost all react at least 100 times slower than the dications and coupling often is not detected at all. A notable exception is the naphthylum ion, $C_{10}H_7^+$, which undergoes dehydrogenative C–C coupling with methane in analogy to reaction (1) with $k_{rel} = 0.06$. In the particular case of the $C_9H_n^{2+}$ dications ($n = 6–8$), we also addressed the question of possible isomers in the dication state.^[13,20] However, the ion/molecule reactions of the corresponding dications generated upon EI of two structurally significantly different neutral precursors, namely, indene and mesitylene, respectively, were virtually superimposable.

Qualitatively, the data in Table 1 reveal the following trends. i) For hydrogen-depleted $C_mH_n^{2+}$ dications ($m > n$),

Table 1. Relative rate constants^[a] and branching ratios^[b] in the reactions of $C_mH_n^{2+}$ dications with neutral methane.

Precursor	Selected ion	k_{rel} ^[a]	PT	ET	HT	CC ₂ H ₂ / CC ₂ H ₂	ϕ_{CC} ^[c]
toluene	$C_7H_6^{2+}$	0.61	5	<1	74	10:11	0.13
	$C_7H_7^{2+}$	0.42	3	19	64	8:6	0.06
	$C_7H_8^{2+}$	0.46	52	1	41	2:4	0.03
<i>p</i> -xylene	$C_8H_6^{2+}$	0.02 ^[d]	2	14	14	62:8	0.01 ^[d]
	$C_8H_7^{2+}$	0.13	54	<1	7	11:28	0.05
	$C_8H_8^{2+}$	0.17	1	<1	44	46:9	0.09
	$C_8H_9^{2+}$	0.42	19	<1	40	35:6	0.17
	$C_8H_{10}^{2+}$	0.05 ^[d]	44	<1	11	30:15	0.02 ^[d]
mesitylene	$C_9H_6^{2+}$ ^[e]	1.00	3	<1	14	83:<1	0.83
	$C_9H_7^{2+}$ ^[e]	0.05	7	20	10	57:6	0.03
	$C_9H_8^{2+}$ ^[e]	0.12	82	<1	1	4:13	0.02
	$C_9H_9^{2+}$	0.11	79	6	1	5:8	0.01
	$C_9H_{10}^{2+}$	0.10	91	2	<1	3:4	0.01
naphthalene	$C_9H_{12}^{2+}$	0.15	87	4	2	4:3	0.01
	$C_{10}H_6^{2+}$	0.05 ^[d]	<1	8	2	84:6	0.05 ^[d]
	$C_{10}H_7^{2+}$	0.95	11	2	15	68:4	0.68
	$C_{10}H_8^{2+}$	0.04	4	60	8	22:6	0.01
1-methyl-naphthalene	$C_{11}H_6^{2+}$	0.62	1	<1	8	90:<1	0.56
	$C_{11}H_7^{2+}$	0.22	7	6	8	65:14	0.17
	$C_{11}H_8^{2+}$	0.60	26	2	6	56:10	0.40
	$C_{11}H_9^{2+}$	0.12	20	12	5	53:10	0.08
	$C_{11}H_{10}^{2+}$	0.20	84	<1	<1	1:15	0.03

[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 $C_9H_6^{2+}$.^[18,19] [b] Normalized to $\Sigma = 100$. [c] Relative efficiency of the C–C coupling expressed as the product of k_{rel} and the branching ratios of the coupling reactions. [d] Lower limit due to overlapping monocations in the parent-ion beam. [e] Within experimental error, identical results were obtained for the dication generated by EI of indene.

HT is more pronounced, whereas PT can compete for less unsaturated $C_mH_n^{2+}$ species ($m \approx n$). ii) ET is inefficient for most dications studied and primarily occurs for those species for which the relative rate constants k_{rel} are low. An exception is $C_7H_7^{2+}$ with $k_{rel} = 0.42$ and 19% ET, which we attribute to the particular stability of the tropylium monocation.^[21] iii) roughly, the efficiency of C–C coupling (ϕ_{CC}) increases with m and decreases with n which can be explained as follows. With increasing m , the recombination energies of the $C_mH_n^{2+}$ dications decrease and hence the driving forces for charge-separation processes in analogy to reactions (3)–(5) decrease.^[17] Further, hydrogen-depleted dications (smaller n) undergo the coupling reactions more readily due to their larger degree of unsaturation and hence increased tendency for condensation processes.

In a more general sense, reaction (2) provides a route for the formation of larger hydrocarbon ions using methane as C_1 building block, provided the conditions enable the formation of molecular dications.^[22–25] Like the CO_2^{2+} dications in the atmosphere of Mars,^[26] vacuum-ultraviolet (VUV) photons as well as energetic particles in the upper atmosphere of Titan may enable the ionization of mono- to dications.^[5,27] As the corresponding monocations react with methane much less efficiently, the dications thus provide a mechanism for the growth of larger hydrocarbons.

With respect to the relevance of these C–C coupling reactions in interstellar environments or the higher regions of methane-rich atmospheres of planets or moons, an important aspect concerns the internal energy of the $C_mH_n^{2+}$ dications serving as reactants, because it might be argued that excess energy imparted in the ionization event and/or electronically excited states of $C_mH_n^{2+}$ are responsible for the C–C coupling. For singly charged ions, the usual strategy to cope with this question is the proper thermalization of the reactant ions.^[28] For dications, however, this approach is more difficult to realize due to the large ionization energies required and the intrinsically high reactivity of $C_mH_n^{2+}$ ions.^[10,11,13] Therefore, we pursued a different approach employing photoionization using synchrotron radiation in conjunction with reactive monitoring.^[29] To this end, neutral toluene is admitted to the ion source of a multipole mass spectrometer,^[30] ionized by VUV photons, the ion of interest, here $C_7H_6^{2+}$ (see Figure 1), is mass-selected and transferred to an octopole collision cell in which it is allowed to react with methane under single-collision conditions (nominal collision energy 0.8 eV), and the dicationic C–C coupling product $C_8H_8^{2+}$ formed according to reaction 6 is then monitored using a second mass filter. While all conditions are otherwise kept constant, the photon energy is scanned from below the threshold of the reactant ion to a few eV higher.

The data shown in Figure 2 reveal two important aspects. At first, the apparent threshold of the coupling product $C_8H_8^{2+}$ somewhat below 26 eV is identical to that of the precursor $C_7H_6^{2+}$ within experimental error; i.e., from the very threshold, the traces overlap with each other and the relative yield is independent of the energy of the ionizing photons up to about 1 eV above threshold. Secondly, the relative yield of coupling product $C_8H_8^{2+}$ tends to decrease at about 27 eV which is ascribed to contributions from rovibrationally and/or electronically excited $C_7H_6^{2+}$ dication precursors. The synchrotron measurements thus proof directly that the observed C–C coupling reactions are nascent to the ground-state reactivity of $C_7H_6^{2+}$.

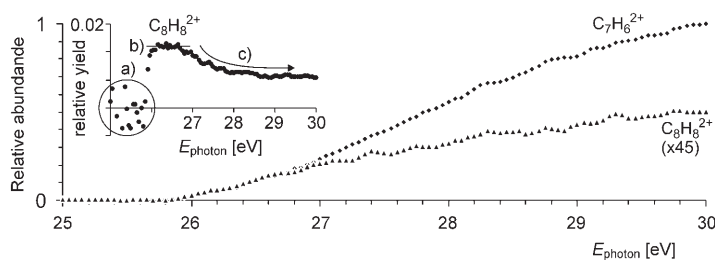
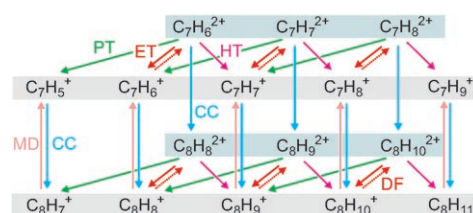


Figure 2. Abundances of the precursor dication $C_7H_6^{2+}$ (◆) and the C–C coupling product $C_8H_8^{2+}$ (▲) in single-ion monitoring as a function of the energy of the ionizing photons (in eV). The inset shows the relative yield of the coupling product, that is, $I(C_8H_8^{2+})/[I(C_7H_6^{2+})+I(C_8H_8^{2+})]$, as a function of photon energy. The encircled region a) of the inset shows random noise as these values are below threshold, the line in region b) indicates a plateau-behavior in the relative yield of the coupling product, and in the arrow in region c) indicates the decrease of conversion due to contributions of “hot” $C_7H_6^{2+}$.

In order to explore the relevance of this scenario, the results were implemented in a kinetic modeling,^[19,31] whose essentials are sketched in Scheme 1. The key assumption is



Scheme 1. Simplified kinetic scheme for the growth of $C_mH_n^+$ monocations in the presence of methane via transient $C_mH_n^{2+}$ dications. For the sake of simplicity, only a partial manifold of C_7 - and C_8 -ions is shown, $(CC,2H_2)$ is left out, the neutral reactant methane and the other neutral or ionic products are omitted. PT: proton transfer, ET: electron transfer, HT: hydride transfer, CC: C–C coupling, DF: dication feed, MD: monocation degradation.

the existence of some event which leads to the formation of $C_mH_n^{2+}$ dications (dication feed, DF), as expressed by a phenomenological parameter k_{DF} which is applied to all monocationic species. The reactions of the $C_mH_n^{2+}$ dications are then determined by the relative rate constants and branching ratios (Table 1). Here, PT, ET, and HT connect the $C_mH_n^{2+}$ dications with the monocations (with varying hydrogen content), whereas the C–C coupling leads from the C_m to the C_{m+1} manifold. The newly formed $C_{m+1}H_{n+2}^{2+}$ dications can then either convert to monocations via PT, ET, and HT or continue growing. Further, the assumption of a dication feed implies that the same energetic conditions enabling double ionization can also lead to monocation degradation (MD) from the C_{m+1} back to the C_m manifold, as expressed by another phenomenological parameter k_{MD} which also is applied to all monocations larger than C_7 . The model fulfils the boundary conditions that i) a quasi-stationary state is rapidly reached for all ions and ii) the results are not very sensitive of the starting conditions. We begin the modeling with $C_7H_n^{2+}$ dications, because toluene is the smallest aromatic hydrocarbon, whose second ionization energy (14.8 eV)^[32] is clearly below the first ionization energy of nitrogen (15.58 eV) which is the predominant component in the atmosphere of Titan.

Figure 3 shows a result of such a modeling.^[33] While the abundances of the higher $C_mH_n^+$ species, of course, crucially depend on the choice of k_{DF} and k_{MD} , several aspects of this model are worth considering with respect to Titan. i) The sum of all dications is far below 1%, consistent with general expectation for such energetic species and the lack of indications for the presence of doubly charged ions from the Titan missions.^[34] ii) Despite low steady-state concentrations of the dications, C–C coupling leads to notable amounts of higher $C_mH_n^+$ species ($n \geq 8$), whereas this fraction is much lower and less extended if dications are excluded (inset in Figure 3). iii) Compared with the conventional EI mass spectra of aromatic hydrocarbons (which are dominated by $[M]^+$

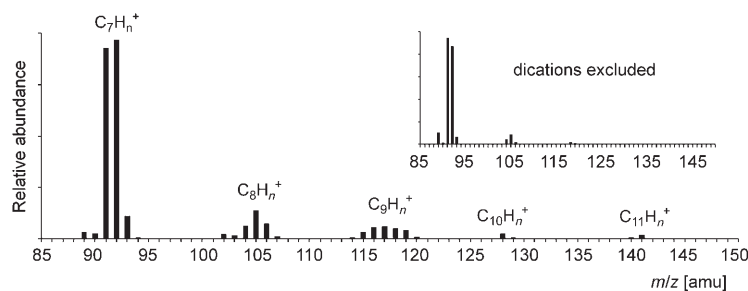


Figure 3. Example of a mass spectrum (m/z 85–150, $C_7H_n^+$ – $C_{11}H_n^+$ ions) derived from the kinetic model sketched in Scheme 1 using the parameters given in Table 1 with $k_{DF}=0.001$ and $k_{MD}=0.0005$. The inset shows the same modeling with exclusion of dicationic intermediates ($k_{DF}=0$).

and $[M-H]^+$ ions), both, single and double dehydrogenation in the coupling reactions and the competition of PT and HT lead to a broadening of the modeled monocation mass spectra with respect to hydrogen content, which is consistent with the Cassini–Huygens data. iv) Inherent to the construction of the kinetic modeling, specifically due to the counteracting parameters k_{DF} and k_{MD} , the modeled abundances of the higher $C_mH_n^+$ species decrease roughly monotonically with m , which agrees with the recent analysis of energy/charge measurements on Titan.^[1b,3] Our suggested mechanism for the growth of hydrocarbon ions can hence account for some key characteristics of Titan's ionosphere. In future laboratory-based studies, it will be of prime importance to probe the relevance of this and similar scenarios for the growth of hydrocarbons ions^[4,5,35,36] by leaving the single-collision regime towards more realistic pressures, consideration of temperature effects, and particularly also extension to nitrogen-containing ions.^[37]

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Keywords: C–C coupling • dications • mass spectrometry • synchrotron radiation • Titan

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