LABORATORNÍ PŘÍSTROJE A POSTUPY

HETEROGENEOUS REACTIONS BETWEEN NITROGEN IONS AND HYDROCARBONS ATTACHED TO SOLID SURFACES

Zdenek Herman[a,b]*, **Martina Harnisch**[b], **Lorenz Ballauf**[b], **Paul Scheier**[b]

[a] *V. Čermák Laboratory, J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Dolejškova 3, 182 23 Prague 8, Czech Republic,* [b] *Institute for Ion Physics and Applied Physics, University of Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria*
zdenek.herman@jh-inst.cas.cz

Keywords: heterogeneous reactions, nitrogen ions, hydrocarbon surfaces, HCN^+ formation

Introduction

The successful Cassini-Huygens mission to Saturn brought large amount of excellent information on this part of the planetary system, on the planet and on several of its moons[1].

The Huygens lander provided valuable data on the moon Titan, among others, on the composition of its atmosphere and ionosphere[2]. Titan atmosphere belongs to nitrogen-rich planetary systems, being composed mostly of molecular nitrogen (above 95 %) with 2–5 % of methane (depending on the altitude), and a small amount of more complex hydrocarbons, traces of nitriles and oxygen compounds[3]. The transmitted data also pointed out the important role of nitrogen chemistry in the upper atmosphere[4]. The data on gas-phase reactions relevant to Titan's atmosphere are plentiful and have been summarized in several recent reviews[4,5].

However, the transmitted data also showed a yellowish haze ascribed to aerosols in Titan's atmosphere[2,6]. Only the elemental composition of these aerosols, referred to as "tholins", is known from the pyrolytic analysis experiment aboard the spacecraft: they are composed from carbon, hydrogen and some nitrogen[7]. Several attempts have been made trying to synthesize in the laboratory aerosols of similar properties as tholins[8], but their character remains to be still unknown. While laboratory data for the gas-phase reactions applicable to the description of Titan's atmosphere and ionosphere are plentiful, there has been virtually no information on possible gas-phase – surface heterogeneous processes relevant to the problem. Faraday discussions in 2014 have been dedicated to astrophysics of heterogeneous processes with dust and, ice and gas in interstellar space[9], but interstellar space is quite different from planetary atmospheres.

In our studies of ion-surface collisions between nitrogen ions and metal surfaces covered with hydrocarbons[10,11], we obtained – in fact as a byproduct of these experiments – information on heterogeneous ion-surface chemical reactions in these systems which may be of interest to astrophysics. Having established first that the reactions were not influenced by the underlying metal surface (tungsten, beryllium, carbon) and being solely due to interaction of the nitrogen ions with the hydrocarbons adsorbed on the surface, we realized that we may have an effective way of investigating heterogeneous reactions of ions relevant to the processes of importance in Titan's ionosphere. Hydrocarbons are, of course, not the mysterious tholins, but they may serve as the first approximation to them.

In our experiments[10,11] we studied impact of argon ions and nitrogen ions N^+ and N_2^+, and NH^+ on surfaces of tungsten, crystalline beryllium, and carbon (carbon-fiber composite) covered by a hydrocarbon layer kept at room temperature, and at 150 °C, and 300 °C. The range of incident energies of the ions was 20–100 eV. In all these experiments, a series of ion-surface reaction was observed, in particular, however, an unusual increase of m/z 27, in comparison with the data obtained with Ar^+ impact, indicating the formation of HCN^+ as the chemical reaction product. The data, corrected for the contribution of $C_2H_3^+$ from collisions with the non-reactive Ar^+, were plotted in dependence on the incident energy.

Experimental

The tandem mass spectrometer apparatus on which the experiments were carried out, was the Innsbruck BESTOF, described several times earlier[10-12]. Briefly (Fig. 1), projectile ions were produced in a Nier-type ions source by electron ionization, extracted from the ionization region and accelerated to 3 keV for mass and energy analysis in the double-focusing two-sector-field mass spectrometer. They were then decelerated to the desired incident energy to impact under the angle of 45° on the solid target. The energy spread of the incident beam was about 0.5 eV (full width at half maximum). A fraction of the product ions from the surface collisions was collected at the scattering angle of 46° after passing through a 1 mm aperture, and subjected to a pulsed deflection-and-acceleration field that initiated the time-of-flight analysis. This was carried out in a linear time-of-flight (TOF) mass spectrometer with an approximately 80 cm long flight tube. The mass-selected ions were then detected on a dou-

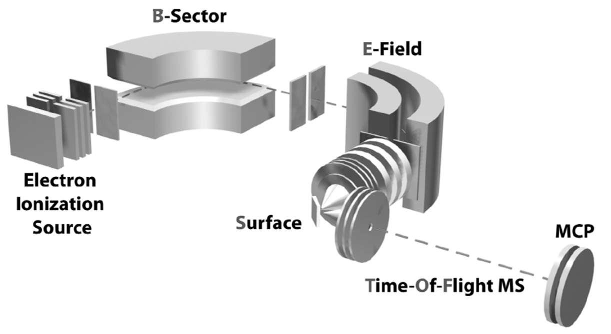

Fig. 1. Schematic view of the tandem apparatus BESTOF

ble-stage multi-channel plate connected to a multi-channel scaler and a computer.

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[14]. The ion current hitting the surface was about 400 pA for the molecular ions and about 5–10 % of it for the fragment ions. Mass spectra from collisions with Ar^+ were recorded for all temperatures and incident energies together with mass spectra of the investigated ions N^+, N_2^+, and NH^+. The product ion intensities were evaluated by integrating the areas under the respective peaks. Both the reaction product HCN^+ and a contribution from background ($C_2H_3^+$) contribute to the investigated m/z 27. To subtract the hydrocarbon contribution, the mass spectra with Ar^+ and with N^+, N_2^+, and NH^+ (N) were mutually compared at all incident energies and all sample temperatures measured, and the ratio $F_{Ar} = (Y[27]/\ Y[29])_{Ar}$ was determined from the Ar^+ mass spectra. The portion of the ion yield at m/z 27 in the mass spectra with the nitrogen ions, corresponding to hydrocarbon sputtering, was then calculated as $Y[27]_{CH,\ N} = F_{Ar}\ Y[29]_N$, and subtracted from the total ion yield at m/z 27 (m/e 29 is a background ion, mostly $C_2H_5^+$). The net yield at m/z 27, ascribed to the formation of HCN^+, was then $Y(HCN^+) = \Delta Y(27)_N = Y(27)_N - Y(27)_{CH,N.}$

Results and discussion

Influence of the underlying substrate. In order to check, if the underlying conducting surface influences the reactions of the surface hydrocarbon layer, reactions of N^+ and N_2^+ leading to HCN^+ were investigated on tungsten, beryllium, and carbon (carbon-fiber composite NB-31) surfaces at several surface temperatures over the incident energy range 20–100 eV[10,11]. In all cases the results were within the experimental error the same, indicating that the underlying conducting surface has negligible effect on the reactions in the hydrocarbon layer on the surface.

Reactions of N^+. Fig. 2 gives as an example mass spectra of product ions from collisions of Ar^+ with hydrocarbons adsorbed on a tungsten sample. Fig. 3 then gives the mass spectra from collisions of N^+ with the hydrocarbon layer on tungsten. The m/z 27 (HCN^+ + $C_2H_3^+$) is denoted by arrows. The ordinate scales are arbitrary and not comparable. The spectrum of product ions from collisions of Ar^+ at room temperature (Fig. 2a) showed mostly aliphatic hydrocarbon species sputtered from the hydrocarbon-covered surface. 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), $C_4H_n^+$ (m/z 53–57), and to a lesser extent $C_5H_n^+$ (m/z 65–69), $C_6H_n^+$ (m/z 77–81), $C_7H_n^+$ (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 (Fig. 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(K^+) and 41 (partly isotope of K^+) appeared in the spectrum (the alkali ions presumably come from alkali in the tungsten sheet). The mass spectrum at 300 °C (Fig. 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

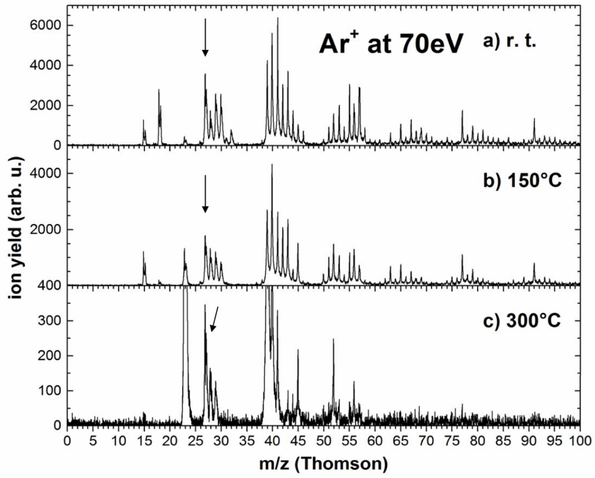

Fig. 2. **Mass spectra of product ions from collisions of Ar^+ with a hydrocarbon-covered tungsten surface kept at (a) room temperature (r.t.); (b) 150 °C; (c) 300 °C; incident energy of the Ar^+ ions was 70 eV.** Position of m/z 27 is denoted by an arrow

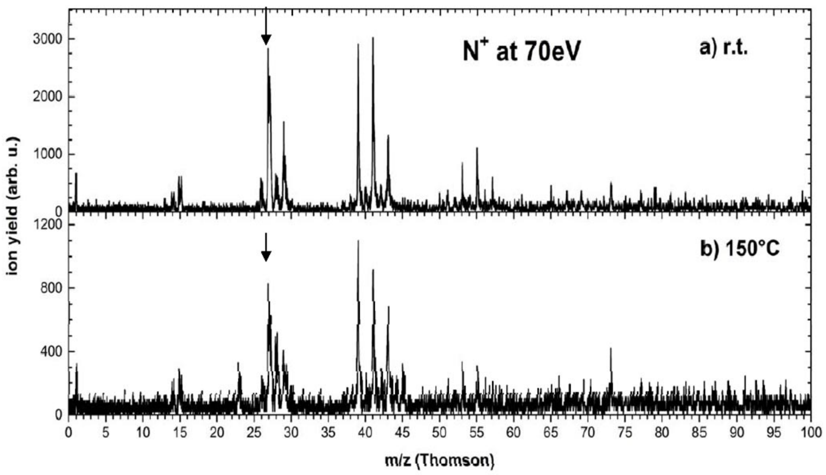

Fig. 3. **Examples of mass spectra of product ions from collisions of N^+-ions with hydrocarbon-covered tungsten surface kept at room temperature (r.t.) and 150 °C, incident energy of N^+ ions was 70 eV**. Position of m/z 27 is denoted by an arrow

tungsten or its compounds) was observed in any of the experiments. Mass spectra from collisions with N^+ (Fig. 3) show small amount of sputtered hydrocarbon ions and a prominent peak at m/z 27 composed of the hydrocarbon background $C_2H_3^+$ and the reaction product HCN^+. The data were treated as described above and Fig. 4 shows the values of ΔY and Y in dependence on the incident energy. The yield of HCN^+ represented 30–70 % of the total m/z 27 yield. The data show positive values over all incident energies. Though due to the experimental limitations it was not possible to measure values below the incident energies of 20 eV, it can be expected that the decreasing part of the energy dependence would extend down to zero. Thus one may conclude from these measurements that in N^+ – hydrocarbon collisions HCN^+ is formed in a heterogeneous reaction, presumably with the terminal groups CH_3 of the adsorbed hydrocarbons, of the type (**S**- for surface)

$$N^+ + CH_3\text{-}C_nH_{2n}\text{-}\mathbf{S} \rightarrow HCN^+ + \\ + (H_2, {}^{\bullet}C_nH_{2n}\text{-}\mathbf{S} / H^{\bullet}, CH_3\text{-}C_{n-1}H_{2(n-1)}\text{-}\mathbf{S}) \qquad (1)$$

In the gaseous phase, reactions of N^+ with lower hydrocarbons (C_1-C_2) are exothermic and represent about 10% of the reaction products[15]. Starting with propane, however, the reaction products observed are only hydrocarbon ions formed in charge transfer and dissociative charge transfer reactions, though energy calculations[16] indicate that reactions with higher alkanes in the gaseous phase are exothermic with exothermicities of 190–200 kJ/mol (ref.[10]). Therefore, one may assume that analogous reactions with alkyl chains bound to the surface are likely to be exothermic and proceed readily even at low incident energies of the N^+ ions. The implications for astrophysics and upper atmosphere of Titan is that the heterogeneous reaction of N^+ may be of importance even for thermal N^+ ions, though the estimation of a possible relevance to astrophysical systems requires extreme caution.

Reactions of N_2^+. Fig. 5 summarizes mass spectra from collisions of N_2^+ with hydrocarbons on the surface of tungsten at three different temperatures (room temperature,

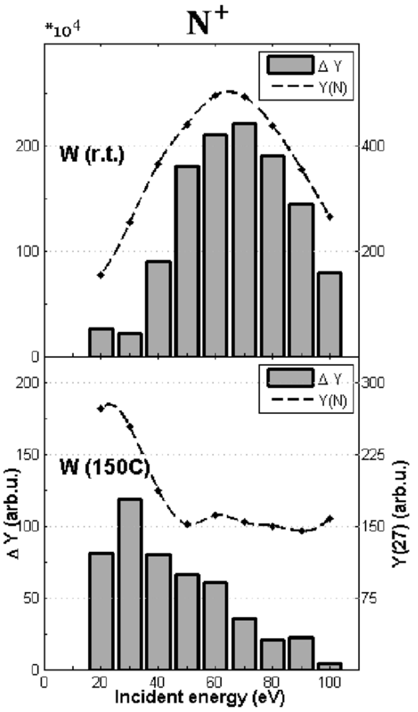

Fig. 4. **Corrected ion yield at m/z 27, Δ*Y*, ascribed to the formation of HCN^+ (histogram), and total ion yield at m/z 27, *Y* (27), (points) from the interaction of N^+ ions of incident energy E_{inc} with a hydrocarbon-covered tungsten surface kept at room (r.t.) and elevated (150 °C) temperature**

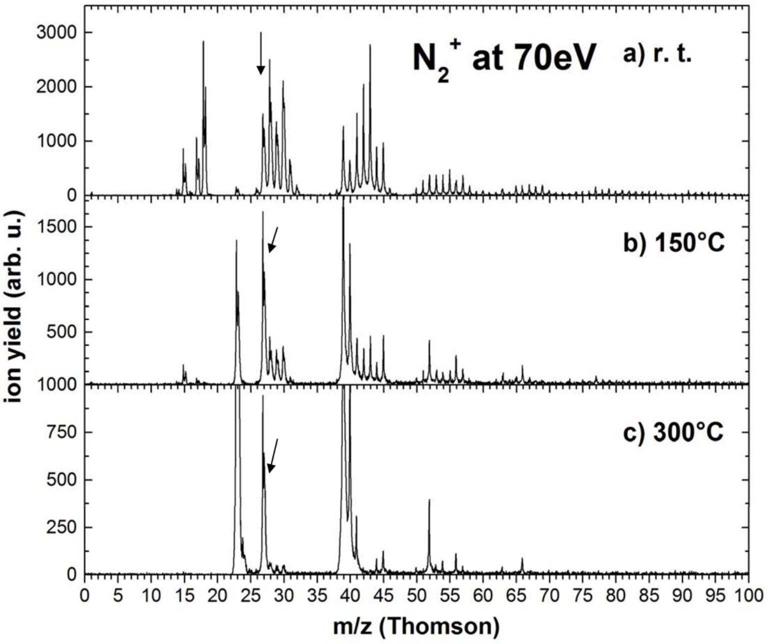

Fig. 5. **Mass spectra of product ions from collisions of N_2^+ with a hydrocarbon-covered tungsten surface kept at (a) room temperature (r.t.); (b) 150 °C; (c) 300 °C; incident energy of the N_2^+ ions was 70 eV.** Position of m/z 27 is denoted by an arrow

150 °C, and 300 °C) and incident energy of 70 eV. At room temperature the spectrum shows contributions of sputtered hydrocarbon ions C_1– C_6. At 150 °C, the relative amounts of hydrocarbon ions decreases and alkali ions Na^+ and K^+ appear in the spectrum, and at 300 °C the alkali ions dominate the spectrum. Plotting *ΔY* and *Y* then gives an entirely different picture than with the projectile N^+ (Fig. 6): HCN^+ appears only at incident energies above about 60 eV, within the experimental error there is no HCN^+ formation below this value. This observation leads us to the conclusion that the heterogeneous reaction between N_2^+ and surface hydrocarbons leading to HCN^+ occurs only at incident energies above about 50 eV and that the reaction below this value is either endothermic or has a high activation barrier.

It followed from our earlier studies of energy partitioning in collisions of small polyatomic ions with surfaces[18,19] and from theoretical model calculations[20] that about 6–8 % of the incident ion energy was converted into internal energy of the projectile ion. If we apply this finding to our problem of N_2^+ – surface hydrocarbon collisions, a roughly estimated endothermicity (or the height of the putative activation barrier) would be about 3–3.5 eV. As the nature of the neutral reaction products is not known, these conclusions are, of course, highly speculative.

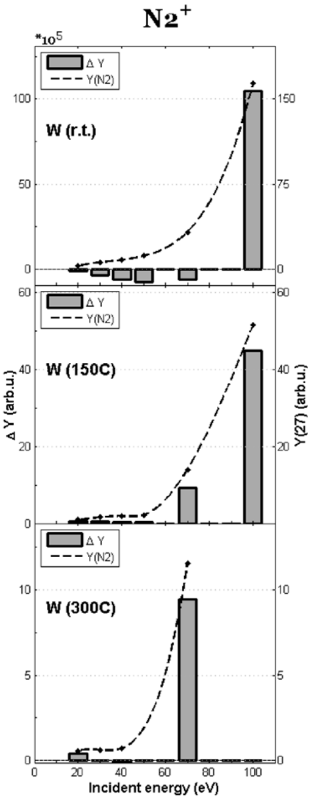

Fig. 6. **Corrected ion yield at m/z 27, Δ*Y*, ascribed to the formation of HCN^+ (histogram), and total ion yield at m/z 27, *Y*(27), (points) from the interaction of N_2^+ ions of incident energy E_{inc} with a hydrocarbon-covered tungsten surface kept at room (r.t.) or elevated (150 °C, 300 °C) temperature**

In the gaseous phase, HCN^+ formation between N_2^+ and hydrocarbons was observed only as a minor channel (3 %) in the reaction with acetylene[15,17], no formation of HCN^+ was observed with aliphatic hydrocarbons. Interestingly, energy calculations[16] suggest that, beginning with ethane, reactions of N_2^+ leading to HCN^+ and neutral amines are only slightly endothermic and become exothermic with increasing hydrocarbon chain length. However, no such reactions were observed in the gaseous phase.

Reactions of NH^+. Fig. 7 shows examples of mass spectra from collisions of NH^+ with hydrocarbons on the surface of tungsten at two surface temperatures (room-temperature and 300 °C)[11]. At room temperature the spectrum showed only sputtered ions of hydrocarbons at m/z 15 (CH_3^+), 27–30 ($C_2H_3^+$ – $C_2H_6^+$), and 39–43 ($C_3H_3^+$-$C_3H_7^+$) and traces of alkali ions at m/z 23 (Na^+) and a contribution to m/z 39 (K^+). However, the abundance of $C_2H_3^+$ at m/z 27 was consistently larger than in the spectra with incident Ar^+. At the surface temperature of 300°C, the spectrum showed large amounts of alkalis at m/z 23 (Na^+) and m/z 39 and 41 (K^+), small amounts of C_2 hydrocarbon ions at m/z 27–29, and a strong increase of the abundance of m/z 27 far beyond what one would expect from $C_2H_3^+$ (as obtained from the ratio of ion yields m/z 27/29 in the spectra of Ar^+ collisions at 300 °C).

The standard subtraction (as described above) of the hydrocarbon background at m/z 27, $Y(C_2H_3^+)$, obtained by comparing the NH^+ spectra with those from Ar^+ collisions, led to the net HCN^+ signal at this m/z. Unlike in Fig. 4 and Fig. 6, Fig. 8 shows the data presented as normalized yields, $\Delta Y = Y(27) - Y(C_2H_3^+)$ divided by the sum of all ion yields in the spectrum (excluding alkali ions Na^+ and K^+), $\Delta Y/\Sigma Y$. To indicate the difference, the values of $\Delta Y/\Sigma Y$ are given in Fig. 8 as points and not as histograms, as in Fig. 4 and 6. The curves of normalized yields of HCN^+, $\Delta Y/\Sigma Y$, in Fig. 8 indicate an increase above zero only at incident energies of NH^+ above about 40 eV. Following the earlier mentioned reasoning, this finding would imply an activation barrier or an endothermicity of the surface reaction leading to HCN^+ of about 2.4–3.2 eV.

No gas phase reactions of NH^+ with aliphatic hydrocarbons have been reported, with the exception of reactions with methane and ethylene[15].

A possible reaction

$$NH^{+\bullet} + C_7H_{16} \rightarrow HCN^{+\bullet} + H_2 + C_6H_{14} \qquad (2)$$

is exothermic by about 3 eV and thus a surface reaction between NH^+ and a terminal CH_3 group of the surface-adsorbed hydrocarbons should be likely to occur. However, reaction (*2*) may not be representative of the surface reaction and neutral products may be different e.g., “healing“ of the defect in the hydrocarbon terminal group may take place, followed by the formation of a shortened saturated hydrocarbon chain.

For instance, another possible reaction

$$NH^{+\bullet} + C_7H_{16} \rightarrow HCN^{+\bullet} + H_2 + H^\bullet + {}^\bullet C_6H_{13} \qquad (3)$$

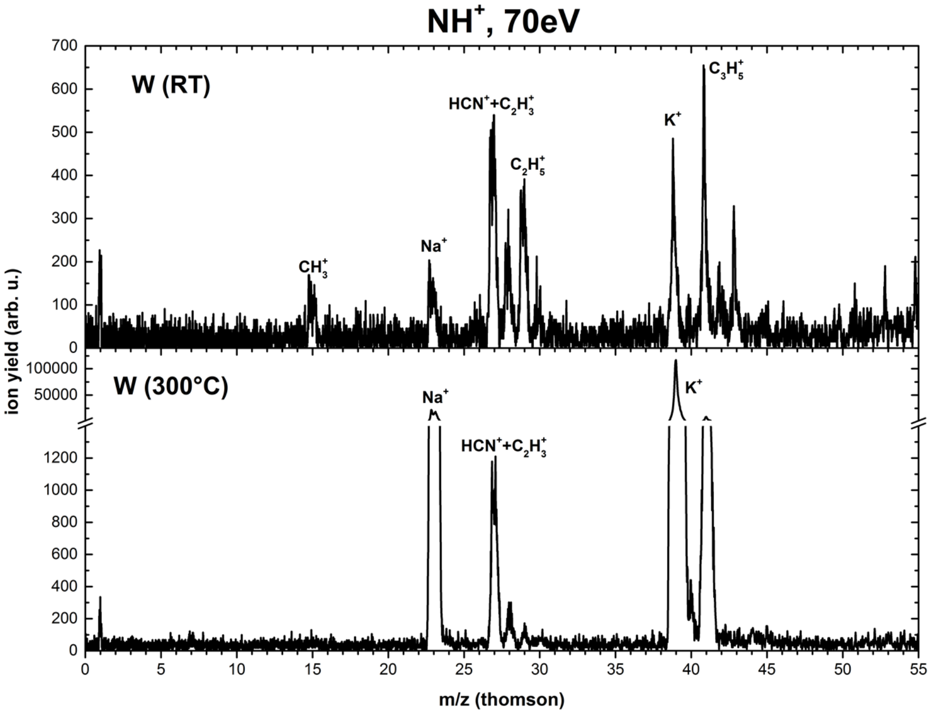

Fig. 7. **Examples of mass spectra of product ions from interactions of NH^+ with surface hydrocarbons adsorbed on the tungsten surface kept at room temperature and 300 °C.** Incident energy of the projectile ions NH^+ was 70 eV

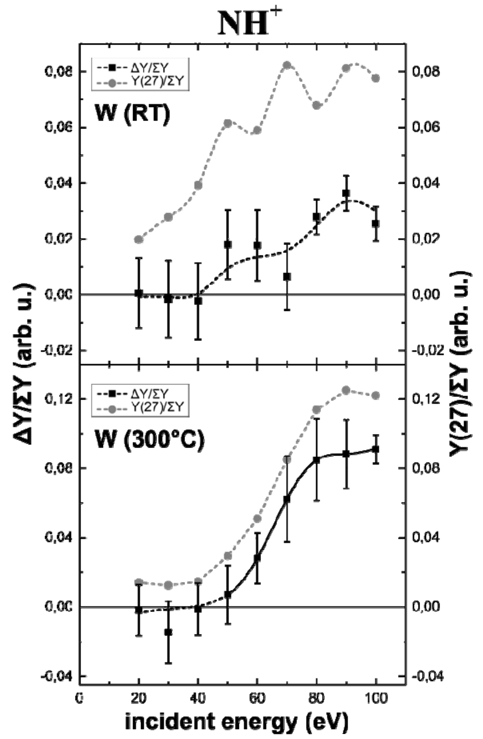

Fig. 8. **Dependence on the incident-energy of the normalized net ion yiel ds, ΔY/ΣY, of the product ion HCN^+ from collisions of NH^+ with surface hydrocarbons adsorbed on a tungsten surface kept at room temperature (RT, top) and at 300 ° C (bottom); the dashed line Y(27)/ΣY shows the total normalized yield of m/z 27 before correction for the $C_2H_3^+$ background**

is endothermic by 1.3 eV, closer to the value derived for the threshold of the surface reaction.

Conclusions

- Heterogeneous reactions between gas phase ions N^+, N_2^+, and NH^+ with hydrocarbons adsorbed on metal substrate (tungsten, beryllium, carbon), leading to HCN^+, were investigated at room surface temperature, and at elevated temperatures of the surface of 150 °C and 300 °C, and over the incident energy of the ions of 20–100 eV.
- The nature of the underlying metal surface did not influence the outcome of the reaction proving that the reaction took place only with the hydrocarbons on the surface.
- With N^+, the reaction was observed at all incident energies, down to 20 eV, and may be presumably occurring down to thermal energies of incident ions.
- With N_2^+ the reaction was observed only at incident energies above about 60eV, indicating an endothermicity or a reaction barrier of about 3–3.5 eV, as inferred form earlier studies of incident-to-internal energy conversion of small ions on hydrocarbon surfaces (6–8 % of the incident energy).
- With NH^+ the reaction was also observed only at higher incident energies, namely above about 40 eV, implying an endothermicity or an activation barrier of about 2.4–3.2 eV.
- Thus for planetary astrophysics or ionosphere of Titan only the reaction with N^+ may be of possible relevance.

We dedicate this paper to Professor Rudolf Zahradník on the occasion of his 90th birthday. One of us (Z.H.) gratefully acknowledges almost 60 years of companionship with the highly respected colleague and friend in the Institute of Physical Chemistry.

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014 –2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

REFERENCES

1. NixonC. A., et al.(24): Planet. Space Sci. (2018). DOI 0.1016/j.pss.2018.02.009 .
2. Tomasko M. G.: Nature *438*, 765 (2005).
3. Cravens T. E., Robertson I. P., Waite Jr. J. H., Yelle R. V., Kasprzak W. T., Keller C. N., Ledvina S. A., Niemann H. B., Luhmann J. G., McNutt R. L., et al.: Geophys. Res. Lett*.* *33*, L07 105 (2006).
4. Vuiton 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 2013.
5. Dutuit O., Carrasco N., Thissen R., Vuitton V., Alcaraz C., Pernot P., Balucani N., Casavecchia P., Canosa A., Le Picard S., Loison J. C., Herman Z., Žabka J., Franceschi P., Tosi P., Price S., Lavvas P.: ApJS *220*, 20 (2013).
6. Tomasko M. G., Doose L., Engel S., Dafoe L. E., West R., Lemmon M., Karkoschka E., See C. A.: Planet. Space Sci. *56*, 669 (2012).
7. 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.: Nature *438*, 796 (2005).
8. Coll P., Navarro-González R., Szopa C., Poch O., Ramírez S. I., Coscia D., Raulin F., Cabane M., Buch A., Isra G.: Planet. Space Sci. *77*, 91 (2013).
9. Faraday Discussion 168, *Astrochemistry of Dust, Ice, and Gas*, Leiden (2014).
10. Harnisch M., Keim A., Scheier P., Herman Z.*:* J. Phys. Chem A *117*, 9653 (2013).
11. Harnisch M., Scheier P., Herman Z.*:* Int. J. Mass Spectrom. *392*, 139 (2015).

12. Mair C., Fiegele T., Biasioli F., Herman Z., Märk T. D.: J. Chem. Phys. *111*, 2770 (1999).
13. Cooks R. G., Ast T., Mabud M. A.: Int. J. Mass Spectrom. Ion Proc. *100*, 209 (1999).
14. Roithová J., Žabka J., Dolejšek Z., Herman Z.: J. Phys. Chem. B *106*, 8293 (2002).
15. Anicich V. G.: *An Index of Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics*. JPL Publication 03-19: Jet Propulsion Laboratory, Pasadena 2003.
16. 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 *17*, Supplement 1 (1988).
17. McEwan M. J., Anicich V. G.: Int. J. Mass Spectrom. Ion Proc. *172*, 209 (1998).
18. Herman Z.: J. Am. Soc. Mass Spectrom. *14*, 1360 (2003).
19. Žabka J., Dolejšek Z., Herman Z.: J. Phys. Chem. A *106*, 10861 (2002).
20. Bosio S. B. M., Hase W. L.: Int. J. Mass Spectrom. *174*, 1 (1998).

Z. Herman[a,b]***, M. Harnisch**[b]**, L. Ballauf**[b]**, and P. Scheier**[b] ([a] *V. Čermák Laboratory, J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic,* [b] *Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria*): **Heterogeneous Reactions between Nitrogen Ions and Hydrocarbons Attached to Solid Surfaces**

Formation of HCN^+ in heterogeneous reactions between gas phase ions N^+, N_2^+, and NH^+ with hydrocarbons adsorbed on conducting substrates (tungsten, beryllium, carbon) was investigated at room temperature, and at elevated temperatures of 150 °C and 300 °C of the surface. The incident energy range of the ions was 20–100 eV. The reaction with N^+ was observed at all incident energies and it may be expected to occur even down to thermal energies, though this extrapolation is tentative and not confirmed by experiments. The reaction with N_2^+ was observed only at incident energies above about 60 eV, and the reaction with NH^+ at incident energies above about 40 eV, indicating an endothermicity or an activation barrier of about 3–3.5 eV (N_2^+) or 2.8–3.2 eV (NH^+). Only the reaction with N^+ may thus be of a possible relevance to astrophysics and the upper atmosphere of Titan.

Keywords: heterogeneous reactions, nitrogen ions, hydrocarbon surfaces, HCN^+ formation