Hydrocyanic Acid from Methane and Ammonia over Pt

Detection of Gas Phase Intermediates using Molecular Beam Mass Spectrometry and Threshold Ionization

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Motivation & Method

Motivation:

The platinum catalyzed formation of hydrocyanic acid from methane and ammonia is an important industrial production process. It is performed in catalytic wall reactors operated at atmospheric pressure and temperatures up to 1300°C. The extraordinary high temperatures are necessary to supply the heat for the highly endothermic reaction:

$$CH_4 + NH_3 \xrightarrow{Pt} HCN + 3H_2 \quad \Delta_r H^{1573K} = +281 kJ/mol$$

The major advantage of the process is the high HCN content of the product gas stream, reducing size and cost of recovery equipment. A drawback of the high reaction temperature are side reactions like the decomposition of ammonia into the elements and under certain conditions the formation of coke:

CH_4 → coke (catalyst deactivation, eventually $CH_x\cdot$ radicals involved)

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NH_3 → $N_2 + H_2$ (limits yield of HCN, eventually $NH_x\cdot$ radicals involved)

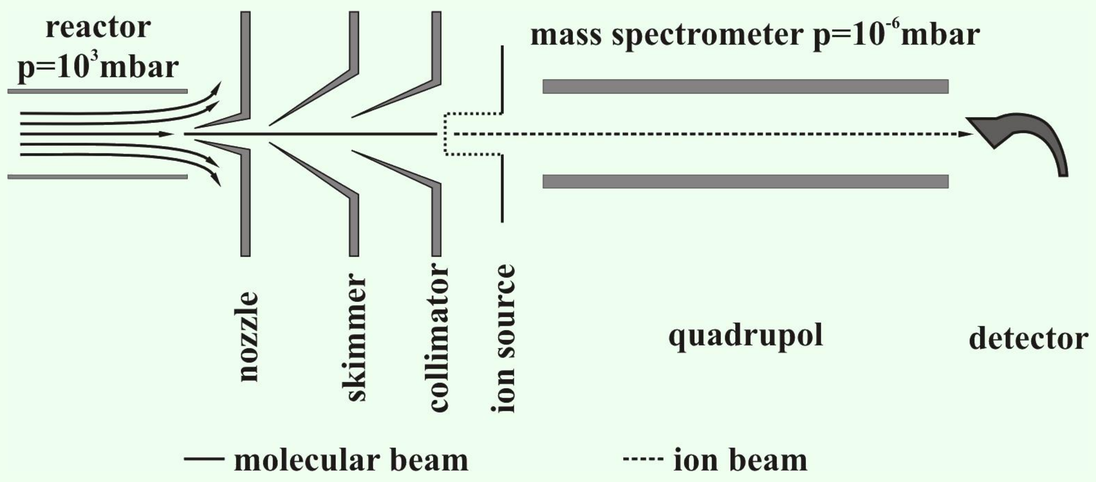
↓

$HCN + 3H_2$ → gas phase route via $CH_2NH \rightarrow HCN + H_2$ predicted[1]

Goal of our work was to investigate the gas phase chemistry in this reaction network, which is assumed to play a vital role under these conditions. Attention was paid to gas phase intermediates along the HCN formation path but also to gas phase radicals, which are possibly involved in the side reactions.

Method:

- molecular beam mass spectrometry



- in situ sampling of the gas phase via molecular beam interface
- adiabatic expansion ⇨ quenching of all gas phase species
- detection of reactive molecules X besides interfering components XY and Z by means of threshold ionization

signal at m/z (X^+) composed of:

$X + e^- \rightarrow X^+$ if $E > IP(X)$

$XY + e^- \rightarrow X^+ + Y$ if $E > AP(X^+/XY)$

$Z + e^- \rightarrow Z^+$ if $E > IP(Z)$

interference if $m/z(Z^+) = m/z(X^+)$

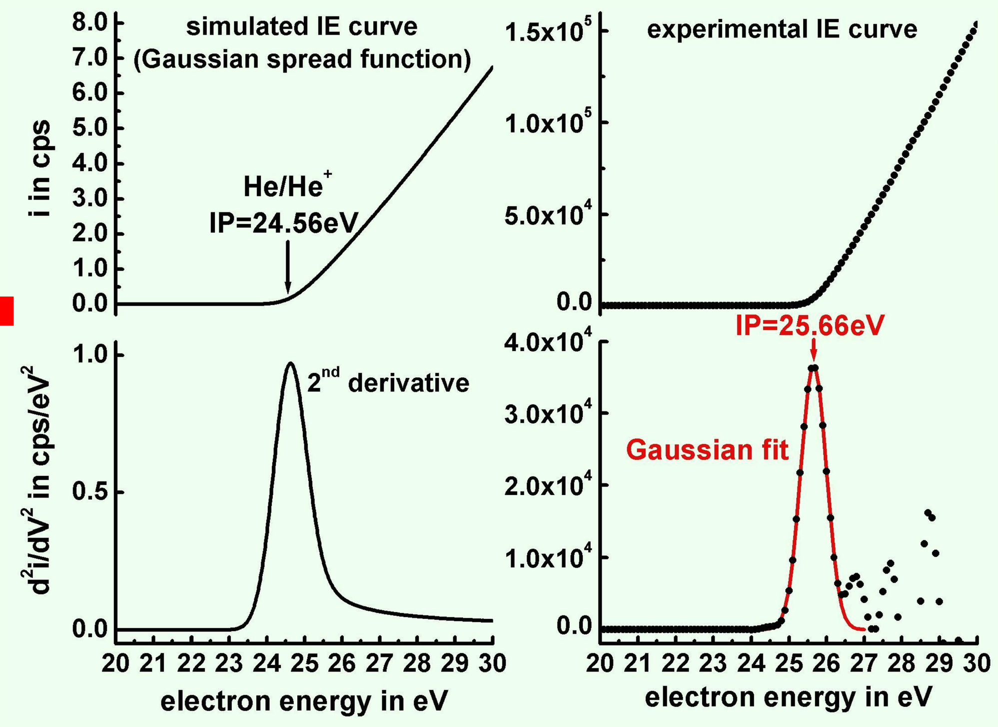
X is detected selectively if the electron energy E is higher than IP(X) but lower than $AP(X^+/XY)$ and IP(Z)

Results & Conclusions

Accuracy of Threshold Potentials

- ionizing electrons are inhomogeneous in energy
- 2nd derivative of a measured He ionization efficiency curve supplies the shape of the underlying electron energy spread function[2]

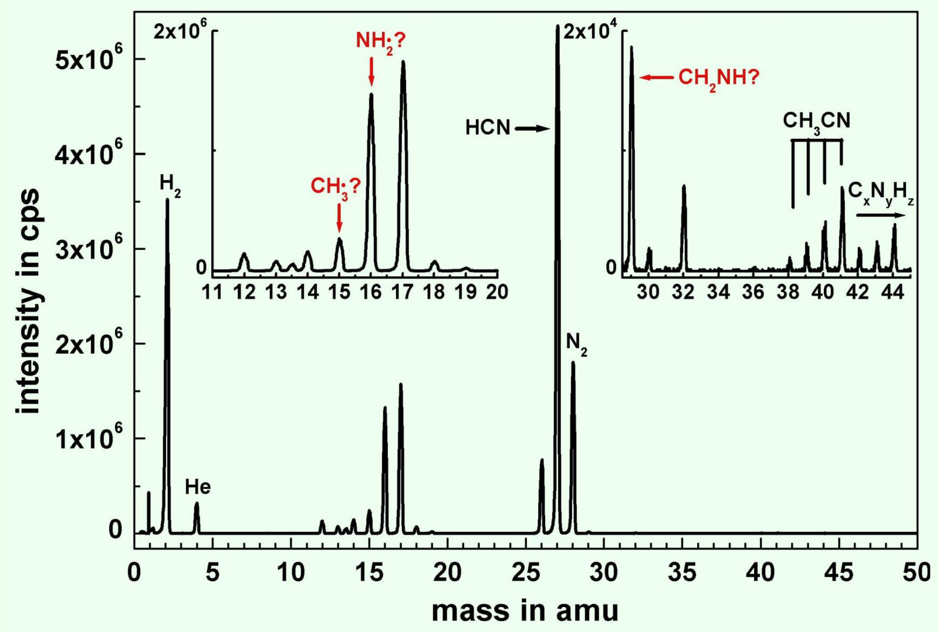
spread follows a Gaussian distribution

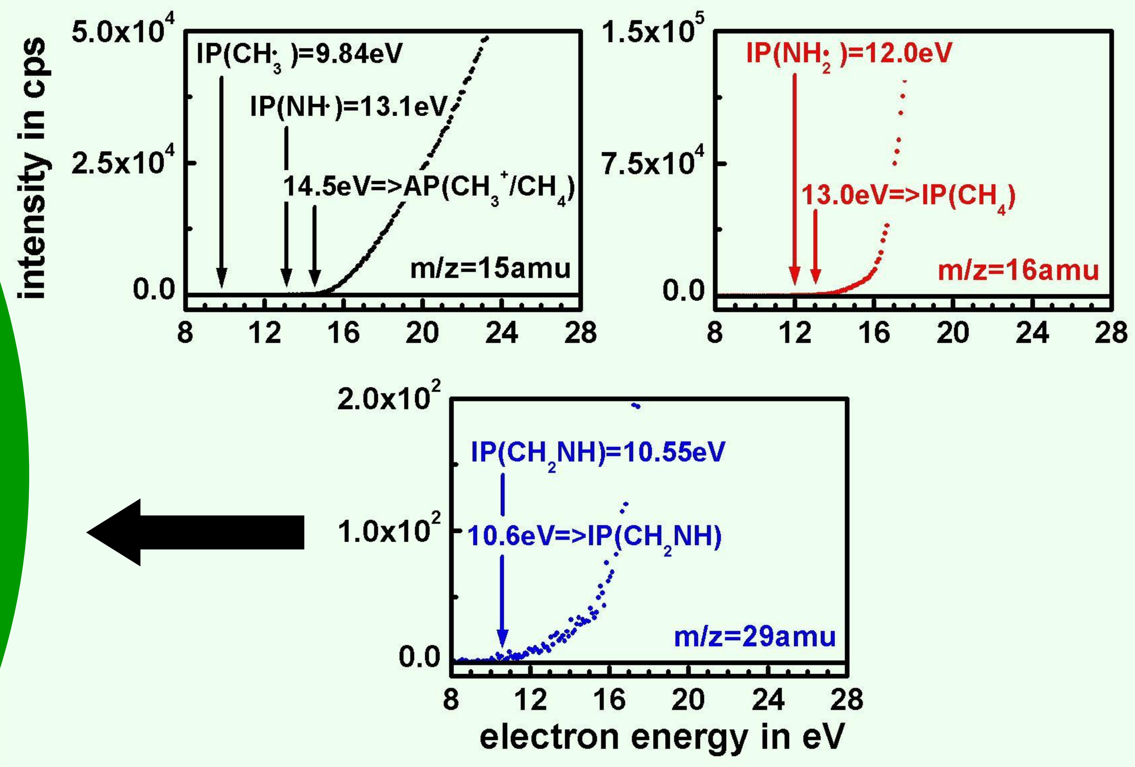


fit of $i(V) = \frac{C}{\sigma\cdot\sqrt{2\pi}} \int_{IP}^{\infty} e^{-\frac{(E-V)^2}{2\sigma^2}} (E-IP)^{1.127} dE$ to experimental IE curve supplies $\sigma = 0.28eV$ ⇨ $IP \pm 2\sigma = IP \pm 0.6eV$

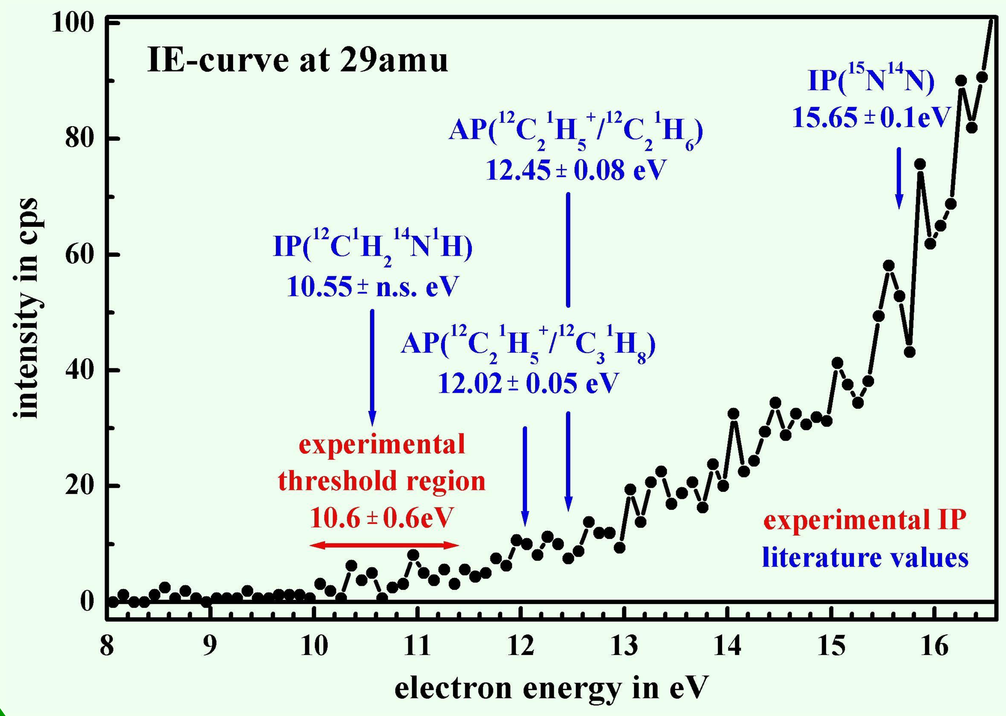
Mass Spectrum and Ionization Efficiency Curves

- peaks > 38amu indicate C-C bond formation
- possible intermediates towards coke
- detection of $CH_3\cdot$, $NH_2\cdot$ and CH_2NH requires threshold ionization technique





molecular beam mass spectrometry allows an in situ study of gas phase contributions to heterogeneous catalysis



$$CH_4 + NH_3 \xrightarrow[\text{catalyst}]{-2H_2} CH_2NH \xrightarrow[\text{gas phase}]{-H_2} HCN$$

Conclusions

- first experimental verification of CH_2NH as gas phase intermediate in the Pt mediated HCN formation ⇨ supports a theoretical prediction of Diefenbach et al.[1]
- reactive double bond ⇨ gas phase precursor for HCN but possibly also for coke formation
- gas phase radicals not detectable, either not present or too short-lived for our sampling process

References

[1]Diefenbach M.; Brönstrup M.; Aschi M.; Schröder D.; Schwarz H.; *J. Am. Chem. Soc.* 1999, *121*, 10614-10625

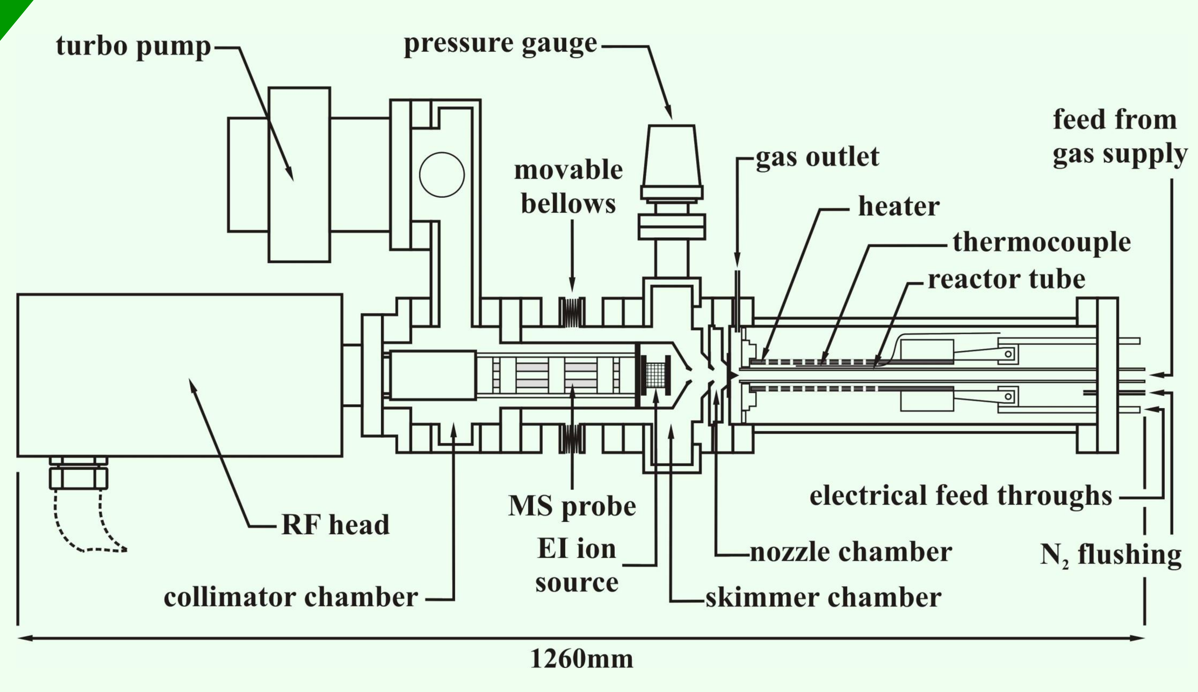
[2]Morrison J. D.; *J. Chem. Phys.* 1953, *21(10)*, 1767-1772

Experimental

Experimental Setup and Reaction Conditions

- catalytic wall reactor (Pt catalyst) at 1300°C and 1013mbar
- total gas flow = 500ml·min^{-1}, 60% NH_3, 30% CH_4, 10% He
- conversion and selectivity: ⇨ $X_{CH4}=Y_{HCN/CH4}=74\%$
- differentially pumped molecular beam interface
- QMS with threshold ionization capability

Setup Scheme



Setup Picture