Growth Of Doubly Ionized C,H,N Compounds in the Presence of Methane[†]

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Received: May 25, 2009; Revised Manuscript Received: July 23, 2009

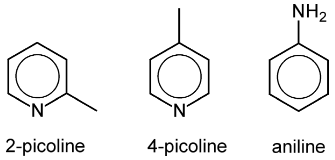
The molecular dications $C_6H_5N^{2+}$ generated via dissociative double ionization of 2- and 4-picoline, respectively, react with methane to form the C−C coupled products $C_7H_7N^{2+}$ concomitant with liberation of molecular hydrogen. Multipole-based mass spectrometric experiments and photoionization studies using synchrotron radiation demonstrate that this bond-forming reaction involves the corresponding dications in their electronic ground states. The reactions might hence be of relevance in the context of the growth of hydrocarbon species at extremely low temperatures and pressures, such as in the atmosphere of Titan. Whereas the parent $[(CH_3)C_5H_4N]^{2+}$ dications of both picolines also show C−C coupling to a limited amount, the molecular dication of aniline, $[C_6H_5NH_2]^{2+}$, is almost unreactive toward methane.

Recently, we have suggested a possible scenario for the growth of hydrocarbon molecules in the higher atmosphere of Titan, which involves dicationic species as reactive intermediates.[1] Whereas the activation of methane, as the major carbon source in Titan's atmosphere, constitutes one of the "holy grails" in chemistry,[2] superelectrophilic reagents,[3] such as molecular dications,[4] are obviously able to master this task.[5] With respect to the chemistry of Titan, the suggested scenario involves, in brief: (i) ionization of preformed hydrocarbon species to monocations $C_mH_n^+$, either by direct ionization with photons or energetic particles or via proton attachment, (ii) photo- or impact-ionization of these monocations to the corresponding dications $C_mH_n^{2+}$, (iii) C−C coupling of the dications with methane to yield $C_{m+1}H_{n+2}^{2+}$ concomitant with molecular hydrogen (reaction 1) eventually followed by consecutive growth reactions in the dication state, and (iv) return to the manifold of singly charged ions and eventually also neutral compounds via electron-, proton-, and hydride-transfer pathways. These bond-forming reactions of molecular dications[6] thus lead to C−C coupling products concomitant with the liberation of molecular hydrogen.

$$C_mH_n^{2+} + CH_4 \rightarrow C_{m+1}H_{n+2}^{2+} + H_2 \qquad (1)$$

Because of the fact that for the nitrogen-rich atmosphere of Titan the formation of nitrogen-containing species has been proposed,[7] here we communicate preliminary data about the reactivity of $C_mH_nN^{2+}$ dications with methane. Specifically, we have chosen the three isomeric C_6H_7N compounds, 2-picoline, 4-picoline, and aniline (Chart 1), as neutral precursors that, upon double ionization, afford the molecular dications $C_6H_7N^{2+}$ as well as $C_6H_5N^{2+}$ fragment ions via dissociative ionization. The choice of these particular compounds in our first approach to nitrogen-containing arene dications was motivated by the previous detailed studies about the energetics, structures, and reactivities of the corresponding all-carbon analogs $C_7H_6^{2+}$ and $C_7H_8^{2+}$ generated upon double ionization of toluene.[8−10]

CHART 1: Structures of the Neutral Precursor Compounds Used in This Work



Experimental Details

Most of the reactivity studies were performed with a TSQ Classic mass spectrometer[10,11] 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 with electrons having 70 eV kinetic energy. 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 that 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 under quasi-thermal conditions or

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[†] Part of the special section "Chemistry: Titan Atmosphere".
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10.1021/jp904859g CCC: $40.75

collision-induced dissociation (CID) at elevated kinetic energies. We performed the ion/molecule reactions of the $C_mH_nN^{2+}$ dications described below by mass-selecting the ions of interest with the first quadrupole (Q1) at a mass resolution fully sufficient to select the corresponding dications. It is pointed out that within the limits of our instrumentation we could not further cool the $C_mH_nN^{2+}$ dications produced via EI. The mass-selected dications were then reacted with neutral methane admitted to the octopole at a typical pressure of 10^{-4} mbar. We adjusted the collision energy by changing the offset between the first quadrupole and the octopole, whereas the offset of Q2 was locked to the sum of the offsets of Q1 and O relative to the source. 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 dications reported here, the beam width at half-maximum was 2.0 ± 0.2 eV in the laboratory frame. The bimolecular reactions reported below were recorded at an ion kinetic energy that corresponds to the point of inflection of the curve obtained by retarding-potential analysis. Because of the kinetic energy distribution of the ions emerging from the source, we refer to this value as a nominal collision energy of 0 eV. 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 Daly-type detector operated in the counting mode. Typically, about 100 scans were accumulated, resulting in an average scan time of 5 min per spectrum.

The photoionization experiments were performed with the CERISES apparatus,[12,13] which was installed on the DESIRS beamline of the synchrotron radiation source SOLEIL (France). This beamline provides monochromatic photons in the range of 5−40 eV by using three different gratings. In the present experiments, the resolution was set to $E/\Delta E = 500$ in the photon-energy range from 20 to 28 eV, that is, ca. 50 meV at $E(\text{photon}) = 25$ eV. We calibrated the photon energy by measuring the ionization energy of argon with an accuracy better than ±10 meV. Samples were introduced via a gas inlet and ionized by photons, and the so-formed dications were extracted by a field of 1 V/cm toward a QOOQ system (Q stands for quadrupole and O for octopole). The photon energy was scanned in steps of 50 meV. Q2 was used to mass-select the ions of interest, whereas Q1, O1, and O2 just served as ion guides. Ions were detected by a multichannel plate operating in the counting mode. During the measurements of the ion yields, electron yields were also simultaneously recorded as well as photon fluxes, which were monitored by photoemission currents from a gold grid. The electron yield helps in monitoring and hence correcting for eventual fluctuations of the pressure in the source. The raw data for the measured ion yields were corrected for the photon flux of the beamline as a function of photon energy.

Results and Discussion

Photoionization Studies. Among much more intense monocations, EI of 4-picoline affords the molecular dication $[M]^{2+}$ ($C_6H_7N^{2+}$, *m/z* 46.5) as well as the dehydrogenated dication $[M\text{-}H_2]^{2+}$ ($C_6H_5N^{2+}$, *m/z* 45.5) in a ca. 1:4 ratio for EI with 70 eV electrons. To achieve further insight into the dication energetics, we determined the threshold for double photoionization using synchrotron radiation. As detailed elsewhere for the case of the toluene dication, an accurate analysis of the double ionization energy (^2IE) requires an explicit consideration of the associated Franck−Condon envelope.[14,15] Because this kind of analysis is a demanding effort and likewise so far limited to the consideration of harmonic frequencies, we have introduced a simplified method for the determination of ^2IE via an empirical fit of the dication yield according to the Wannier law for double photoionization with ^2IE of the molecular ions derived from the first derivative of the photoionization efficiency. (See insets a and b in Figure 1 as an example.)[16,17] The appearance energy of the $[M\text{-}H_2]^{2+}$ fragment due to dissociative double ionization is given for the first point above the noise level, where we employ a conservative error estimate of ±0.2 eV.

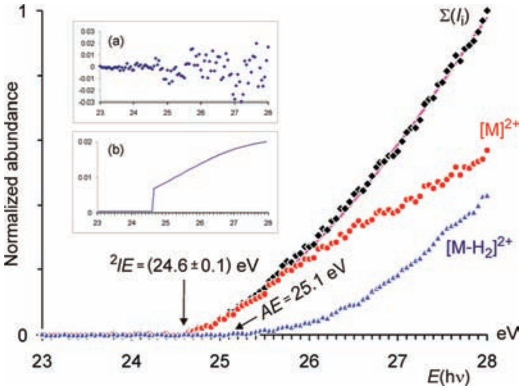

Figure 1. Photoionization threshold for the double ionization of 4-picoline with synchrotron photons from 23−28 eV to afford the molecular dication ($[M]^{2+}$, ●) and the dehydrogenated dication ($[M\text{-}H_2]^{2+}$, ▲) as well as the sum of $[M]^{2+}$ and $[M\text{-}H_2]^{2+}$ (◆). The solid purple line is the Wannier fit of the dication threshold from which ^2IE is derived. Inset a shows the deviation of the fit from the sum of ions, and inset b shows the derivative of the Wannier fit used for the determination of the second ionization threshold.

Figure 1 shows the yields of the dications $[M]^{2+}$ and $[M\text{-}H_2]^{2+}$ for 4-picoline in the photon-energy range from 23 to 28 eV. The best fit using the Wannier law yields $^2IE(\text{4-picoline}) = (24.6 \pm 0.1)$ eV for the molecular dication and a phenomenological appearance energy of $AE(C_6H_5N^{2+}) = (25.1 \pm 0.2)$ eV for dissociative double photoionization. In conjunction with the first ionization energy $IE(\text{4-picoline}) = (9.04 \pm 0.03)$ eV,[18,19] for the molecular ion of 4-picoline, this implies $IE(\text{4-picoline}^+) = (15.6 \pm 0.1)$ eV. In comparison with toluene,[14] we note that all values are somewhat larger than those for the corresponding all-carbon compound, that is, $IE(\text{toluene}) = (8.828 \pm 0.001)$ eV, $IE(\text{toluene}^+) = (14.8 \pm 0.1)$ eV, and $^2IE(\text{toluene}) = (23.81 \pm 0.06)$ eV. To a first approximation, the increased ionization energies of the *N*-heterocyclic compound can be attributed to the electronegative nitrogen atom embedded in the aromatic skeleton, which lowers the HOMO energies.[20] We explicitly note, however, that a more elaborate analysis of the photoionization threshold of the C_6H_7N isomers studied in this work will require further theoretical studies because the singlet/triplet splitting of the dication states and the associated Franck−Condon effects may have a considerable effect in the ionization threshold and thereby influence the apparent threshold.[14] Above a photon energy of about 26 eV, the $[M\text{-}H_2]^{2+}$ fragment due to dissociative photoionization with maintenance of the two-fold charge makes a considerable contribution to the double photoionization cross section of 4-picoline, which indicates that the dehydrogenation is thermochemically as well as kinetically facile.

In marked contrast with 4-picoline, the ratio of the molecular dication $[M]^{2+}$ and the dehydrogenated dication $[M\text{-}H_2]^{2+}$ is inverted to ca. 3:1 upon EI (70 eV) of the isomeric 2-picoline; dehydrogenation is obviously more hindered for this isomer. This qualitative observation from the EI mass spectra finds quantitative support from the photoionization data in that the $[M\text{-}H_2]^{2+}$ fragment is much less intense in the entire range of

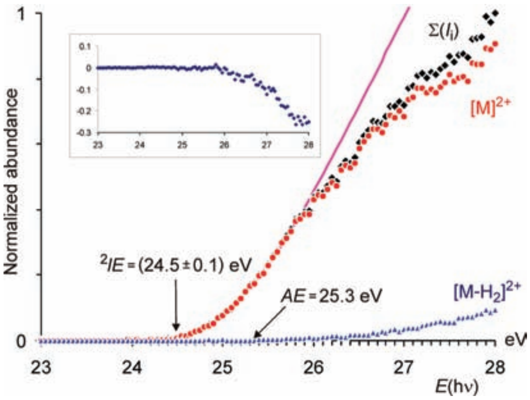

Figure 2. Photoionization threshold for the double ionization of 2-picoline with synchrotron photons from 23−28 eV to afford the molecular dication ($[M]^{2+}$, ●) and the dehydrogenated dication ($[M\text{-}H_2]^{2+}$, ▲) as well as the sum of $[M]^{2+}$ and $[M\text{-}H_2]^{2+}$ (◆). The solid purple line is the Wannier fit of the dication threshold from which ^2IE is derived; the inset shows the deviation of the fit from the sum of ions.

photon energies studied (Figure 2). However, the derived double ionization energy ^2IE(2-picoline) = (24.5 ± 0.1) eV is almost identical to that of 4-picoline, and $AE(C_6H_5N^{2+})$ = (25.3 ± 0.2) eV is also quite close to the corresponding value for 4-picoline. These observations point to a considerable kinetic hindrance of the dehydrogenation channel in the case of 2-picoline, which can be due to either an entropically particularly demanding transition structure or competing processes. Indirect evidence of the latter comes from the metastable-ion studies discussed further below and the deviation of the Wannier fit (purple line in Figure 2) from the sum of dication signals. Whereas one may well argue that the Wannier law is not valid across such an extended energy range, the Wannier fits for 4-picoline (Figure 1) as well as aniline (see below) span more than 3 eV, whereas in Figure 2, the deviation already occurs at about 1.5 eV above threshold. Therefore, we propose that the deviation in the case of 2-picoline is due to competing charge-separation processes that lead to pairs of monocations. In our photoionization experiment, these singly charged fragment ions cannot be monitored separately because in the range of photon energies employed, large amounts of these monocations are produced by dissociative single ionization of the neutral arenes. In conjunction with IE(2-picoline) = (9.02 ± 0.03) eV,[18,19] from ^2IE(2-picoline) = (24.5 ± 0.1) eV, we can further derive $IE(\text{2-picoline}^+)$ = (15.5 ± 0.1) eV, which is again significantly larger than in the case of toluene.

In contrast with the picolines, aniline bears the heteroatom outside of the ring. Therefore, unlike the σ-electron-withdrawing character of nitrogen within the ring, the exocyclic amino group can act as a π donor. This substituent effect is already reflected in the first ionization energy of aniline IE(aniline) = (7.720 ± 0.002) eV,[18] which is about 1.5 eV lower than that of the parent compound benzene (9.24378 ± 0.00007 eV).[18] It is therefore not surprising that with ^2IE(aniline) = (21.9 ± 0.1) eV, the threshold for double ionization of aniline (Figure 3) is also substantially lower than that for the picolines. Accordingly, $IE(\text{aniline}^+)$ = (14.2 ± 0.1) eV is derived, which is significantly lower than $IE(\text{phenol}^+)$ = (14.75 ± 0.3) eV[21] and $IE(\text{benzene}^+)$ = (15.35 ± 0.1) eV,[22] as is expected from the general trends of substituent effects in arenes. The loss of either atomic or molecular hydrogen from the aniline dication does not occur to a significant extent in the photon-energy range investigated, whereas the EI (70 eV) mass spectrum of aniline shows a $[M\text{-}H_2]^{2+}$ signal in a ratio of ca. 1:3 relative to the molecular dication $[M]^{2+}$.

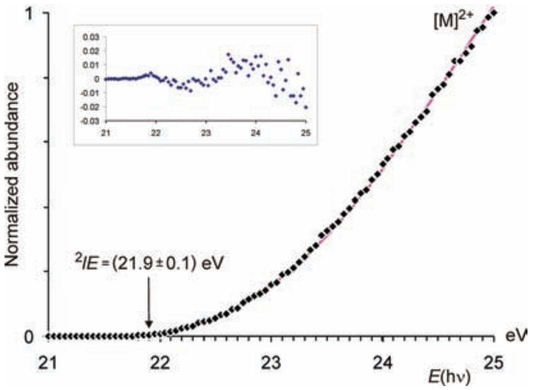

Figure 3. Photoionization threshold for the double ionization of aniline with synchrotron photons from 21−25 eV to afford the molecular dication ($[M]^{2+}$, ◆). The solid purple line is the Wannier fit of the dication threshold from which ^2IE is derived; the inset shows the deviation of the fit from the sum of ions.

Unimolecular Dissociations of the $C_6H_nN^{2+}$ Dications. Before addressing the bimolecular reactions of these $C_6H_nN^{2+}$ dications (n = 5, 7) with methane, the ions are characterized by their unimolecular dissociation reactions. To this end, the dications generated via EI in the ion source were mass-selected and guided through the octopole at a nominal collision energy of 0 eV to realize a maximal residence time in the octopole, thereby allowing most of the metastable ions to dissociate; for the $C_6H_nN^{2+}$ species studied here, contributions from CID are negligible under these conditions.[5,17,23] In addition to the unimolecular loss of H_2 from the metastable dications (reaction 2), a series of charge-separation channels are observed (reactions 3−7). We note in passing that sequential losses of two hydrogen atoms, rather than molecular hydrogen, appear very unlikely for two reasons. At first, the AEs determined above for the doubly charged dehydrogenation products lie only slightly above the second ionization energies of the neutral precursors, whereas sequential bond homolysis concomitant with expulsion of H atoms will require several electronvolts. Second, whereas losses of atomic hydrogen have indeed been observed for hydrocarbon dications $C_mH_n^{2+}$,[8,16,24] their abundances follow an odd/even electron pattern.[25,26] Sequential H-atom losses are therefore unlikely to take place without detection of the intermediates $C_mH_{n-1}^{2+}$, and the corresponding $C_6H_{n-1}N^{2+}$ were not observed in our PI experiments with the nitrogen analogs.

$$C_6H_nN^{2+} \rightarrow C_6H_{n-2}N^{2+} + H_2 \tag{2}$$

$$C_6H_nN^{2+} \rightarrow C_5H_{n-3}N^+ + CH_3^+ \tag{3}$$

$$C_6H_nN^{2+} \rightarrow C_4H_{n-3}N^+ + C_2H_3^+ \tag{4a}$$

$$\rightarrow C_5H_{n-1}^+ + HCN^+ \tag{4b}$$

$$C_6H_nN^{2+} \rightarrow C_4H_{n-4}N^+ + C_2H_4^+ \tag{5a}$$

$$\rightarrow C_5H_{n-2}^+ + HCNH^+ \tag{5b}$$

$$C_6H_nN^{2+} \rightarrow C_3H_{n-3}N^+ + C_3H_3^+ \tag{6}$$

$$C_6H_nN^{2+} \rightarrow C_4H_{n-4}^+ + C_2H_4N^+ \tag{7}$$

In the case of reactions 4a and 5a, without additional labeling data or high-resolution MS/MS experiments we cannot assign

TABLE 1: Species Lost upon Unimolecular Dissociation of Mass-Selected, Metastable $C_6H_nN^{2+}$ Dications ($n = 5, 7$) from Different Precursors[a,b]

precursor	2-picoline		4-picoline		aniline	
	$C_6H_5N^{2+}$ *m/z* 45.5	$C_6H_7N^{2+}$ *m/z* 46.5	$C_6H_5N^{2+}$ *m/z* 45.5	$C_6H_7N^{2+}$ *m/z* 46.5	$C_6H_5N^{2+}$ *m/z* 45.5	$C_6H_7N^{2+}$ *m/z* 46.5
x_{MI}[c]	0.015	0.024	0.013	0.035	0.015	0.016
$-H_2$	27	8	5	20	25	30
$-H^+$	15	7	20	10	10	20
$-CH_3^+$	6	30	1	9	8	12
$-NH_4^+$						10
$-HCN^+$/ $-C_2H_3^+$	22	37	5	12	1	5
$-CH_2N^+$/ $-C_2H_4^+$	28	13	68	45	50	8
$-C_3H_3^+$		3		3	6	15
$-C_2H_4N^+$	2	2	1	1		

[a] Branching ratios normalized to $\Sigma = 100$. [b] Because of mass-discrimination effects in charge-separation reactions,[5,17,23,28] only the abundances of the heavier ions were analyzed, whereas the corresponding lighter fragments ions were also observed experimentally. [c] Metastable fraction of the mass-selected ion beam (the rest is the intact parent ion).

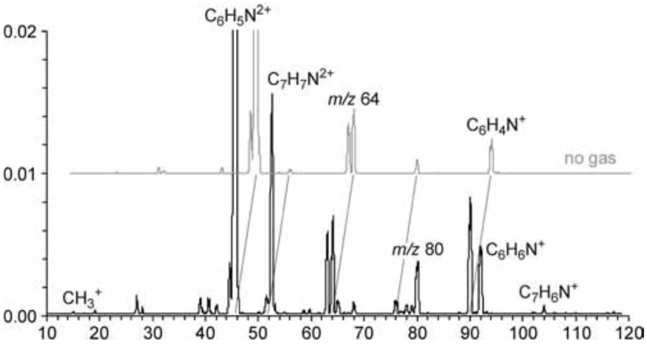

Figure 4. Reaction of the mass-selected $C_6H_5N^{2+}$ dication generated by dissociative electron ionization of 2-picoline with 0.16 μbar methane at a nominal collision energy of 0 eV. In the same scaling, but with shifts upward and to the right, the gray trace in the background shows the unimolecular dissociation pattern $C_6H_5N^{2+}$ in the absence of methane.

the elemental composition of the pair of ions formed. As a rough guideline, however, the even-electron rule[26] implies a preference for reaction 4a over 4b and 5b over 5a, respectively, because reactions 4a and 5b can yield closed-shell ions, whereas reactions 4b and 5a afford pairs of radical ions. The formation of protonated hydrocyanic acid in reaction 5b is also implied by the high proton affinity of HCN; accordingly, the connectivity $HCNH^+$ appears to be most plausible for the ionic species formed. Furthermore, monocation signals due to formal loss of a free proton (reaction 8) are observed for all dications under study, which may well be due to a unimolecular expulsion of H^+;[27] but is certainly also due to traces of water being present in the background of the mass spectrometer (reaction 9), which is evidenced by the observation of the complementary signal due to H_3O^+ in the low-mass range.

$$C_6H_nN^{2+} \rightarrow C_6H_{n-1}N^+ + H^+ \qquad (8)$$

$$C_6H_nN^{2+} + H_2O \rightarrow C_6H_{n-1}N^+ + H_3O^+ \qquad (9)$$

Notwithstanding the uncertainties in the assignment of the formula of the ionic fragments, the data in Table 1 demonstrate that unlike many hydrocarbon dications,[8,25,27] the $C_6H_nN^{2+}$ ions made from the precursors shown in Chart 1 are all well distinguished from each other. In other words, the precursor structures do indeed matter for the heteroatom-containing hydrocarbon dications.

Most indicative for the differentiation of the isomeric ions is the ratio of the losses of $C_2H_3^+$ (reaction 4a) and $HCNH^+$ (reaction 5b), in that the former channel is much more preferred for both $C_6H_nN^{2+}$ ions generated from 2-picoline compared with the isomeric 4-picoline. For the molecular dications of 2- and 4-picoline, for example, the ratios of the corresponding fragments at *m/z* 65 and 66 change from ca. 1:3 in the case of 2-picoline to ca. 4:1 for 4-picoline. Also notable is the significant amount of methyl cation lost from the molecular dication of 2-picoline, which may be seen as an indication that the methyl group stays intact in the dication rather than being involved in hydrogen rearrangements, as is the case for the toluene dication.[8] In comparison, the amount of CH_3^+ expulsion from doubly ionized 4-picoline is much lower. Furthermore and fully consistent with the photoionization data, the absolute efficiency for the loss of neutral dihydrogen to afford $C_6H_5N^{2+}$ is most pronounced for the dication of 4-picoline. The aniline dication can clearly be distinguished from the two other $C_6H_7N^{2+}$ by a characteristic loss of ammonium ion; also, the rest of the fragmentation pattern is different from the picoline dications. The same holds true for the $C_6H_5N^{2+}$ dication generated from aniline, whose ca. 50:1 ratio of the fragments at *m/z* 63 and 64 very much differs from the dehydrogenation products of the picoline dications. We hence conclude that the dications emerging from the various precursors bear different structures and do not (fully) interconvert into a common mixture of isomers during the time-of-flight from the ion source to the octopole ion guide. As far as dication structures are concerned, however, no direct conclusions based on the precursors can be drawn because the dications formed may indeed bear very different structures.[8,9b]

Bimolecular Reactions of the $C_6H_nN^{2+}$ Dications with Methane. After having characterized the energetics and the unimolecular dissociations of these selected C,H,N-dications, we can address their reactivity toward methane. To this end, the mass-selected dications generated via EI were allowed to react with methane at a nominal collision energy of $E_{CM} = 0$ eV. Specifically, the octopole potential was set to the point of inflection obtained in a retarding-potential analysis scan of the dication signals, which reveals a kinetic energy width of ca. 2.0 eV in the laboratory frame (ca. 0.3 eV in the center-of-mass frame). We have previously demonstrated that under such conditions thermal ion reactivity can be assessed reasonably well.[29] Note, however, that the incident dications produced upon EI can by no means be considered to be equilibrated to ambient conditions. Therefore, the branching ratios and rate constants derived should primarily be considered as a guidance for the assessment of the relative reactivities of the dications under study.

Figure 4 shows the reaction of the $C_6H_5N^{2+}$ dication generated via dissociative EI of 2-picoline as an example. In comparison with the metastable ion decay (gray trace in Figure 4), the presence of methane gives rise to several processes in which new bonds are formed. Most interesting with respect to possible relevance for chemical processes in the atmosphere of Titan are the dehydrogenation reactions 10 and 11 under the maintenance of the two-fold charge; reaction 11 gives rise to the small signal left to the $C_7H_7N^{2+}$ peak in Figure 4. Another new feature in the presence of methane is a monocation at *m/z* 80, which can be due to either reaction 12a or reaction 12b, which yield isobaric pairs of ions. By analogy to the arguments raised above in the context of reactions 4a, 4b, 5a, and 5b, the occurrence of reaction 12b appears to be more likely because only closed-shell cations can be formed. Accordingly, the ion with *m*/*z* 80 most likely corresponds to protonated pyridine. Reactions 13 and 14 do not involve the formation of new C−C or C−N bonds but just represent proton transfer from the dication (reaction 13) and hydride transfer from methane to $C_6H_5N^{2+}$ (reaction 14).[30] With respect to the possible growth of C,H,N species in the atmosphere of Titan, reactions 13 and 14 in fact represent sinks as they deplete the population of the reactive dications in favor of nonreactive monocations. We further note in passing that single-electron transfer from methane to the dication does not occur to any significant extent, as demonstrated by the absence of a peak due to $C_6H_5N^+$, *m*/*z* 91, in Figure 4. Although single-electron transfer putatively is exothermic ($IE(CH_4) = 12.61$ eV),[18] like in most bimolecular reactions of dications,[6] a Coulomb barrier suppresses this channel when other pathways are available.

$$C_6H_5N^{2+} + CH_4 \rightarrow C_7H_7N^{2+} + H_2 \qquad (10)$$

$$C_6H_5N^{2+} + CH_4 \rightarrow C_7H_5N^{2+} + 2H_2 \qquad (11)$$

$$C_6H_5N^{2+} + CH_4 \rightarrow C_6H_8^+ + HCN^+ \qquad (12a)$$

$$\rightarrow C_5H_6N^+ + C_2H_3^+ \qquad (12b)$$

$$C_6H_5N^{2+} + CH_4 \rightarrow C_6H_4N^+ + CH_5^+ \qquad (13)$$

$$C_6H_5N^{2+} + CH_4 \rightarrow C_6H_6N^+ + CH_3^+ \qquad (14)$$

$$C_7H_7N^{2+} + CH_4 \rightarrow C_7H_6N^+ + CH_5^+ \qquad (15)$$

Using the well-established rate constant of 1.14×10^{-9} cm^3 s^{-1} for the reaction of N_2^+ with CH_4 as an internal reference[31] for the overall reaction of methane with the $C_6H_5N^{2+}$ dication made from 2-picoline, a rate constant of $k_{\Sigma(10-14)} = (1.7 \pm 0.5) \times 10^{-10}$ cm^3 s^{-1} is obtained, which corresponds to ca. 8% of the gas-kinetic collision rate of the $C_6H_5N^{2+}$ dication with methane. Furthermore, a weak signal at *m*/*z* 104 is observed, which is assigned as the secondary reaction 15 of the $C_7H_7N^{2+}$ dication formed in reaction 10. Whereas all other dications investigated in this preliminary essay, that is, the $C_6H_5N^{2+}$ ions derived from 4-picoline and aniline, respectively, and the molecular dications of 2- and 4-picoline as well as aniline, undergo similar reactions, the proton and hydride transfer channels predominate for these $C_6H_nN^{2+}$ ions, and the overall rate constants are lower. Consequently, the C−C coupling processes are much less efficient for these ions than in the case of the $C_6H_5N^{2+}$ dication made from 2-picoline (Table 2).

Reactive Monitoring Using Synchrotron Radiation. Prior to a brief discussion of these preliminary results in the context of their possible relevance for the chemistry in the atmosphere of Titan, a key concern arises from the ionization method. Specifically, EI is a very efficient means for generating cationic species in a mass spectrometer, but because the energy of the ionizing electrons very much exceeds the ionization thresholds, the ions formed can contain substantial amounts of internal energy, also including the formation of high-lying, quasi-isolated electronic states.[32] Given the condition that multipole-based studies of ion/molecule reactions are best conducted in the single-collision regime and thus the resulting overall conversion of the reactant ion is low,[33] a small percentage of excited species may already dominate the observed reactivity if these ions react much faster than the ground-state species.

TABLE 2: Summary of the Products Formed in the Reactions of Methane with Mass-Selected $C_6H_nN^{2+}$ Dications ($n = 5, 7$) from Different Precursors[a,b,c]

precursor	2-picoline		4-picoline		aniline	
	$C_6H_5N^{2+}$ *m*/*z* 45.5	$C_6H_7N^{2+}$ *m*/*z* 46.5	$C_6H_5N^{2+}$ *m*/*z* 45.5	$C_6H_7N^{2+}$ *m*/*z* 46.5	$C_6H_5N^{2+}$ *m*/*z* 45.5	$C_6H_7N^{2+}$ *m*/*z* 46.5
k_Σ[d]	1.7	0.6	0.6	0.2	1.0	0.1
$-H_2$	50	33	25	20	20	10
$-2H_2$	3	5	7	2	2	4
$-C_2H_3^+$	12		8		20	1
$-CH_5^+$	20	40	45	24	54	75
$-CH_3^+$	15	22	15	54	4	10
$\phi_{CC,rel}$[e]	1.00	0.27	0.21	0.06	0.25	0.02

[a] Branching ratios (BR) normalized to $\Sigma = 100$. [b] Because of mass-discrimination effects in charge-separation reactions, only the abundances of the heavier ions were analyzed, whereas the corresponding lighter fragment ions were also observed experimentally. [c] Fragments due to metastable dications were subtracted prior to analysis; several small product (BR < 5) were neglected. [d] Given in 10^{-10} cm^3 s^{-1}. [e] Relative efficiency of the C−C coupling defined as $\phi_{CC,rel} = k_{i,max}[BR(-H_2) + BR(-2H_2)]/100$.

To clarify this point of outmost importance for the chemistry in extraterrestrial atmospheres or interstellar media, we applied reactive monitoring using synchrotron radiation.[34] To this end, suitable neutral precursors are admitted to the ion source of a multipole mass spectrometer[13] ionized by vacuum-ultraviolet photons; the ions of interest, here $C_6H_5N^{2+}$ from either 2- or 4-picoline, are mass-selected and transferred to an octopole collision cell in which they are allowed to react with methane under single collision conditions (nominal collision energy 0.35 eV in the laboratory frame), and the dicationic C−C coupling product $C_7H_7N^{2+}$ formed according to reaction 10 is then monitored using a second mass filter. Whereas all conditions are otherwise kept constant, the photon energy is varied from below the threshold of the reactant ion to a few electronvolts higher (Figure 5a). Because of extremely low ion currents in the present experiments, both due to the low abundances of the precursor dications and their moderate tendency for C−C coupling, the photon energy could not be scanned continuously but was instead varied in steps of 0.5 eV to achieve increased time for signal averaging. Whereas the corresponding experimental data obtained have low counting rates, Figure 5b,c demonstrates that within the experimental error, the apparent onsets of the coupling products are identical to those of the corresponding $C_6H_5N^{2+}$ precursor dications. If instead only a high-lying excited state or isomer would be responsible for reaction 10, then the threshold would accordingly be delayed, which is not the case within the energy resolution of the monitoring experiment (0.5 eV). We thus conclude that the growth of the $C_6H_5N^{2+}$ species in the presence of methane is a genuine process of the electronic ground states of the dications. Therefore, these coupling reactions may also occur under conditions such as those in the atmosphere of Titan, provided that the dications are formed at all.

Implications for the Chemistry of the Atmosphere of Titan. Finally, let us briefly address the results in the context of the Titan atmosphere. Provided that any double ionization events can take place in this environment, several comparisons between the pure hydrocarbon dications and the $C_6H_nN^{2+}$ congeners with respect to their putative coupling reactions with methane can be made. At first, the ionization energies of the two picolines studied in this work are significantly larger than

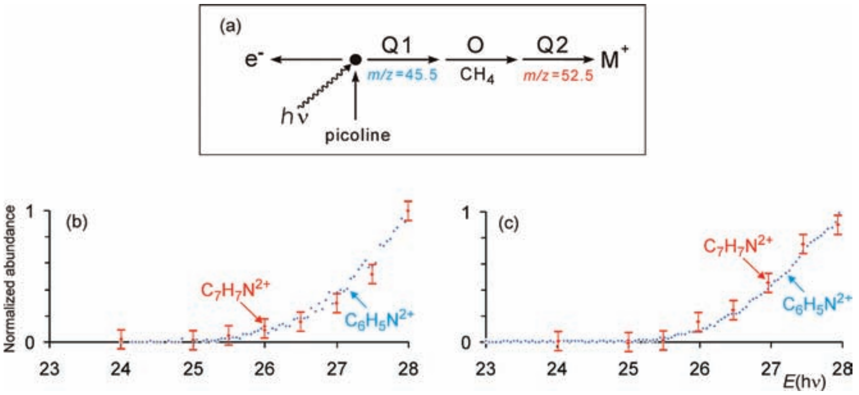

Figure 5. (a) Schematic illustration of reactive monitoring using synchrotron radiation and a tandem mass spectrometer: The photons (*hν*) ionize neutral picoline, the precursor cation $C_6H_5N^{2+}$ (*m/z* 45.5) is mass-selected by means of the quadrupole analyzer Q1 and allowed to react with methane in the octopole, and the product is mass-selected using Q2 and detected. (b,c) Abundances of the precursor dications $C_6H_5N^{2+}$ (♦) and of the resulting C−C coupling products $C_7H_7N^{2+}$ (●) for (b) 2-picoline as the neutral precursor and (c) 4-picoline as the neutral precursor in single-ion monitoring as a function of the energy of the ionizing photons (in electronvolts).

that of toluene as the all-carbon analogue. Considering that nitrogen, as the major component of Titan's atmosphere, sets a harsh cutoff at $IE(N_2) = 15.581$ eV[18] to energetic photons penetrating the moon's atmosphere, the derived values of $IE(\text{2-picoline}^+) = (15.5 \pm 0.1)$ and $IE(\text{4-picoline}^+) = (15.6 \pm 0.1)$ eV indicate that these particular dications are unlikely to be formed because only a very narrow window of photon energies can master this task. In contrast, $IE(\text{toluene}^+) = (14.8 \pm 0.1)$ eV lies significantly lower. Aniline with a nitrogen-containing substituent outside of the ring has a significantly lower threshold, $IE(\text{aniline}^+) = (14.2 \pm 0.1)$ eV, but at least the molecular dication reacts only very sluggishly with methane (Table 2). Second, the dications of C,H,N compounds suffer from a decreased stability with respect to charge-separation reactions not only because the *N*-heterocyclic dications are less stable but also because the neutral counterparts are usually strong bases with considerable proton affinities, such that the resulting monocations are more stable than their all-carbon analogs. This aspect is indeed reflected in the significance of proton and hydride transfers in the reactions of the $C_6H_nN^{2+}$ dications with methane (Table 2). Future work on larger $C_mH_nN^{2+}$ dications will have to show if these two disadvantages can be overcome and species can be found that undergo more efficient coupling reactions with methane.

Conclusions

In this work, we extend previous experimental and theoretical studies on the growth of hydrocarbon dications in the presence of methane to $C_6H_nN^{2+}$ species ($n = 5, 7$) as the first nitrogen-containing dications. These species do indeed undergo coupling reactions with methane under the maintenance of the two-fold charge. Whereas the occurrence of the coupling reactions may be regarded as a proof of principle, it is quite obvious that this work is only a first step toward a more complete understanding of the chemistry of C,H,N dications and their possible role in the formation of more complex molecules under extreme conditions. Specifically, the set of compounds has to be extended; moreover, the electronic states of nitrogen-containing arene dications and the structures of the gaseous ions, both precursors and products, need to be addressed in future work. Last but not least, the observation that the reactivities of the $C_6H_nN^{2+}$ ions depend on the structures of the precursor compounds indicates that in attempts to kinetically model the ion chemistry of interstellar media or ionospheres, the mere consideration of the gross formula may be insufficient, and isomer-specific contributions need to be included instead.

Acknowledgment. This work was supported by a L'Oreal "For Women in Science" stipend for J.R. Further support was provided by the Czech Academy of Sciences (Z40550506), the Grant Agency of the Czech Republic (203/09/1223), and the Ministry of Education of the Czech Republic (MSM0021620857, RP MSMT 14/63). The access to the European Multiuser facility SOLEIL was enabled in the framework of the TNA Scheme of the European Commission. D.A., C.A., and D.S. thank SOLEIL for allocation of beam time (proposal 20080481), the team of the beamline DESIRS for kind assistance during the synchrotron measurements, and M. Elhanine and B. Miranda for their help in the preparation of the CERISES setup.

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JP904859G