

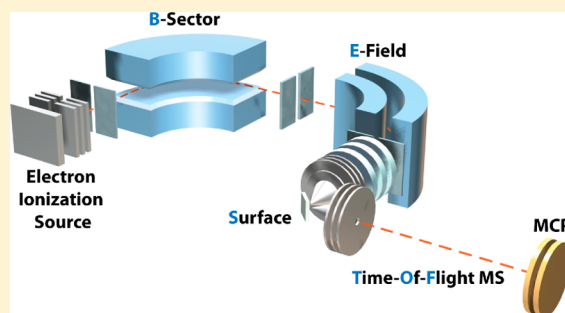
Formation of HCN^+ in Heterogeneous Reactions of N_2^+ and N^+ with Surface Hydrocarbons

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ABSTRACT: A significant increase of the ion yield at m/z 27 in collisions of low-energy ions of N_2^+ and N^+ with hydrocarbon-covered room-temperature or heated surfaces of tungsten, carbon-fiber composite, and beryllium, not observed in analogous collisions of Ar^+ , is ascribed to the formation of HCN^+ in heterogeneous reactions between N_2^+ or N^+ and surface hydrocarbons. The formation of HCN^+ in the reaction with N^+ indicated an exothermic reaction with no activation barrier, likely to occur even at very low collision energies. In the reaction with N_2^+ , the formation of HCN^+ was observed to a different degree on these room-temperature and heated (150 and 300 °C) surfaces at incident energies above about 50 eV. This finding suggested an activation barrier or reaction endothermicity of the heterogeneous reaction of about 3–3.5 eV. The main process in N_2^+ or N^+ interaction with the surfaces is ion neutralization; the probability of forming the reaction product HCN^+ was very roughly estimated for both N_2^+ and N^+ ions to about one in 10^4 collisions with the surfaces.



INTRODUCTION

Information from space missions has provided motivation for a wide range of laboratory experiments and modeling calculations. The results of the Cassini–Huygens mission to Saturn and especially the rich data on Titan’s atmosphere and surface from the Huygens probe and lander have turned considerable attention to studying the ionosphere and atmosphere of this object. The atmosphere of Titan is composed mostly of molecular nitrogen (above 95%) with 2–5% of methane and small amounts of more complex hydrocarbons (ethane, ethylene, acetylene, propane), traces of nitriles, and oxygen-containing compounds.¹ The transmitted data revealed a rich chemical composition of the ionosphere² and led to emphasis of importance of nitrogen chemistry in the upper atmosphere. Present data on gas phase processes relevant to the atmosphere of Titan are plentiful and have been summarized in several recent reviews.^{3,4}

The direct observations of the satellite revealed also the existence of aerosols forming the organic haze in the atmosphere.^{1,5} Pyrolytic analysis suggested a chemical composition that includes carbon, hydrogen, and nitrogen.⁶ Considerable effort has been put into synthesizing the laboratory analogues of these aerosols,⁷ referred to as tholins, but up to now the problem remains open. However, the existence of aerosols brought up the question of heterogeneous reactions of ions and neutrals on their surface. Though information on reaction of ions and neutrals in the gaseous phase, relevant to the atmosphere of Titan, is plentiful,

information on possible heterogeneous processes appears to be very limited.

We report here on an observation of elementary heterogeneous chemical reactions of N_2^+ and N^+ ions with surface hydrocarbons that lead to the formation of the HCN^+ ion. Experimental information comes from our work on the ion–surface interaction of slow (up to 100 eV) Ar^+ , N_2^+ , and N^+ ions with surfaces covered with adsorbed hydrocarbons. The principal aim of the studies was to provide data on collisions of selected low-energy seeding gas ions (argon and nitrogen) with surfaces relevant to construction of fusion devices (carbon, tungsten, beryllium).

Our previous investigation of collisions of molecular ions of energies from several electronvolts up to about 100 eV with solid surfaces has provided information on the neutralization (or survival probability) of ions,^{8,9} on dissociation processes and chemical reactions at surfaces,^{10,11} on partitioning of energy in these processes,¹¹ and on the low-energy sputtering of the surface material.¹²

Chemical reactions between low-energy incident ions and surface material have been observed in many systems. The reaction described most often is hydrogen atom transfer between some incident ions (e.g., polyatomic organic cations)

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and hydrogen-containing surface material,¹³ leading to protonated incident ions. Other reactions (e.g., formation of CsCO^+ , CsOH^+ ,¹⁴ XeF^+ , XeCF^+ , XeCF_2^+ ¹⁵) have been observed in specific systems. Collisions of molecular ions N_2^+ with surfaces have been studied in particular in connection with surface modification (nitridation),¹⁶ scattering results concerned neutralization and dissociation at higher incident energies.¹⁷ To our knowledge, however, no chemical reactions of low-energy N_2^+ or N^+ ions at surfaces have been so far reported.

The observation of HCN^+ formation in heterogeneous reactions of the nitrogenous ions with surface hydrocarbons can be of interest from the point of view both of chemical reactivity of nitrogenous ions at surfaces and of astrophysics. However, the relevance to the conditions of space and planetary atmospheres (Titan) should be regarded with caution. We believe that the formation of the molecular ion HCN^+ in the observed heterogeneous processes is worth reporting, though the probability of the reactions is rather small. The reaction of N^+ has been observed clearly at all measured incident energies, it appears to be exothermic and thus it may be expected to occur even at very low N^+ energies relevant to space conditions. On the other hand, the reaction of N_2^+ seems to have a high activation barrier (or endothermicity) as inferred from its observation only at incident energies of N_2^+ above about 50 eV. The occurrence of ions of such high energies in planetary atmospheres is unlikely and this limits the relevance of the N_2^+ reaction to conditions of the astrophysical systems.

■ EXPERIMENTAL SECTION

The experiments were carried out on the tandem apparatus BESTOF in Innsbruck, described in detail in our previous publications (e.g., ref 18). It consists of two mass spectrometers arranged in tandem geometry (Figure 1). Projectile ions were

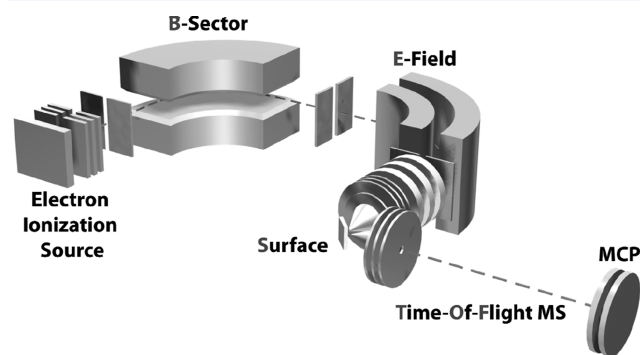


Figure 1. Schematics of the tandem apparatus BESTOF: a mass-selected ion beam interacts with a surface, and product ions are detected by a time-of-flight (TOF) mass spectrometer.

produced in a Nier-type ion source by electron ionization (75 eV energy) of argon or nitrogen. The ions produced were extracted from the ion source region and accelerated to 3 keV for mass and energy analysis by the double-focusing two-sector-field mass spectrometer. After passing the mass spectrometer exit slit, the ions were refocused by an Einzel lens and decelerated to the required incident energy, before interacting with the target surface. The incident impact angle of the projectile beam was kept at 45° and the scattering angle was fixed at 46° (with respect to the plane of the surface). The energy spread of the projectile ion beam was about 0.5 eV (full

width at half-maximum). A fraction of the product ions formed at the surface left the shielded chamber through a 1 mm diameter orifice. The ions were then subjected to a pulsed deflection-and-acceleration field that initiated the time-of-flight analysis of the ions. The second mass analyzer was a linear time-of-flight (TOF) mass spectrometer with a flight tube about 80 cm long. The mass selected ions were detected by a double-stage multichannel plate connected to a multichannel scaler and a computer. The product ion yields were obtained by integration of the area under the recorded peaks in the mass spectra.

The pressure in the ion source was $(4\text{--}9) \times 10^{-5}$ mbar, the bakeable surface chamber and the TOF analyzer were maintained under ultrahigh-vacuum conditions (10^{-8} mbar) by a turbo-pump. However, even these ultrahigh-vacuum conditions did not exclude deposition of a layer of hydrocarbons on the surface, kept at room temperature, whenever the valve between the sector-field mass spectrometer and the surface chamber was opened and the pressure in the surface region increased to the 3×10^{-8} mbar range. To investigate the dependence of product ion signals on surface temperature, the surface samples could be heated during measurements up to 450°C by a heating wire located inside the surface sample holder.

The hydrocarbons adsorbed on the surface of the solid samples are generally assumed to be cracked pump oil aliphatic hydrocarbons of chain length of about C8.¹³ The hydrocarbon coverage at room temperature is quite stable and constantly renewable by adsorption from the hydrocarbon background. At higher surface temperatures it may be viewed as a surface covered largely or partially with islands of hydrocarbons, which decrease in size with increasing temperature of the sample. At 600°C the surface is practically devoid of any hydrocarbons, as checked by the absence of H-atom transfer reactions with radical cations.¹⁰

The metal samples were cut from a 0.25 mm tungsten (Alfa Aesar, #10415) and beryllium (Alfa Aesar, #41642) foils, respectively. The carbon-fiber composite NB-31 (CFC) sample was obtained from the Max-Planck Institute for Plasma Chemistry, Garching. It is a carbon–carbon composite with interwoven carbon fibers densified by pyrocarbon.

Ionization of N_2 by electrons produces N_2^+ ions in the ground state $\text{X}^2\Sigma_g^+$ as well as in the $\text{A}^2\Pi_u$, $\text{B}^2\Sigma_u^+$, and $\text{C}^2\Sigma_u^+$ electronic excited states. The excited states pass in fast radiative transitions to the ground state (B,C), the lifetime of the A-state is of the order of microseconds,¹⁹ short in comparison with the passage time of the beam to the surface (longer than about 5×10^{-5} s). The C-state is also partially dissociative. Therefore, it is generally assumed that the N_2^+ ions in the beam are practically only in their electronic ground state $\text{X}^2\Sigma_g^+$.

The beam of atomic ions N^+ formed by electron dissociative ionization of N_2 is composed mostly of ions in the ground state ^3P , about 15% is expected to be in the long-lived metastable excited state ^1D .²⁰ A small admixture of doubly charged ions N_2^{2+} could be avoided by measuring at electron energies of 40 eV, below the ionization energy of the dication.

■ RESULTS AND DISCUSSION

Reactions of N_2^+ . As an example, Figure 2 shows mass spectra of product ions resulting from the interaction of Ar^+ with the tungsten target kept at room temperature (a), heated to 150°C (b), and heated to 300°C (c). The mass spectra were measured at a series of incident energies of Ar^+ between

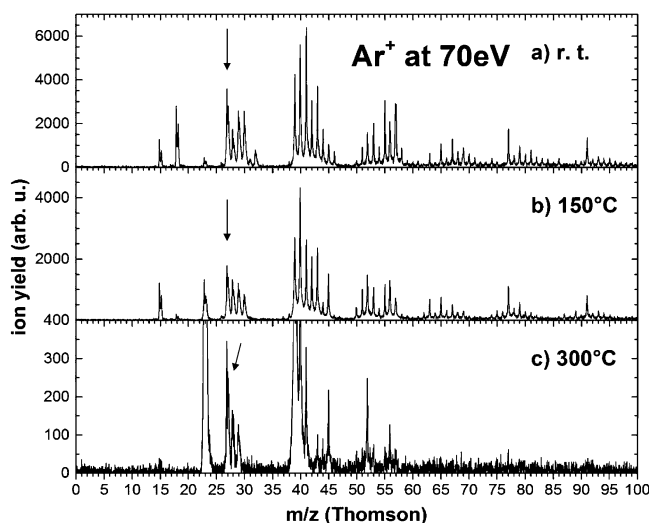


Figure 2. Mass spectra of product ions from collisions of Ar^+ with a hydrocarbon-covered tungsten surface kept at (a) room temperature (rt), (b) 150 °C, and (c) 300 °C. The incident energy of the Ar^+ ions was 70 eV. The position of m/z 27 is denoted by an arrow.

20 and 100 eV. Figure 2 shows the result at 70 eV. The ion yields are mutually comparable, because they were normalized to the same projectile beam intensity and measurement time.

The spectrum of product ions at room temperature (Figure 2a) showed mostly aliphatic hydrocarbon species sputtered from the surface, covered by adsorbed hydrocarbons. Hydrocarbon ions CH_3^+ (m/z 15), C_2H_3^+ and C_2H_5^+ (m/z 27 and 29), C_3H_n^+ (m/z 39–43), and C_4H_n^+ (m/z 53–57), and to a lesser extent C_5H_n^+ (m/z 65–69), C_6H_n^+ (m/z 77–81), and C_7H_n^+ (m/z 91) can be identified. In addition to the hydrocarbon ions, the spectra indicated the presence of surface contaminants: water (m/z 18) and traces of oxygen-containing compounds from the sample cleaning procedure (m/z 30–32, parts of ion yields at m/z 42–45 and 57–58). The spectrum at the surface temperature of 150 °C (Figure 2b) showed a relative decrease of the hydrocarbon ion yields. At the same time, alkali ions at m/z 23 (Na^+) and m/z 39 and 41 (K^+) appeared in the spectrum. The alkali ions are regarded as sample contaminants whose conspicuous appearance in the spectra was due to their easy and disproportionate ionization efficiency. They were not taken into consideration in the discussion of the ion yields. The mass spectrum at 300 °C (Figure 2c) was dominated by strong ion signals of these alkali ions. Aliphatic hydrocarbon ions were reduced even more, only the C2 group at m/z 27–29 was clearly observable. No sputtering of the basic material (ions of tungsten or its compounds) was observed at these low incident energies in any of the experiments.

Figure 3 shows the analogous mass spectra from collisions of N_2^+ projectiles with the same tungsten surface, at the same incident energy of 70 eV, and at the three surface temperatures. Much the same as what was said about Ar^+ collisions holds for the N_2^+ interaction: at room temperature, sputtering of hydrocarbon ions of the groups C1–C7 of approximately comparable yields. The yield of m/z 28 was higher (surviving N_2^+ projectile ions). At 150 °C the ion yields decreased with one notable exception: the ion yield at m/z 27 dramatically increased in comparison with the ion yield at m/z 29. Alkali contaminants Na^+ and K^+ appeared in the spectra, too. At 300 °C the yields of hydrocarbon ions decreased to very small

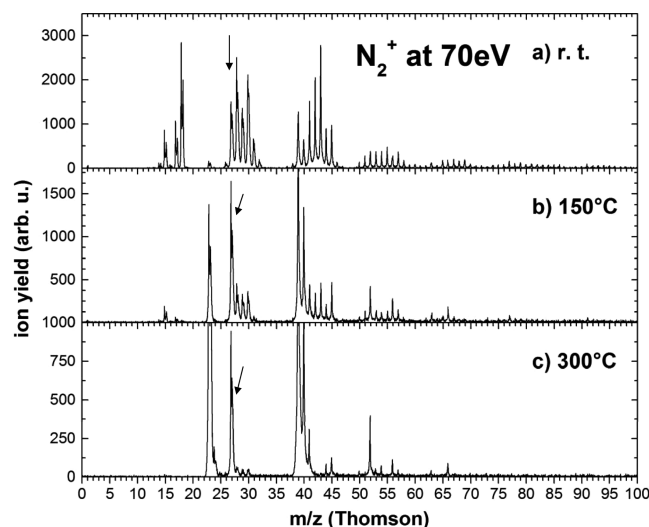
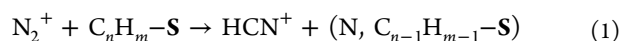


Figure 3. Mass spectra of product ions from collisions of N_2^+ with a hydrocarbon-covered tungsten surface kept at (a) room temperature (rt), (b) 150 °C, and (c) 300 °C. The incident energy of the N_2^+ ions was 70 eV. The position of m/z 27 is denoted by an arrow.

values, whereas the alkali contaminants increased even more. Most significantly, however, the ion yield of m/z 27 strongly increased in comparison with the yield of other hydrocarbon product ions.

This strong increase of the ion yield at m/z 27 was not observed in the Ar^+ spectra, and we interpret it as being due to the product of a surface reaction of the projectile ion N_2^+ with the surface hydrocarbons, namely formation of HCN^+ in a heterogeneous ion–surface chemical reaction of the type ($\text{C}_n\text{H}_m\text{--S}$ denotes hydrocarbon chain attached to the surface S)



Correct assessment of the ion yield of m/z 27 due to HCN^+ required subtraction of the hydrocarbon background on m/z 27. The ion yields at m/z 27 and 29 in the mass spectra with Ar^+ originated only from sputtered hydrocarbon fragments C_2H_3^+ and C_2H_5^+ and sputtering of surface hydrocarbons with N_2^+ may be regarded as very similar to that by Ar^+ . To cross check this assumption, the ratio of yields of another pure hydrocarbon ion pair, m/z 53 (C_4H_5^+) and m/z 55 (C_4H_7^+), was measured (the yields at m/z 41 and 43 were obstructed by the signals of Ar^+ and K^+ ions). The ratio $Y(53)/Y(55)$ was found to be practically the same for both Ar^+ and N_2^+ collisions at all measured incident energies and temperatures, thus justifying the above-mentioned assumption.

To subtract the hydrocarbon contribution, the mass spectra with Ar^+ and with N_2^+ were mutually compared at all incident energies and all sample temperatures measured, and the ratio $F_{\text{Ar}} = (Y[27]/Y[29])_{\text{Ar}}$ was determined from the Ar^+ mass spectra. The portion of the ion yield at m/z 27 in the mass spectra with N_2^+ , corresponding to hydrocarbon sputtering, was then calculated as $Y[27]_{\text{CH,N}_2} = F_{\text{Ar}}Y[29]_{\text{N}_2}$, and subtracted from the total ion yield at m/z 27. The net yield at m/z 27, ascribed to the formation of HCN^+ , was then $Y(\text{HCN}^+) = \Delta Y(27)_{\text{N}_2} = Y(27)_{\text{N}_2} - Y(27)_{\text{CH,N}_2}$. The value of F_{Ar} was found to increase slowly at room temperature from about 1.1 to 1.4 for incident energies 20–100 eV, more steeply at higher

surface temperatures (at 300 °C from 1.5 at 20 eV to 2.8 at 100 eV).

The net yield ascribed to HCN^+ formation in the N_2^+ -tungsten surface collisions, $\Delta Y(27)$, is plotted in Figure 4 as a

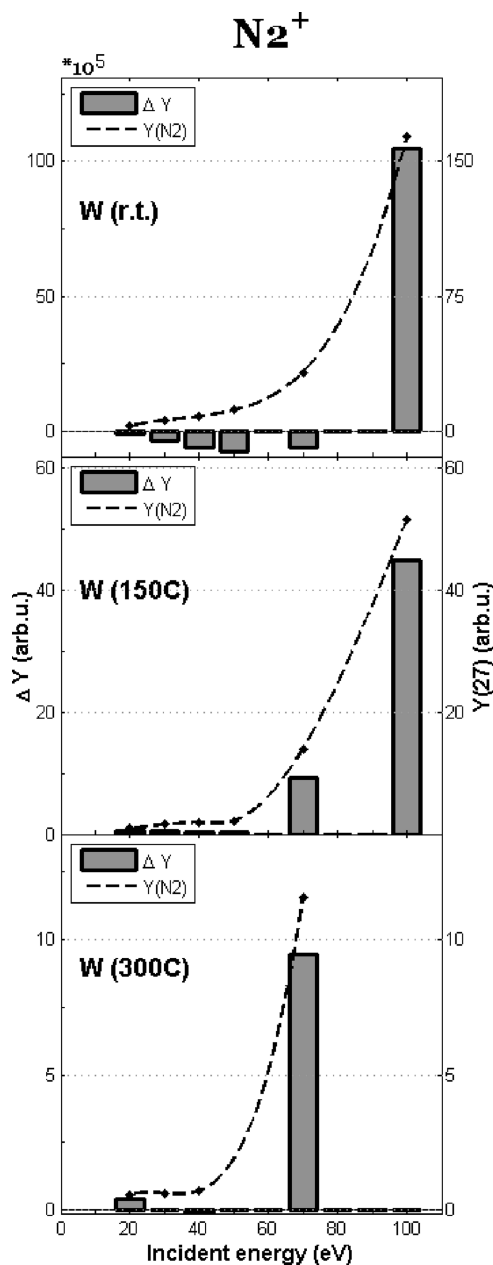


Figure 4. Net ion yield at m/z 27, ΔY , ascribed to the formation of HCN^+ (histogram), and total ion yield at m/z 27, $Y(27)$ (points), from the interaction of N_2^+ ions of incident energy E_{inc} with a hydrocarbon-covered tungsten surface kept at room (rt) or elevated (150 °C, 300 °C) temperature.

function of the incident energy of N_2^+ for the three temperatures of the surface (histograms), and (for comparison) the total yield of m/z 27, $Y(27)$, is plotted, too. The error in determination was fairly large, as indicated by the alternating positive and negative values of $\Delta Y(27)$ at low incident energies (in principle, $\Delta Y(27)$ should not be negative). The estimated error is about ± 150 arb.u. for the room-temperature data and ± 10 arb.u. for the data at 150 and 300 °C. However, the data clearly show a strong increase of $\Delta Y(27)$ at incident energies

above about 50 eV. At 70–100 eV the yield ascribed to the reaction product HCN^+ represents from 40% (room temperature) to 80% (300 °C) of the total ion yield at m/z 27.

No indication of formation of N_2H^+ (m/z 29) by H-atom transfer from surface hydrocarbons could be discerned from the comparison of the Ar^+ and N_2^+ mass spectra and from the analysis of the ion yields at m/z 28 and 29.

If these considerations are correct, one should observe the reaction between N_2^+ and surface hydrocarbons also in experiments with other hydrocarbon-covered surfaces, though possibly to a different extent. Figure 5 (upper part) shows the results of an analogous analysis of our experiments on Ar^+ and N_2^+ collisions with hydrocarbon-covered surfaces of carbon,

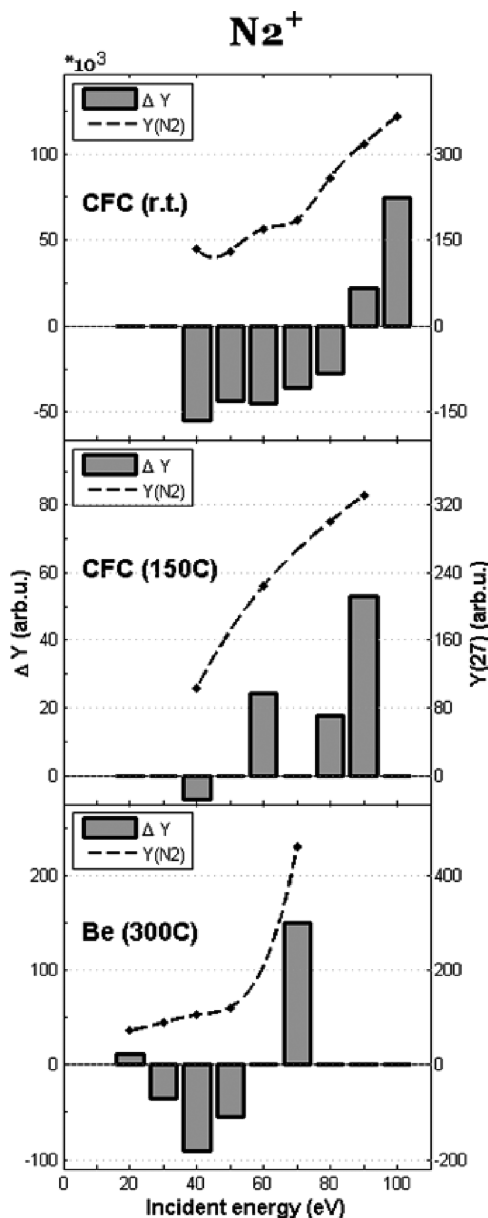


Figure 5. Net ion yield at m/z 27, ΔY , ascribed to the formation of HCN^+ (histogram), and total ion yield at m/z 27, $Y(27)$ (points), from the interaction of N_2^+ ions of incident energy E_{inc} with a hydrocarbon-covered carbon-fiber composite (CFC) surface kept at room (rt) or elevated (150 °C) temperature (upper and middle part); analogous data for interaction of N_2^+ ions with a hydrocarbon-covered surface of beryllium at 300 °C (lower part).

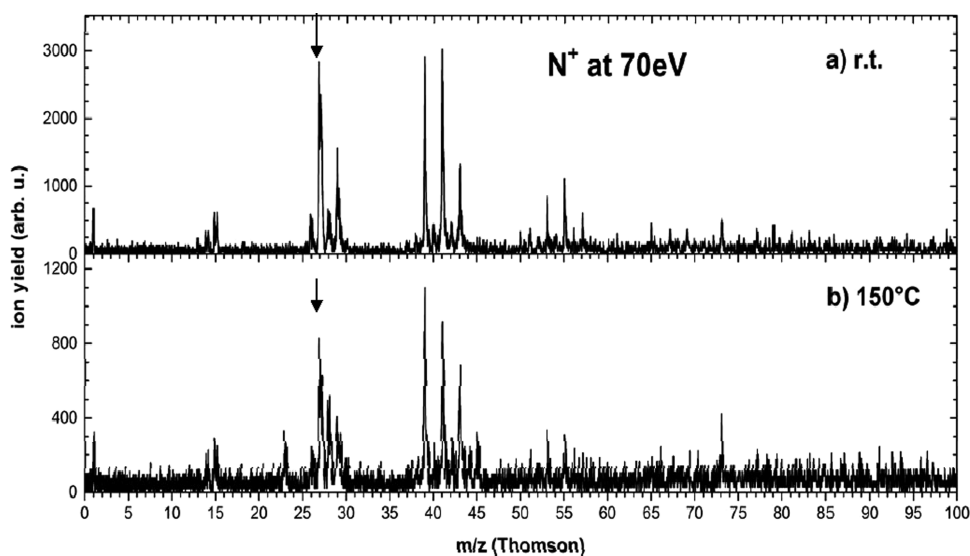


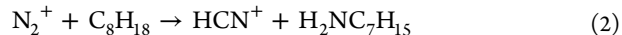
Figure 6. Examples of mass spectra of product ions from collisions of N^+ ions with a hydrocarbon-covered tungsten surface kept at room temperature (rt) and $150\text{ }^\circ\text{C}$. The incident energy of the N^+ ions was 70 eV. The position of m/z 27 is denoted by an arrow.

namely of the carbon-fiber composite (CFC) surface, kept at room temperature and at $150\text{ }^\circ\text{C}$. The signals were much weaker and the increase of the ion yield ascribed to HCN^+ was much more buried in the hydrocarbon background (about 20% of the total yield of m/z 27 at room temperature and $150\text{ }^\circ\text{C}$) but showed a noticeable increase above about 50–70 eV. Finally, Figure 5 (lower part) gives as an example of our analysis of the data from Ar^+ and N_2^+ collisions with a hydrocarbon-covered beryllium surface, the results of the measurements at $300\text{ }^\circ\text{C}$. The increase of the ion yield at m/z 27 due to the HCN^+ formation shows up in the positive value of $\Delta Y(27)$ at 70 eV (30% of the total yield at m/z 27). In the measurements with the room-temperature Be surface and the surface heated to $150\text{ }^\circ\text{C}$ the $\Delta Y(27)$ signals were obstructed by high hydrocarbon background, the values oscillated between small positive and negative values and though they showed a tendency to go up to positive with increasing energy they remained below the error limits, and thus the identification was inconclusive. Therefore, the data are not shown in the figure. Different efficiency of forming the ion product of reaction 1 on different surfaces, in comparison with the sputtered hydrocarbon background, is presumably due to the differences in binding of surface hydrocarbons to the underlying surface and/or to different efficiency of sputtering from the surfaces.

The data presented in Figures 2–5 led us to the conclusion that in collisions of N_2^+ with hydrocarbons adsorbed on surfaces, HCN^+ was formed in a heterogeneous reaction of the type of reaction 1 at incident projectile energies above 50 eV. The experimental evidence came from the observation of an increase of the ion yield at m/z 27 with the N_2^+ projectile, in comparison with the data using Ar^+ as the projectile, on three different hydrocarbon-covered surfaces (clearly on the W surface, partially on carbon and Be surfaces) and its dependence on the incident energy of the projectile ion and the surface temperature. In this connection, some further considerations may be useful.

Energy Considerations. In the gaseous phase, HCN^+ formation in reactions of N_2^+ with hydrocarbons was observed only as a minor channel (3%) in the reaction with acetylene in ICR experiments.^{21,22} No formation of HCN^+ was observed in

reactions of N_2^+ with aliphatic hydrocarbons. Product ions were only molecular and fragment hydrocarbon ions formed in charge transfer and dissociative charge transfer processes.²² Interestingly, energy calculations²³ show that, starting with ethane, reactions of N_2^+ with alkanes, leading to HCN^+ and neutral amines, are only slightly endothermic and with the increasing chain length become thermoneutral and slightly exothermic; e.g., the reaction



is exothermic in the gaseous phase by about 5 kJ/mol. However, no such reactions were observed in the gaseous phase.

Data in Figures 4 and 5 indicate that the formation of HCN^+ increased significantly at incident energies of the N_2^+ projectile above about 50 eV. This behavior suggests either that the reaction between N_2^+ and surface hydrocarbons in which HCN^+ is formed is strongly endothermic or that it has an activation barrier. It follows from studies of surface scattering of small polyatomic ions and partitioning of incident energy at surfaces^{11,24} and from theoretical model calculations²⁵ that less than 10% of the incident energy, usually about 6–8%, is transformed into internal energy of the projectile in the surface collision. If this finding is applied to the molecular N_2^+ projectile, the roughly estimated height of the putative activation barrier (or the endothermicity of the reaction) would be about 3–3.5 eV. An activation barrier that high may be connected with breaking the very strong N–N bond of the ion. The nature of the neutral reaction products of reaction 1 is not known and this prevents any conclusions concerning the endothermicity or activation barrier of the reaction. However, embedding the other nitrogen atom into the surface and formation of nitrogen-containing surface compounds from surface hydrocarbons appears to be an interesting possibility.

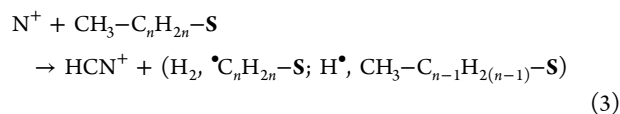
Reaction Probability. The probability of reaction 1 is difficult to estimate, because the area (“concentration”) occupied by hydrocarbons on the surface is not known. However, from the ion yields in the mass spectra, one may approximately estimate that the reaction probability is of the same order of magnitude as the survival probability of N_2^+ ions,

S_a , in collisions with the hydrocarbon-covered surfaces. More specifically, on the tungsten surface the ratio $Y(\text{HCN}^+)$ to $S_a(\text{N}_2^+)$ was 1:5, 2:3, and 1:1 at 70 eV and room temperature, 150 °C, and 300 °C, respectively. The survival probability, $S_a(\%)$, the percent ratio of the sum of the intensities of product ions to the intensity of the incident projectile beam, measured for N_2^+ on hydrocarbon-covered tungsten⁸ and beryllium⁹ surfaces led to the values of 0.0015 and 0.018, respectively. Obviously, the main process in the interaction of N_2^+ with the surfaces is neutralization of the projectile ions (at least formally analogous to electron transfer in the gaseous phase). The formation of the reaction product HCN^+ should thus very approximately occur in about one in 10^4 collisions of N_2^+ with the surface.

Reactions of N^+ . Figure 6 gives, as an example, the mass spectra of product ions from interaction of the atomic ion N^+ with hydrocarbon-covered tungsten surfaces at room temperature and heated to 150 °C, and incident energy of 70 eV. The product ions and their relative ratios were very similar to those obtained in collisions of Ar^+ and N_2^+ with tungsten, as discussed in the previous paragraph, namely at room-temperature hydrocarbon ion groups C1–C5, and to a lesser extent C6 and C7. The signal at m/z 14 corresponded to surviving N^+ , the signals of contaminants from the cleaning procedure (m/z 30–32 and 45) and alkali ions were very small. At 150 °C only hydrocarbon ion groups C1–C4 and alkali ions Na^+ and K^+ could be identified. A substantial increase of the yield at m/z 27 (arrows in Figure 6) was clearly observable. The net yield at this m/z ascribed to the formation of HCN^+ was estimated in the same way as described in the previous paragraph and the results are summarized in Figure 7. The dependence of $\Delta Y(27)$ on the incident energy of N^+ was entirely different from that one for N_2^+ collisions. It showed positive values over all incident energies that peaked at 70 eV (room temperature) or 30 eV (150 °C). Though for technical reasons values below 20 eV could not be measured, it can be expected that the decreasing part of the dependence would extend down to zero.

Similarly as with N_2^+ experiments, formation of HCN^+ in reactions with surface hydrocarbons was confirmed by experiments on hydrocarbon-covered surface of carbon, a room-temperature and heated surface of carbon-fiber composite (CFC). The formation of HCN^+ was clearly observable even with the room-temperature surface over all incident energies of N^+ (Figure 8). The yields of HCN^+ represented 30–70% of the total yield at m/z 27 and thus the result was much more convincing than in the case of the reaction after N_2^+ impact. The shape of the dependence HCN^+ yield vs incident energy of N^+ has to be regarded as very approximate and a discussion of it was deliberately avoided. More precise data from a series of repeated measurements are necessary to determine it.

It can be concluded from these observations that in collisions of N^+ with surface hydrocarbons, HCN^+ is formed in a heterogeneous reaction, probably with terminal CH_3 groups of the adsorbed hydrocarbons, of the type



Reaction 3 could be clearly observed at all incident energies of N^+ , down to 20 eV.

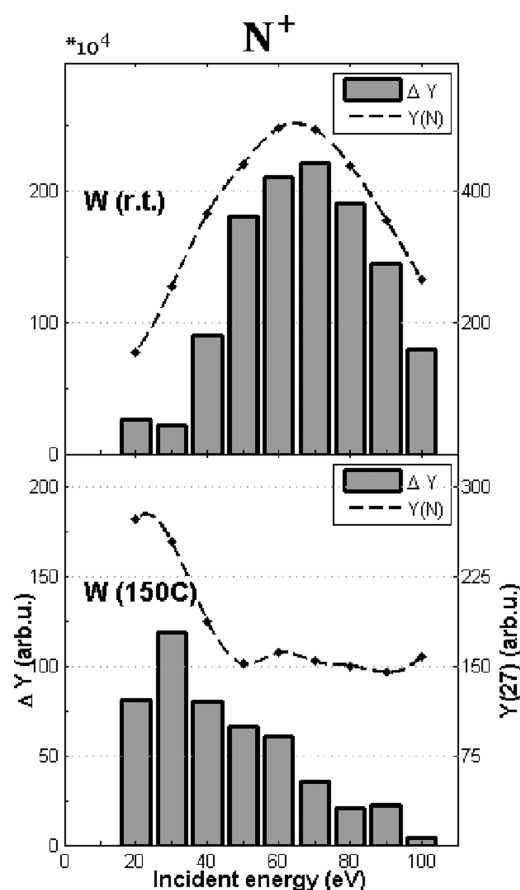
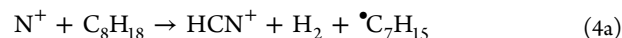


Figure 7. Net ion yield at m/z 27, ΔY , ascribed to the formation of HCN^+ (histogram), and total ion yield at m/z 27, $Y(27)$ (points), from the interaction of N^+ ions of incident energy E_{inc} with a hydrocarbon-covered tungsten surface kept at room (rt) and elevated (150 °C) temperature.

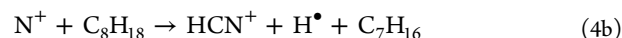
Formation of protonated hydrogen cyanide, HCNH^+ (m/z 28), could not be convincingly identified in the mass spectra.

Energy Considerations. Reactions of N^+ with lower hydrocarbons in the gaseous phase giving HCN^+ are exothermic and HCN^+ represents about 10% of the products with CH_4 , C_2H_2 , and C_2H_4 .²² The fraction of the protonated product, HCNH^+ , is even somewhat higher forming 32% with CH_4 and 15% of the products with C_2H_4 . Starting with C_3H_8 , only hydrocarbon product ions are formed in charge transfer and dissociative charge transfer reactions.

However, energy calculations²³ show that reactions with higher alkanes in the gaseous phase are exothermic. With octane, e.g., two reactions are possible



or



giving as the neutral product either a pair hydrogen molecule–alkyl radical or hydrogen atom–alkane. The reaction exothermicities are fairly high, 201 kJ/mol for reaction 4a and 188 kJ/mol for reaction 4b. Therefore, we may assume that analogous reactions with alkyl chains bound to the surface, presumably with the terminal CH_3 groups, are likely to be exothermic, too, and to proceed readily even at low energies of N^+ ions.

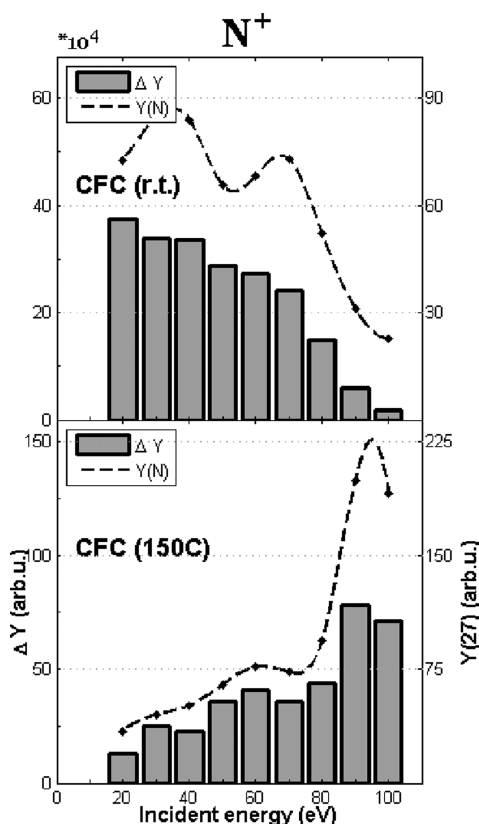


Figure 8. Net ion yield at m/z 27, ΔY , ascribed to the formation of HCN^+ (histogram), and total ion yield at m/z 27, $Y(27)$ (points), from the interaction of N^+ ions of incident energy E_{inc} with a hydrocarbon-covered surface of carbon-fiber composite (CFC) kept at room (rt) and elevated (150 °C) temperature.

Reaction Probability. Similarly as with N_2^+ , the signals corresponding to the yields of HCN^+ in the mass spectra are comparable to the total yield of product ions. The survival probability $S_a(\text{N}^+)$ on room-temperature tungsten surfaces, as estimated from the correlation between S_a and ionization energy,⁸ should be about 0.005. This leads to similar values of the reaction probability of the heterogeneous reactions N^+ –surface hydrocarbons as for the reaction with N_2^+ , i.e., of the order of about one in 10^4 collisions of the N^+ ion with the surface, the main process at the surface being incident ion neutralization.

CONCLUSIONS

A significant increase of the ion yield at m/z 27 in collisions of N_2^+ and N^+ ions with surfaces covered by adsorbed hydrocarbons, not observed in analogous collisions of Ar^+ ions, was ascribed to heterogeneous reaction between N_2^+ or N^+ and surface hydrocarbons leading to HCN^+ formation.

In the case of N^+ , the formation of HCN^+ was clearly observed, after subtraction of the hydrocarbon background, on hydrocarbon-covered surfaces of tungsten and carbon (CFC) at room and elevated (150 °C) surface temperatures for all incident energies between 20 and 100 eV, implying that the reaction is likely to occur even at very small energies of the N^+ ions.

In the case of N_2^+ , the formation of HCN^+ was observed on hydrocarbon-covered surfaces of tungsten at all surface temperatures (room temperature, 150 °C, and 300 °C) and on surfaces of carbon and beryllium at some surface

temperatures, in all cases the signal increased above background at incident energies above about 50 eV. This suggested endothermicity or an activation barrier of the heterogeneous reaction of about 3–3.5 eV. The main process in the interaction of N_2^+ or N^+ with hydrocarbons on the surfaces is incident ion neutralization; with both nitrogenous ions the formation of HCN^+ may be very approximately estimated to occur in about one in 10^4 surface collisions.

Among the scarce information on heterogeneous processes relevant to planetary atmospheres, the formation of HCN^+ in reactions of N^+ and N_2^+ and surface hydrocarbons appears to be the first description of such heterogeneous processes with nitrogenous ions. However, the estimation of a possible relevance of the reactions to astrophysical systems requires caution. The reaction of N^+ with surface hydrocarbons is very probably exothermic and likely to occur even with ions of very small energies relevant to the conditions in interstellar space and nitrogen-containing planetary atmospheres (e.g., Titan). On the other hand, the reaction with N_2^+ appears to have a high activation barrier (or an endothermicity) estimated to about 3–3.5 eV and thus takes place only with rather energetic ions (above 50 eV) whose presence in the astrophysical systems mentioned above is unlikely.

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Notes

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REFERENCES

- (1) Tomasko, M. G. Rain, Winds and Haze during the Huygens Probe's Descent to Titan's Surface. *Nature* **2005**, 438, 765–778.
- (2) Cravens, T. E.; Robertson, I. P.; Waite, J. H., Jr.; Yelle, R. V.; Kasprzak, W. T.; Keller, C. N.; Ledvina, S. A.; Niemann, H. B.; Luhmann, J. G.; McNutt, R. L.; et al. Composition of Titan's Ionosphere. *Geophys. Res. Lett.* **2006**, 33, L07 105.
- (3) Vuitton, V.; Dutuit, O.; Balucani, N.; Smith, M. A. In *Titan*; Müller-Wodarg, I. C. F.; Caitlin, A. G.; Lellouch, E.; Cravens, T. E., Eds.; Cambridge University Press: Cambridge, U.K., 2013.
- (4) Dutuit, O.; Carrasco, N.; Thissen, R.; Vuitton, V.; Alcaraz, C.; Pernot, P.; Balucani, N.; Casavecchia, P.; Canosa, A.; Le Picard, S.; et al. Critical Review of N , N^+ , N_2^+ , N_2^{+2} and N_2^{+2} Main Production Processes and Reactions of Relevance to Titan's Atmosphere. *Astrophys. J., Suppl. Ser.* **2013**, 220, 20–65.
- (5) Tomasko, M. G.; Doose, L.; Engel, S.; Dafoe, L. E.; West, R.; Lemmon, M.; Karkoschka, E.; See, C. A Model of Titan's Aerosols Based on Measurements Made inside the Atmosphere. *Planet. Space Sci.* **2012**, 56, 669–707.
- (6) Israel, G.; Szopa, C.; Raulin, F.; Cabane, M.; Niemann, H. B.; Atreya, S. K.; Bauer, S. J.; Brun, J. F.; Chassefière, E.; Coll, J. P.; et al. Complex Organic Matter in Titan's Atmospheric Aerosols from in Situ Pyrolysis and Analysis. *Nature* **2005**, 438, 796–799.
- (7) Coll, P.; Navarro-González, R.; Szopa, C.; Poch, O.; Ramírez, S. I.; Coscia, D.; Raulin, F.; Cabane, M.; Buch, A.; Isra, G. Can Laboratory Tholins Mimic the Chemistry Producing Titan's Aerosols?

A Review in Light of ACP Experimental Results. *Planet. Space Sci.* **2013**, *77*, 91–103.

(8) Herman, Z.; Žabka, J.; Pysanenko, A. Correlations between Survival Probabilities and Ionization Energies of Slow Ions Colliding with Room-Temperature and Heated Surfaces of Carbon, Tungsten, and Beryllium. *J. Phys. Chem. A* **2009**, *113*, 14838–14834.

(9) Herman, Z.; Žabka, J.; Pysanenko, A. Survival Probability of Slow Ions Colliding with Room-Temperature and Heated Surfaces of Beryllium. *Mol. Phys.* **2012**, *110*, 1669–1673.

(10) Roithová, J.; Žabka, J.; Dolejšek, Z.; Herman, Z. Collisions of Slow Polyatomic Ions with Surfaces: Dissociation and Chemical Reactions of CD_5^+ , CD_4^+ , and CD_3^+ and their Isotopic Variants on Room-Temperature and Heated Carbon Surfaces. *J. Phys. Chem. B* **2002**, *106*, 8293–8301.

(11) Herman, Z. Collisions of Slow Polyatomic Ions with Surfaces: The Scattering Method and Results. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 1360–1372.

(12) Keim, A.; Rasul, B.; Endstrasser, N.; Scheier, P.; Märk, T. D.; Herman, Z. Interaction of Small Hydrocarbon Ions and Ar^+ with Carbon-Fiber-Composite Surfaces at Room Temperature. *Int. J. Mass Spectrom.* **2011**, *306*, 204–209.

(13) Cooks, R. G.; Ast, T.; Mabud, M. A. Collisions of Polyatomic Ions with Surfaces. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209–266.

(14) Kang, H.; Yang, M. C.; Kim, K. D.; Kim, K. Y. Reactive Scattering of Cs^+ from Chemisorbed Molecules on a $\text{Ni}(100)$ Surface. *Int. J. Mass Spectrom. Ion Processes* **1998**, *174*, 143–154.

(15) Luo, H.; Miller, S. A.; Cooks, R. G.; Pachuta, S. J. Soft Landing of Polyatomic Ions for Selective Modification of Fluorinated Self-Assembled Monolayer Surfaces. *Int. J. Mass Spectrom. Ion Processes* **1998**, *174*, 193–217.

(16) Lancaster, G. M.; Rabalais, J. W. Chemical Reactions of N_2^+ Ion Beams with First-Row Transition Metals. *J. Phys. Chem.* **1979**, *83*, 209–212.

(17) Heiland, W. The Interaction of Molecular Ions with Surfaces. In *Low Energy Ion-surface Interaction*; Rabalais, J. W., Ed.; Wiley: New York, 1994; p 313 (see also references therein).

(18) Mair, C.; Fiegele, T.; Biasioli, F.; Herman, Z.; Märk, T. D. Surface-Induced Reactions of Acetone Cluster Ions. *J. Chem. Phys.* **1999**, *111*, 2770–2778.

(19) Peterson, J. R.; Moseley, J. T. Time-of-Flight Determination of Lifetimes of the $\text{N}_2^+(\text{A}^2\Pi_u)$ Meinel Band System. *J. Chem. Phys.* **1973**, *58*, 172–177.

(20) Nicolas, C.; Alcaraz, C.; Thissen, R.; Vervloet, M.; Dutuit, O. Dissociative Photoionization of N_2 in the 24–32 eV Photon Energy Range. *J. Phys. B-At. Mol. Opt. Phys.* **2003**, *36*, 2239–2251.

(21) McEwan, M. J.; Anicich, V. G. Ion–Molecule Reactions Relevant to Titan's Atmosphere. *Int. J. Mass Spectrom. Ion Processes* **1998**, *172*, 209–219.

(22) Anicich, V. G. *An Index of Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics*; JPL Publication 03-19; Jet Propulsion Laboratory: Pasadena, CA, 2003; p 299.

(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1.

(24) Žabka, J.; Dolejšek, Z.; Herman, Z. Energy Partitioning in Collisions of Slow Polyatomic Ions with Surfaces: Ethanol Molecular Ions on Surfaces Covered by Self-Assembled Monolayers (CF-SAM, CH-SAM, COOH-SAM). *J. Phys. Chem. A* **2002**, *106*, 10861–10869.

(25) Bosio, S. B. M.; Hase, W. L. Simulations of Energy Transfer in $\text{Cr}(\text{CO})_6^+$ Surface-Induced Dissociation. *Int. J. Mass Spectrom.* **1998**, *174*, 1–9.