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Ni^+ Reactions with Aminoacrylonitrile, A Species of Potential Astrochemical Relevance

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The reaction of aminoacrylonitrile, a species of astrochemical interest, with $Ni^+(^2D_{5/2})$ was investigated by means of mass spectrometry techniques and density functional theory calculations. The dominant fragmentations in the MIKE spectrum correspond to the loss of $[C_2,N,H_3]$, HCN, and NH_3, the loss of H_2 being very minor. The structure and bonding of the different aminoacrylonitrile$-Ni^+$ complexes were investigated at the B3LYP/6-311G(d,p) level of theory. The same approach was employed in our survey of the corresponding potential energy surface. This survey indicates that the $[C_2,N,H_3]$ neutral product can be formed either as ketenimine ($CH_2{=}C{=}NH$) or acetonitrile. The formation of the latter is significantly more exothermic but involves slightly higher activation barriers; so very likely, both isomers are produced along the reaction process. The lost of HNC is not competitive with the loss of HCN, because when the former is formed the products lie higher in energy and the corresponding mechanisms involve energy barriers above the entrance channel. The loss of NH_3 is associated with the formation of a complex between cyanoacetylene, $HC{\equiv}C{-}CN$, which is very abundant in the interstellar media, and Ni^+.

Introduction

Various saturated or alkynylnitriles have been observed in the interstellar medium (ISM), in comets or in the atmosphere of Titan, the largest moon of Saturn. Aminoacetonitrile has been recently detected in the ISM.[1] Acrylonitrile derivatives are potentially important species in interstellar chemistry as well as in planet atmosphere chemistry. Among other things these latter are supposed to be good starting materials for the formation of more complex astrochemical species[2] or building blocks of life on the primitive Earth.[3,4] In spite of their relevance in astrochemistry very little is known on their chemistry, and only very recently, an investigation on the gas-phase basicity and acidity of aminoacrylonitrile and crotononitrile, probably the most relevant ones in the interstellar space or in the planet atmospheres, was reported in the literature.[5]

Aminoacrylonitrile (3-amino-2-propenenitrile: $H_2N{-}CH{=}CH{-}CN$) is particularly interesting because it can be easily formed by reaction of cyanoacetylene ($HC{\equiv}C{-}C{\equiv}N$)[6,7] with ammonia,[8−10] two abundant species in these media. As well as aminoacetonitrile is a potential precursor of glycine, aminoacrylonitrile is a potential precursor on the primitive Earth of two amino acids, asparagine and aspartic acid.[11] However, the investigation of the intrinsic reactivity of aminoacrylonitrile is not only of interest in interstellar or space chemistry but also from a more fundamental point of view. The introduction of a cyano group alters significantly the physical and chemical properties of the unsubstituted compound, vinylamine ($H_2C{=}CH{-}NH_2$), from which it derives. Actually, aminoacrylonitrile is a robust and kinetically a quite stable compound, whereas vinylamine is unstable at −80 °C in the condensed phase, and it decomposes in the presence of several reactants. At the same time, aminoacrylonitrile is a much stronger acid than vinylamine, because the presence of the cyano group preferentially stabilizes the deprotonated anion. Also, the presence of the cyano group modifies its behavior as a base, because in aminoacrylonitrile the basic site is the cyano group rather than the amino group.[5]

Up to now, aminoacrylonitrile has never been observed in the ISM, but its microwave and infrared spectra have been only recently recorded.[9,10] No barrierless gas-phase synthesis of this compound has been found[10] nor for the recently detected aminoacetonitrile. Interestingly, a synthesis on icy grain mantles has recently been proposed[12] based on density functional theory (DFT) calculations. This theoretical approach is consistent with previously reported experiments.[13] It is usually accepted that the formation of interstellar molecules occurs in the gas phase by reaction between molecules smaller than the formed compound or of a comparable size in atoms. However a rich chemistry is probably also performed on the grains, but the subsequent vaporization of the formed adducts remains difficult. The formation of molecules on grains under UV irradiation and then the breaking in smaller ones associated to the vaporization of one of them could be envisaged to explain the presence or the abundance of several compounds in these media.

The aim of this paper is to investigate the intrinsic reactivity of aminoacrylonitrile with respect to Ni^+. Although this transition metal is not among the most abundant in the ISM, we have chosen it because it can be a good model to investigate the specific interactions with open-shell transition metal ions and because lately we have paid particular attention to reactions involving this metal ion.[14−17] The interactions between relatively

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small molecules and metal cations may take place on the surface of dust particles or meteorites but also in the gas phase. Hence, the study of the unimolecular reactivity of aminoacrylonitrile−Ni^+ adducts provides important clues on the most favorable reactions occurring between these kind of derivatives and metal cations. In particular, the high abundance of hydrogen isocyanide (HNC) in dense interstellar clouds relative to its more stable isomer hydrogen cyanide (HCN) has been a subject that intrigued the scientists for long time;[18,19] hence it is of special relevance to investigate, in this example, whether HCN or HNC are produced in these reactions and which one is the dominant product.

Experimental Section

The synthesis of aminoacrylonitrile was performed as previously reported.[20]

All experiments were carried out using a VG Analytical ZAB-HSQ hybrid mass spectrometer of BEqQ geometry, which has been described in detail previously.[21] Complexes were generated by the CI-FAB method.[22−27] The CI-FAB source was constructed from VG Analytical EI/CI and FAB ion source parts with the same modifications described by Freas et al.[22] The conventional FAB probe tip has been replaced by a nickel foil of high purity. "Naked" metal ions were generated by bombardment with fast xenon atoms (Xe gas 7−8 keV kinetic energy, 1−2 mA of emission current in the FAB gun). The organic samples were introduced via a probe in a nonheated source. We can assume that due to the relatively high pressure in that source (10^2−10^3 Pa) efficient collisional cooling of the generated ions takes place. Therefore we will consider that excited states of the Ni^+ ions that could be formed in these experimental conditions are not likely to participate in the observed reactivity as already postulated by Hornung et al.[26] The ion beam of the Ni^+ adduct complexes formed with aminoacrylonitrile were mass selected (using an acceleration voltage of 8 kV) with the magnetic analyzer B. The ionic products of unimolecular fragmentations, occurring in the second field-free (second FFR) region following the magnet, were analyzed by means of mass-analyzed ion kinetic energy (MIKE)[28,29] by scanning the electric sector E.

The collision activated dissociation experiments were carried out in the same fashion but with the introduction of argon in the cell as the collision gas. The pressure of argon in the collision cell was adjusted so that the main beam signal was reduced by approximately 30%. The spectra were recorded at a resolving power (R) of ∼1000.

Computational Details

Standard DFT calculations have been carried out to optimize the geometries and to obtain the final energies of the different stationary points of the aminoacrylonitrile−Ni^+ potential energy surface (PES). The hybrid B3LYP functional, as implemented in the Gaussian03 series of programs,[30] has been chosen for this purpose due to its good performance in the description of the interactions between transition metal ions and neutral molecules. For geometry optimizations we have employed the all-electron basis (14s9p5d/9s5p3d) of Wachters[31] and Hay[32] augmented by a set of *f* functions for Ni and the 6-311G** basis set for remaining atoms of the system. Harmonic vibrational frequencies were evaluated at the same level of theory in order to classify the stationary points of the PES as local minima or transition states and to evaluate the corresponding zero-point energies (ZPE), which were scaled by the empirical factor 0.9806.[33] Since Ni^+ is an open shell system, we have verified that in all cases the $\langle S^2 \rangle$ expectation value showed that the spin contamination of the unrestricted wave function was always very small. All these calculations have been carried out with the B3LYP hybrid DFT method.[34,35]

TABLE 1: Product Distribution for the Unimolecular Reactivity of the Ni^+/Aminoacrylonitrile Complex

observed peak	relative intensity (%)[a] MIKE	MIKE/CAD	eliminated fragment[b]
m/z 125	15	11	$H^\bullet$ (1 Da)
m/z 124	18	5	H_2 (2 Da)
m/z 109	9		NH_3 (17 Da)
m/z 99	89	11	HCN or HNC (27 Da)
m/z 85	*100*	36	CH_2=C=NH or CH_3CN (41 Da)
m/z 68		9	Ni^0 (58 Da)
m/z 58	38	*100*	H_2N−CH=CH−CN (68 Da)
m/z 52		7	$[Ni^+NH_2]$ (74 Da)
m/z 41		5	$[Ni^+CN]$ (85 Da)

[a] Intensities are normalized relative to the base peak (italicized). [b] See text for details.

The association of a metal cation to a neutral system leads to significant electron density rearrangements that are usually reflected in bond reinforcement or bond weakening effects. To analyze these bonding perturbations we have used the atoms in molecules (AIM) theory, [36] which allowed us to locate the bond critical points (BCPs) that together with the bond paths define the corresponding molecular graph. This AIM analysis was carried out using the AIMPAC series of programs.[37] An alternative and useful way to look into these bonding changes is by means of second order perturbation analysis in the framework of the natural bond orbital (NBO) approach.[38] This analysis permits the identification of the interactions between occupied orbitals of the base and empty orbitals of the metal, involved in the dative bonds from the former to the latter and between occupied orbitals in the metal and empty orbitals in the base, associated with possible back-donations from the latter to the former. Since all complexes are open-shell systems, the NBO analysis has to be carried out for both the α and β sets of MOs. However, for the sake of simplicity, hereafter we will provide only the information corresponding to orbital interactions within the β subset, because this is the subset that contains the 3d as well as the 4s unoccupied orbitals. The α natural orbital set exhibits a similar behavior, although in this case only the empty 4s orbital is within the subset.

Results and Discussion

Mass Spectra. $^{58}Ni^+$ ions react with neutral aminoacrylonitrile to produce $[^{58}Ni{-}NC{-}CH{=}CH{-}NH_2]^+$ adduct ions at m/z 126. The unimolecular decomposition of this adduct has been investigated by means of MIKE analysis to obtain information related to the structure and reactivity of this complex. The overall fragmentation pattern is summarized in Table 1. The $[^{58}Ni{-}NC{-}CH{=}CH{-}NH_2]^+$ ion dissociates according to several dissociation pathways. Under metastable conditions, the main fragmentation corresponds to the loss of $[C_2,N,H_3]$ concomitant with the formation of a $[Ni{-}H,C,N]^+$ ion at m/z 85. Another important fragmentation corresponds to the elimination of a 27 Da neutral (m/z 99) that may be attributed to either loss of HCN or HNC. Such an elimination has been already observed not only with aminoacetonitrile ($NC{-}CH_2{-}NH_2$)[17] but also for α- and β-unsaturated alkenenitriles.[39] By contrast,

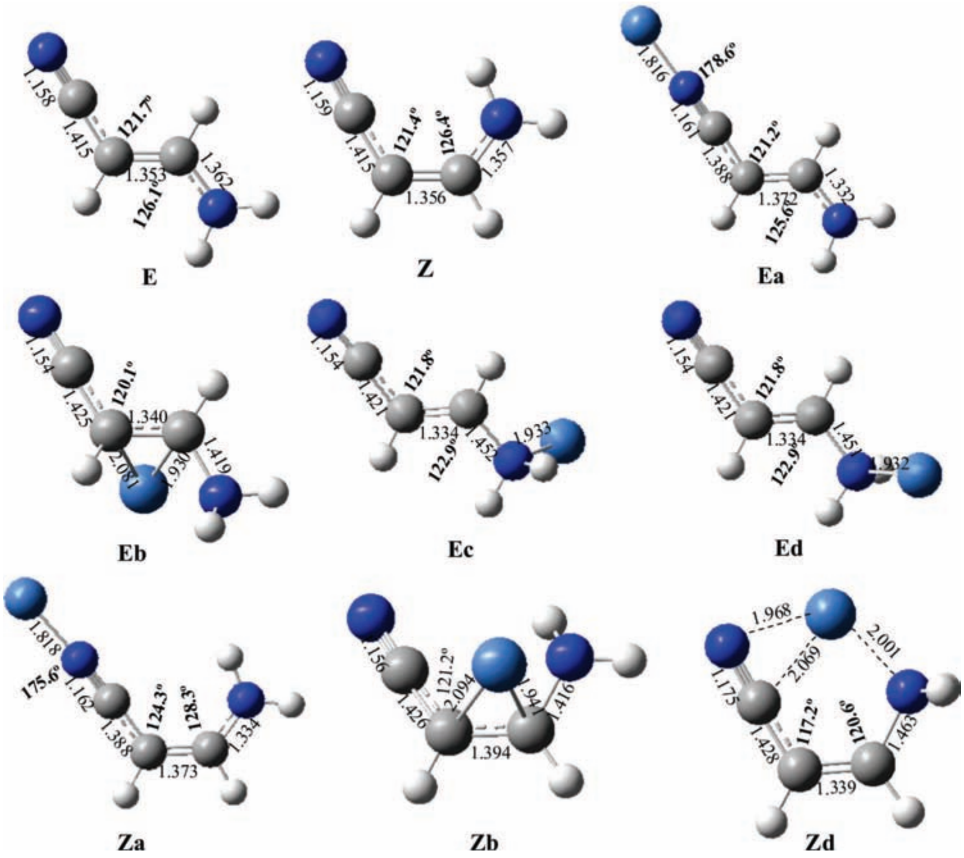

Figure 1. B3LYP/6-311G(d,p)-optimized geometries of the two isomers, *E* and *Z*, of aminoacrylonitrile and their Ni^+ adducts. Bond lengths are in angstroms and bond angles in degrees.

alkanenitriles do not exhibit loss of 27 Da; their unimolecular reactivity is characterized by loss of the intact ligand leading to bare Ni^+ ion.[40−43] It is worth noting that formation of Ni^+ (*m*/*z* 58) is also presently observed in significant amounts, while it was not detected on the MIKE spectrum of the [^{58}Ni(aminoacetonitrile)]$^+$ complex. To complete this survey, three minor processes are also observed, namely, elimination of H, H_2, and ammonia. The dehydrogenation process has been already observed for both alkanenitriles[40−42] and primary amines[44−46] and recently for aminoacetonitrile,[17] but its intensity is, in this case, particularly weak compared to what has been reported for these molecules. Loss of NH_3 corresponds to the less abundant fragment ion, but interestingly, this dissociation route was observed neither for nitriles nor for primary amines, or for aminoacetonitrile. Finally, another significant difference between unimolecular reactivity of Ni^+/aminoacrylonitrile Ni^+/amine systems is the absence of elimination of nickel hydride NiH in the former case.

Under CAD conditions, one can note changes in the branching ratio for the three most important dissociation routes (Table 1). The most intense ion is now bare Ni^+ (*m*/*z* 58), showing that elimination of intact aminoacrylonitrile is favored when energy is provided. Formation of *m*/*z* 85 (loss of [C_2,N,H_3]) may be attributed to the elimination of either ketenimine ($CH_2{=}C{=}NH$) or acetonitrile ($CH_3{-}C{\equiv}N$), while *m*/*z* 99 ions may correspond to the loss of HCN or HNC. Since the ability of transition metal ions to be dicoordinated is well known, the competitive losses of neutral 41 and 27 mass units might arise from Ni^+-bound heterodimers such as [$HCN{-}Ni{-}NH{=}CH_2$] or [$HNC{-}Ni^+{-}N{\equiv}C{-}CH_3$] for example, which may undergo competitive dissociations leading to the two fragment ions at *m*/*z* 85 and 99. Increasing the energetic conditions also results in the onset of few additional fragments of very weak intensities, at *m*/*z* 41, 52, and 68, which might correspond to [$H_2N{-}CH{=}CH$]$^+$, [$NC{-}CH{=}CH$]$^+$, and [$H_2N{-}CH{=}CH{-}CN$]$^{+\bullet}$, respectively. Finally, unlike the Ni^+/aminoacetonitrile system, the formation of H_2Ni^+ (*m*/*z* 60) is not observed.

To assess the mechanisms behind the aforementioned experimental findings, we have carried out a detailed study on the stability and reactivity of the [aminoacrylonitrile−Ni^+] system by means of DFT calculations.

Ni^+ Adducts. Structure and Bonding. The optimized structures of the different adducts that can be formed by the direct interaction of Ni^+ with aminoacrylonitrile are schematized in Figure 1 together with those of the two isomers (*Z* and *E*) of the neutral compound. As it has been reported previously,[20] the *Z* isomer of aminoacrylonitrile lies slightly lower in energy than the *E* isomer. This was explained as the result of the enhanced conjugation of the amino lone-pair with the π-system in the former through an interaction between the nitrogen lone pair and the C═C π^* antibonding orbital. The association of aminoacrylonitrile with Ni^+ significantly changes the relative stabilities of both conformers, and the most stable aminoacrylonitrile−Ni^+ adduct is the **Ea** isomer, in which Ni^+ is attached to the cyano group of the *E* isomer, whereas the equivalent local minimum involving the *Z* isomer (**Za**) of the neutral lies 8.7 kJ mol^{-1} higher in energy. This is likely a result of the aforementioned conjugation between the amino lone pair and the π system in the *Z* conformer, which results in a decrease in the intrinsic basicity of the cyano group. As a matter of fact, it has been found that 100% of the protonated species in the gas phase should correspond to the *E* conformer.

The third adduct in decreasing stability order is **Zd**, in which Ni^+ bridges between the two basic sites of aminoacrylonitrile.

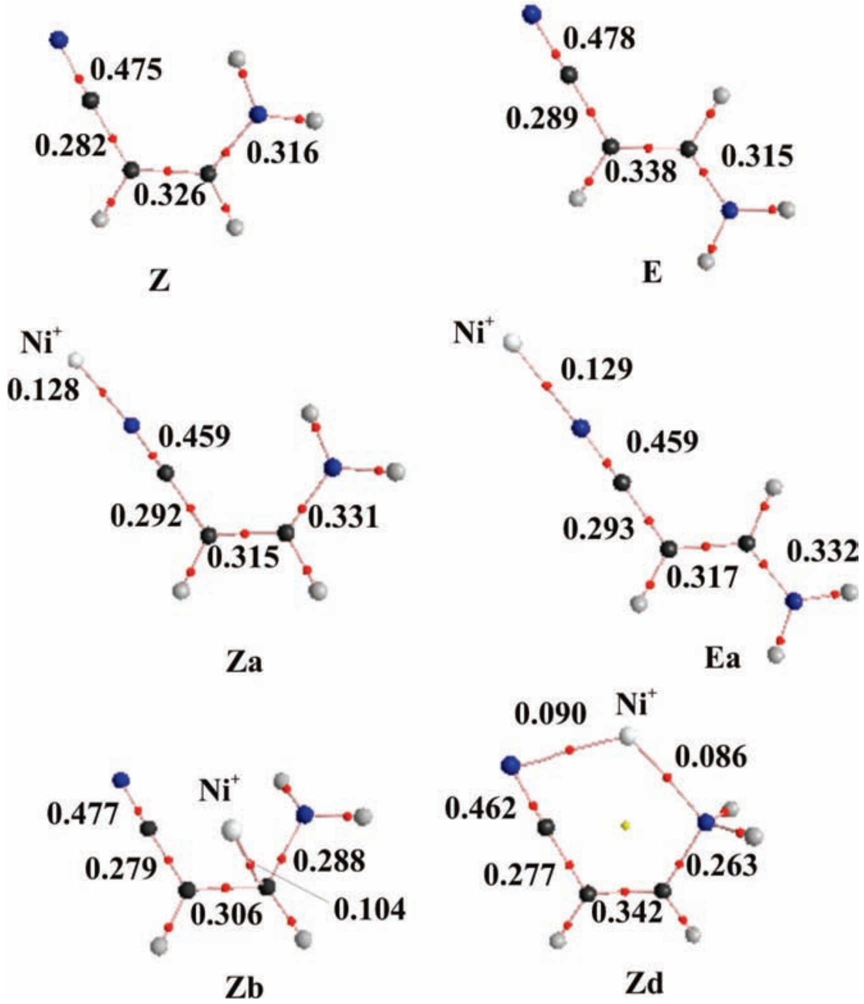

Figure 2. Molecular graphs, showing the BCPs and the bond paths of the two isomers, *E* and *Z*, of aminoacrylonitrile and their most stable Ni$^+$ adducts. Electron densities are in au.

Despite the fact that in this structure the metal cation is bisligated (BCPs are found between Ni and the two nitrogens (see Figure 2)), the adduct is 33.4 kJ mol^{-1} above **Ea** because the amino group strongly pyrimidalizes and the conjugation with the π system disappears.

The interaction of Ni$^+$ with the base in **Ea** and **Za**, although essentially electrostatic, has a non-negligible covalent character, through a dative bond from the cyano N lone pair to an empty sd (91% s, 9% d) hybrid on Ni$^+$, which is followed by a small back-donation from an occupied d orbital of Ni toward the π_{CN}* antibonding orbital of the cyano group. Consistently, the electron density at the N—Ni BCP is rather large in both cases, as well as the Wiberg bond order (0.39). The donation and back-donation just mentioned is also mirrored in a decrease in the electron density at the C≡N BCP (see Figure 2) and in the corresponding Wiberg bond order (from 2.81 in the neutral to 2.52 in the complex).

Previous studies about the reactivity of transition metal ions with nitriles have suggested the coexistence of both "end-on" and "side-on" coordination modes.[41,42,47] For the particular case of the Z isomer, this form collapses to structure **Zd** already discussed. For the *E* isomer, the "side-on" structure is not a stationary point of the PES as it collapses to the global minimum **Ea**. We have found, however, local minima in which the metal cation interacts with the C═C double bond (**Eb** and **Zb**), although these species lie very high in energy. In fact, according to the NBO analysis, a covalent bond between the C attached to the CN group (with 81% of participation from the C atomic orbitals) is formed, and consequently the CC bond order decreases significantly (from 1.64 in the neutral to 1.30 in the complex) as well as the electron density at the BCP (see Figure 2).

Unimolecular Reactivity of the [Aminoacrylonitrile—Ni]$^+$ Adducts. In this section we will analyze the [aminoacrylonitrile—Ni]$^+$ PES obtained at the B3LYP level in order to identify the reaction mechanisms associated with the loss of HCN, NH$_3$, [C$_2$,N,H$_3$] (CH$_2$═C═NH or CH$_3$CN), the latter being, as mentioned above, the dominant one in the MIKE spectrum, and the first two are the second and the third dominant process, respectively. For the sake of clarity, the loss of HNC and H$_2$ will be discussed separately from the aforementioned processes, not to overload the figures associated with the corresponding PESs. The total energies and the zero-point vibrational energies of all the stationary points involved in the PESs discussed here are summarized in Table S1 of the Supporting Information.

Previous experimental studies on the reactivity of nitriles with metal cations suggested that a single type of interaction could not account for all the fragmentation processes experimentally observed.[39,41] Hence, we have considered different [aminoacrylonitrile—Ni]$^+$ adducts as starting points in our survey. Nevertheless, it must be noted that these adducts are interconnected through activation barriers (see Figure S1 of the Supporting Information) which lie lower in energy than the

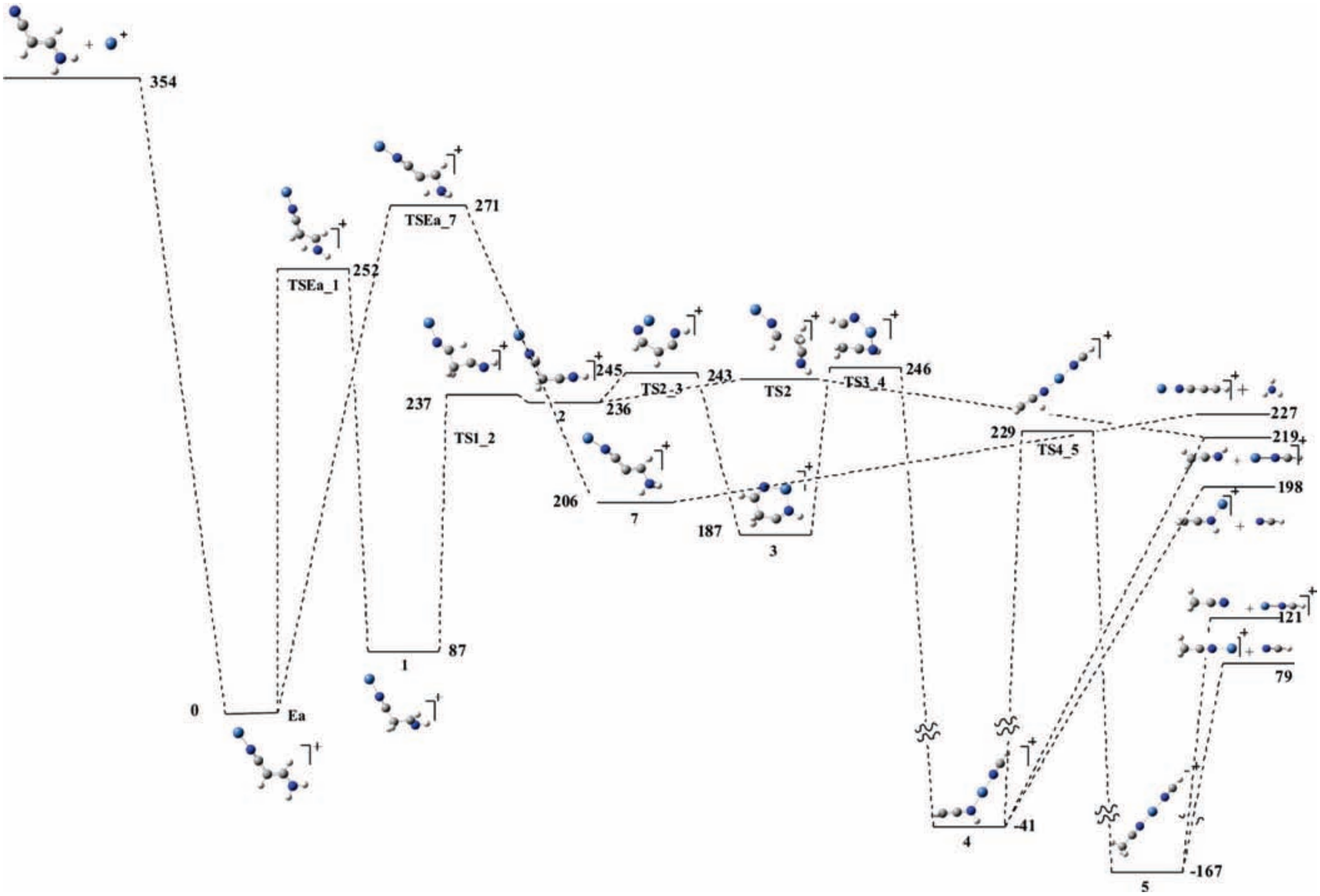

Figure 3. Energy profile of the mechanisms associated with the loss of HCN, C_2, N, H_3, and NH_3. Relative energies are in kJ/mol.

entrance channels. This means that many other possible mechanisms than those discussed in detail here have been explored, but they were discarded because either the corresponding products lie very high in energy or the activation barriers involved were much higher in energy than the entrance channels or both. This is, for instance, the case of the mechanisms with origin in **Za**, which as already indicated, is the second stable adduct. As illustrated in Figure S2 of the Supporting Information, the hydrogen shifts that can be envisaged with origin in this adduct involve activation barriers that are higher in energy than the entrance channels and lead to dissociation products that although being lower than the entrance channels are much higher in energy than products with the same mass produced through alternative mechanisms.

Losses of [C_2,N,H_3], HCN, and NH_3. The energy profiles associated with the loss of [C_2,N,H_3], HCN, and NH_3, with origin in the most stable **Ea** adduct is presented in Figure 3. It should be remembered here that these mechanisms can have also origin in both the **Za** and the **Zd** adducts, because they are connected to the global minimum through barriers well below 354 kJ/mol, which is the energy of the entrance channel. Two 1,3-H shifts can be envisaged for the global minimum, from the amino group toward the CH group to which the CN substituent is attached, or from this group toward the amino group. The possible 1,2-H shifts involve necessarily much higher activation barriers and therefore they are not shown in the figure.

The first of the two processes mentioned above leads to intermediate **1**, which after a second 1,3-H shift from the CH group attached to the imino nitrogen toward the C of the CN group yields a new intermediate **2**. Minimum **2** is easily connected, through a rather low activation barrier associated with the internal rotation around the CH_2—CH bond, with the cyclic local minimum **3**. It is worth noting that the atom connectivity in this local minimum is already consistent with the most abundant products. Hence, the cleavage of the H_2C—CH bond in this cycle yields a very stable structure **4** in which Ni is bisligated to CH_2=C=NH and to HCN. The fragmentation of this local minimum would produce precisely the two more abundant products, HCN + CH_2=C=NH···Ni^+ and CH_2=C=NH + HCN···Ni^+. Alternatively, a 1,3-H shift from the imino group to the CH_2 group in **4** leads to the global minimum of the PES, in which Ni^+ is connected simultaneously to HCN and CH_3CN. The eventual dissociation of the global minimum would yield HCN + $CH_3C{\equiv}N\cdots Ni^+$ or CH_3CN + $HCN\cdots Ni^+$.

In summary, our results indicate that the loss of 41 Daltons may correspond to either ketenimine or to acetonitrile. Although the production of acetonitrile through the intermediate **5** involves an activation barrier slightly higher in energy than the exit channels yielding HCN + CH_2=C=NH···Ni^+ or HCN···Ni^+ + CH_2=C=NH, a definite answer on which of the two processes dominates would require an adequate kinetic analysis, which is out of the scope of this paper. Our data also demonstrate that expectedly acetonitrile has a greater affinity for Ni^+ than hydrogen cyanide. The same is true for ketenimine, although the difference in affinity is less pronounced.

It is worth mentioning that two of the products detected in the Ni^+ + aminoacrylonitrile reaction, ketenimine and acetonitrile, are astrochemically related since it is assumed that the former is likely formed from the latter by tautomerization driven

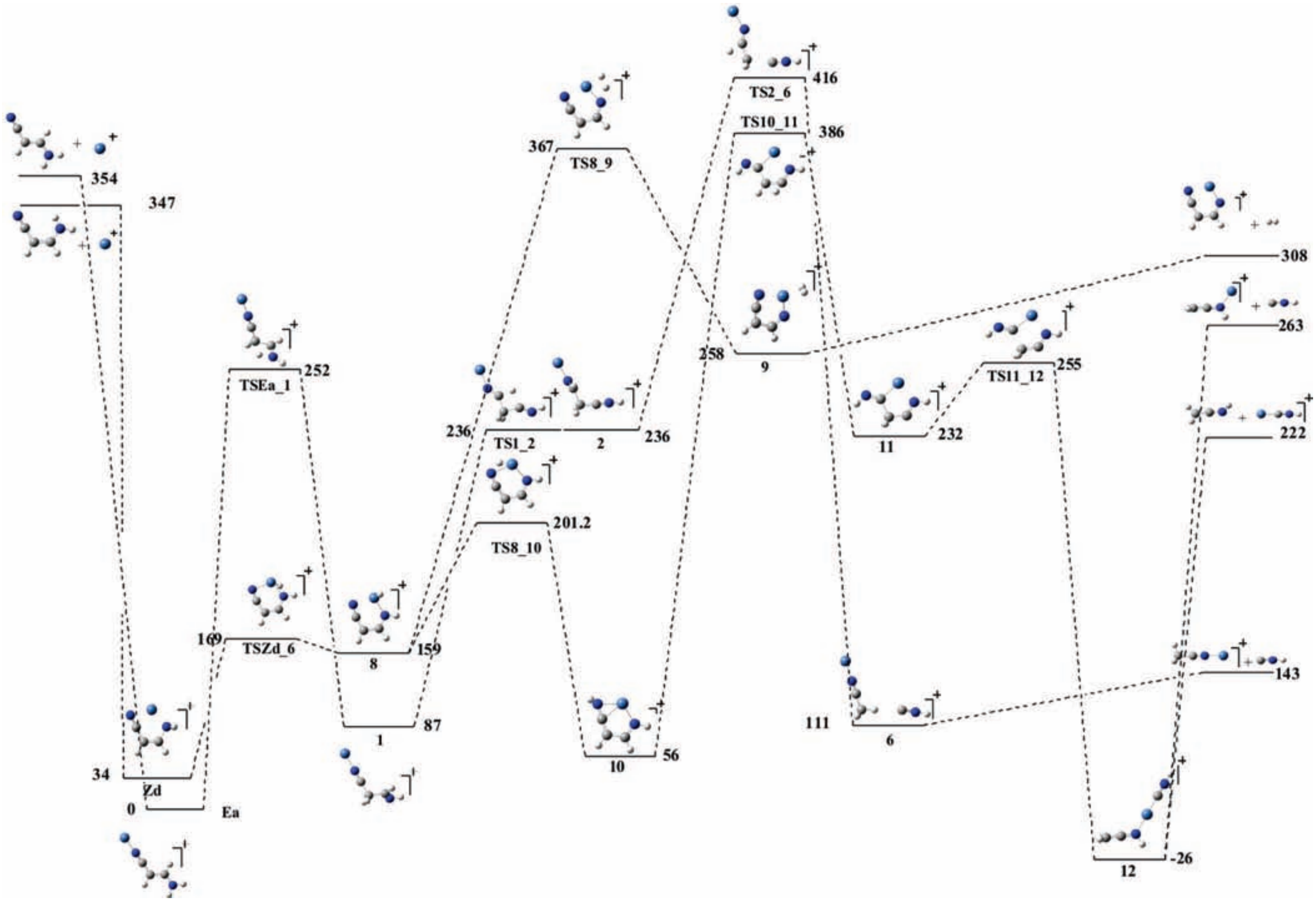

Figure 4. Energy profile of the mechanisms associated with the loss of HNC and H_2. Relative energies are in kJ/mol.

by shocks that pervade the star-forming region.[48] Also interestingly, ketenimine has been recently detected in Sagittarius B2(N) hot cores.[48]

The less favorable 1,3-H shift with origin in adduct **Ea** would lead to the local minimum **7**, which would eventually lose NH_3 to yield a linear $HC{\equiv}C{-}C{\equiv}N{\cdots}Ni^+$ ion. In agreement with the experimental observation, the loss of ammonia is less favorable than the loss of HCN or $CH_2{=}CN{-}H$ ($CH_3C{\equiv}N$) because the activation barriers involved are larger and the products are thermodynamically less stable.

Losses of H_2 and HNC. Molecular hydrogen interacts quite well with metal cations, so when looking for the possible intermediates leading to the loss of H_2 we have considered as the more likely possibility that in which two hydrogens migrate toward the metal. This possibility is particularly favorable starting from the **Zd** adduct due to the proximity of the amino group to the metal, as shown in Figure 4. As a matter of fact, the migration of one of the amino group hydrogens toward the Ni atom involves a rather low activation barrier to yield the intermediate **8**. From **8**, the migration of the second hydrogen would yield structure **9**, which would lose H_2. It is worth noting that the formation of **9** requires an activation barrier, which is slightly above the entrance channel, that would be consistent with the experimental observation that this is very minor process. The local minimum **8** can act also as an intermediate in a H-carrier process through the metal, since the H atom attached to Ni can move further (through **TS8_10**) to yield a quite stable local minimum **10**. A further hydrogen shift involving the two CH groups within the cycle would lead to **11**, an intermediate that has the connectivity of the most abundant product (CH_2CNH), where the second fragment would have a HNC rather than a HCN arrangement. Indeed, minimum **11** evolves, through the **TS11_12** transition state, toward a very stable complex in which Ni^+ is bonded to a HNC and to a $CH_2C{=}N{-}H$ subunits, and therefore its fragmentation would yield $CH_2C{=}NH$ + $HNC{\cdots}Ni^+$ or $CH_2C{=}N{-}H{\cdots}Ni^+$ + HNC. Examination of Figure 4 also shows that ketenimine has a greater affinity for Ni^+ than HNC.

One important question would be whether there is some competitive mechanism to lead to the loss of HNC with origin in the most stable adduct **Ea**. This possibility is also shown in Figure 4. Once the local minimum **2** is formed, besides the cyclization of the system yielding structure **3** (shown in Figure 3), there is the possibility of a hydrogen shift through the **TS2_6** transition state to yield **6**, a weakly bound complex between HNC and $CH_3C{\equiv}N{\cdots}Ni^+$, that would lose HNC.

It is worth noting however, that the two possible mechanisms for the loss of HNC involve not only activation barriers much higher than those discussed above for the loss of HCN but barriers that are above the entrance channels. This means that most of the products will be in the form of HCN, although some HNC cannot be absolutely discarded, mainly when considering the MIKE−CAD spectra.

Conclusions

The dominant fragmentations in the MIKE spectra of the [aminoacrylonitrile−Ni]$^+$ complexes correspond to the loss of [C_2,N,H_3], HCN, and NH_3, the loss of H_2 being very minor.

Our B3LYP/6-311G(d,p) calculations indicate that the most stable adducts correspond to the association of the Ni^+ to the nitrogen of the cyano group (end-on), either when the neutral is in its **Z** or in its **E** conformation. Interestingly, Ni^+ attachment reverses the stability order of the isomers. For the [aminoacrylonitrile−Ni]$^+$ complex, the most stable conformer is **Ea**, in which Ni^+ is bonded to the cyano nitrogen of the **E** isomer, which is less stable than the **Z** isomer as far as neutral species are concerned. This is consistent with the fact that the cyano group of the **E** isomer has a greater intrinsic basicity than that of the **Z** isomer.

A survey of the [aminoacrylonitrile−Ni]$^+$ PES carried out at the B3LYP/6-311G(d,p) level allows us to propose suitable mechanisms for the experimentally observed fragmentations. Two mechanisms, with origin in the most stable adduct **Ea**, lead to the observed loss of [C_2,N,H_3]; one corresponds to the loss of CH_2CNH and the other to the loss of CH_3CN. The formation of the latter is significantly more exothermic but involves slightly higher activation barriers, so very likely, both isomers are produced along the reaction process. Interestingly, ketenimine has been recently detected in Sagittarius B2(N) hot cores.

Two mechanisms are also envisaged for the lost of HNC with origin in the most stable adduct **Ea** or on the cyclic adduct **Zd**. Both mechanisms, however, involve energy barriers higher in energy than the entrance channel and lead to products which are above those obtained when HCN is lost. Hence, it must be concluded that the lost of HNC is not competitive with the lost of HCN. The loss of NH_3 is associated with the formation of a complex between cyanoacetylene and Ni^+.

The loss of H_2 takes place from complexes in which two hydrogen atoms reach this precursor lie slightly higher than the entrance channel, which is consistent with the experimental observations.

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Supporting Information Available: A table containing the total energies, ZPE, relative energies of the different stationary points of the [aminoacrylonitrile−Ni^+] PES and a figure depicting the energy profile corresponding to the connection between the different aminoacrylonitrile−Ni^+ adducts. This material is available free of charge via the Internet at http://pubs.acs.org.

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