

Carbon–Carbon Bond Activation in Saturated Hydrocarbons by Field-Assisted Nitrogen Fixation

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**Depanjan Sarkar
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Alkanes are the most abundant organic compounds in nature. They are readily combusted but chemically unreactive.

The stability of the chemical bonds in saturated hydrocarbons makes them generally unreactive. But the invention of processes in which carbon–hydrogen (C–H) bonds in hydrocarbons can be activated is allowing chemists to exploit organic compounds in previously unimaginable ways. NATURE/Vol 446/22 March 2007

Conversion of alkanes to functionalized compounds forms the basis for the chemical industry.

Selective activation and functionalization of alkanes is very difficult.

Organometallic catalyzed C-H bond activation was reported by Janowicz and Bergman. Although the bond dissociation energy for C-H bond is very high e.g. CH_3 –H bond dissociation energy is 432.5 kJ/mol.

Activation of C-C bonds is even more challenging because metal–hydride bonds are generally 60–100 kJ/mol stronger than metal–alkyl bonds.

The direct insertion of a metal into C-C bonds of noncyclic alkanes has not yet been reported.

Metal based functionalization of alkanes is known.

Practical challenges for the organometallic approach to hydrocarbon functionalization are more expense, toxicity and less activity of organometallic catalysts (usually palladium and platinum).

These facts make metal-free alkane transformations (“green chemistry”) highly desirable.

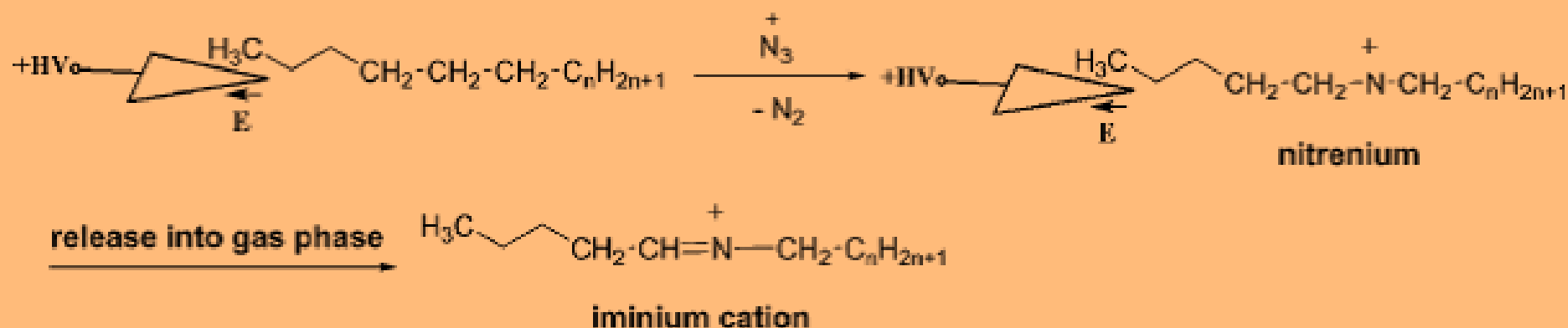
Nitrogen is an inert gas...

In this paper...

They reported a strategy for the direct insertion of nitrogen into C-C bonds of saturated alkanes to form iminium salts without involving metal species.

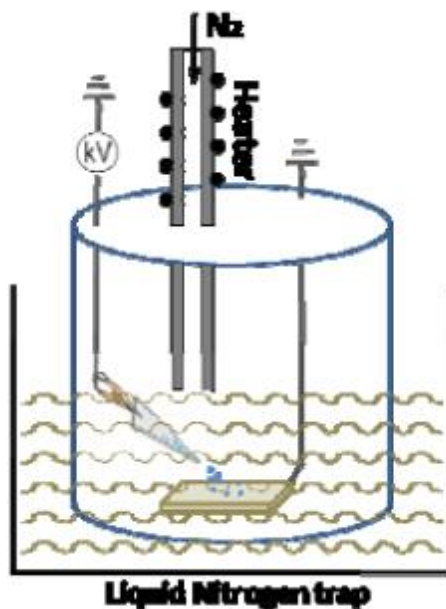
Although the reaction occurs on a very small scale but product was collected and characterized.

Scheme of the reaction



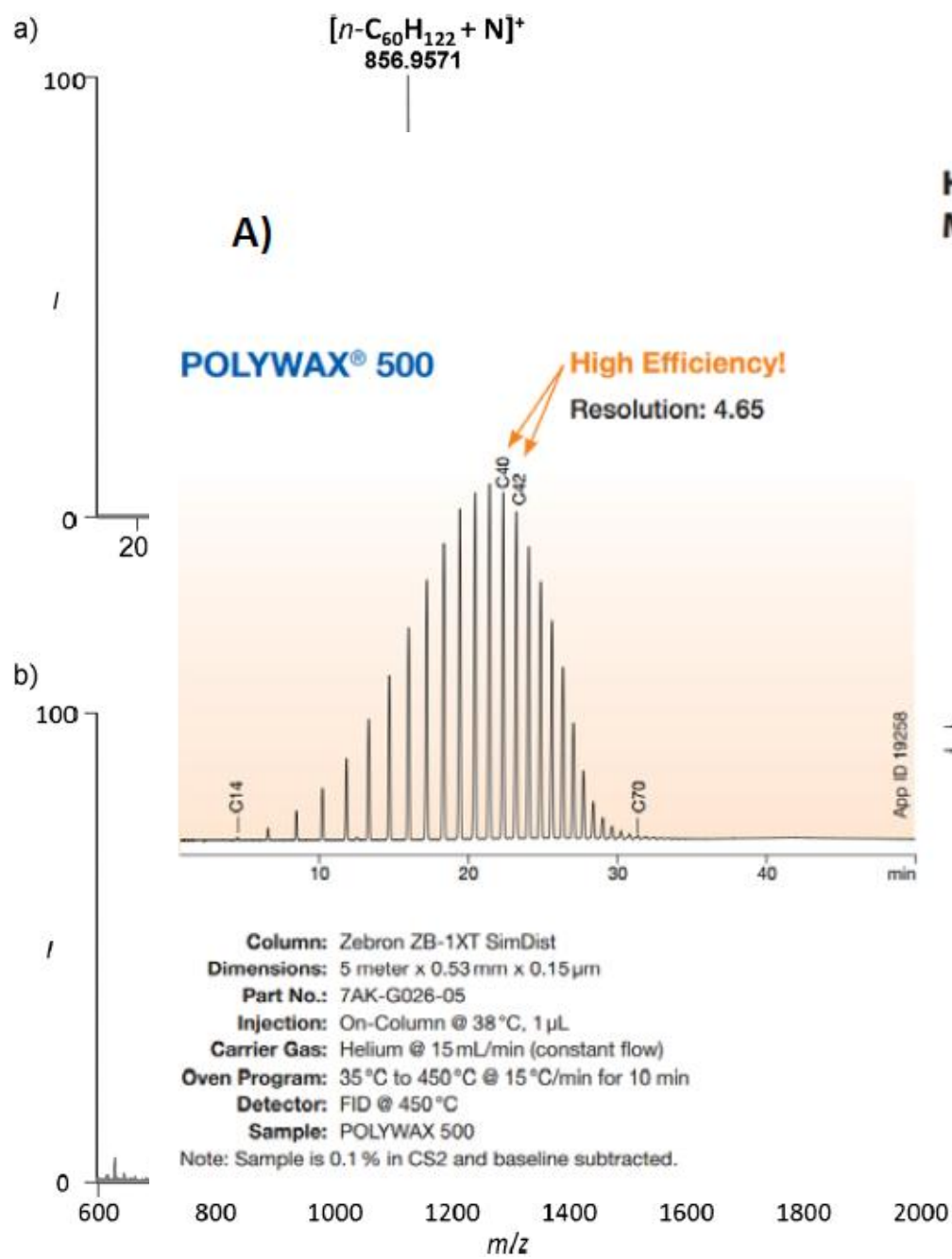
Deposited on a surface and analyzed independently

Sucked into the vacuum system of a mass spectrometer for on-line analysis.



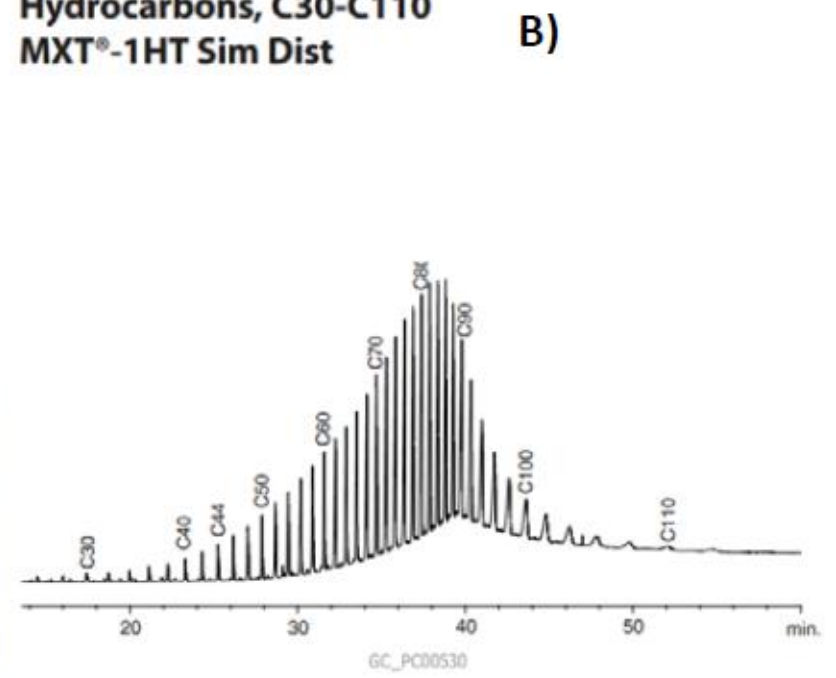
Sample collection apparatus:
the nitrogen gas stream carries the functionalized alkane

Introduction Experimental Section Results & Discussion Summary



The online analysis of the product gave

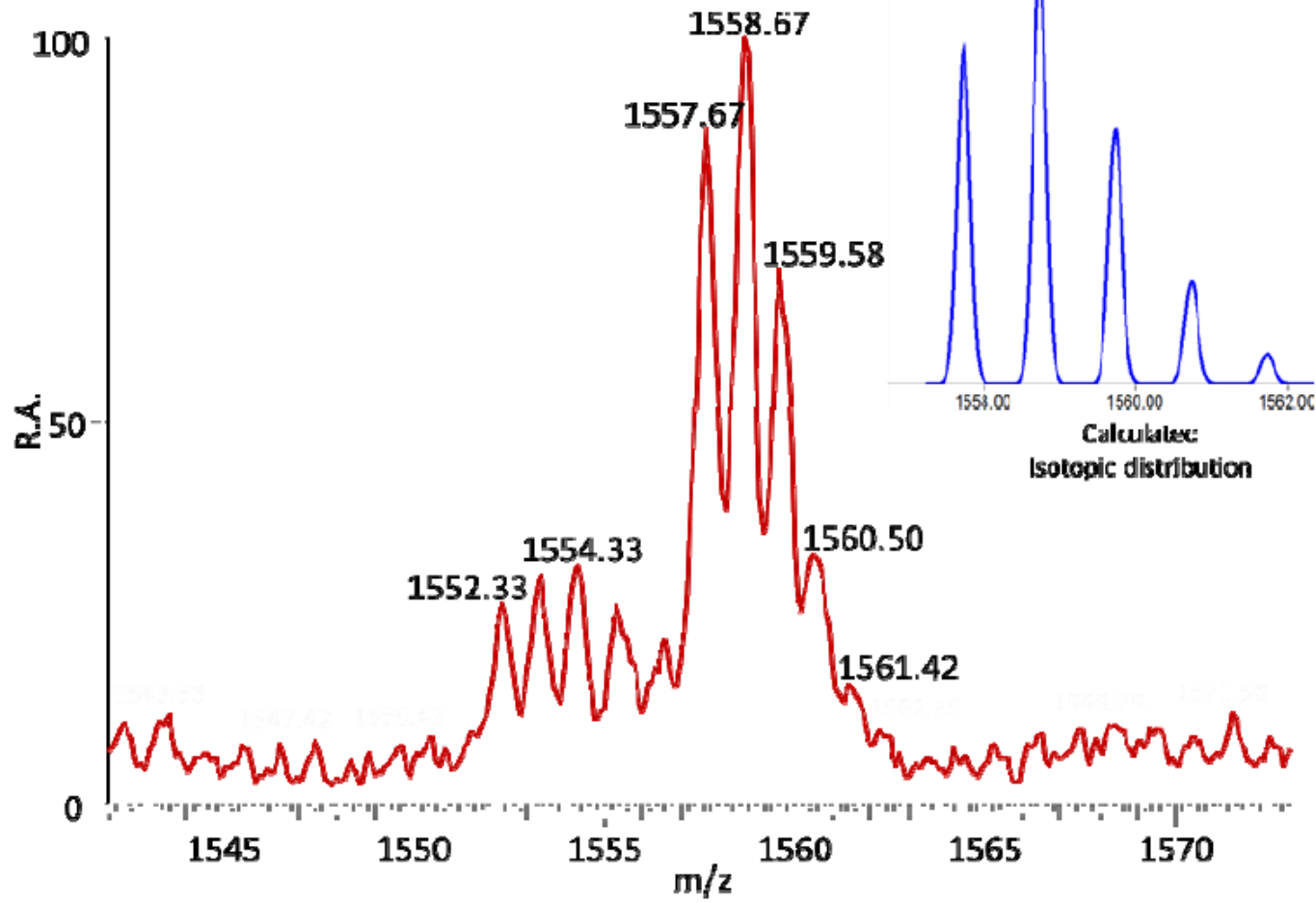
Hydrocarbons, C30-C110
MXT®-1HT Sim Dist



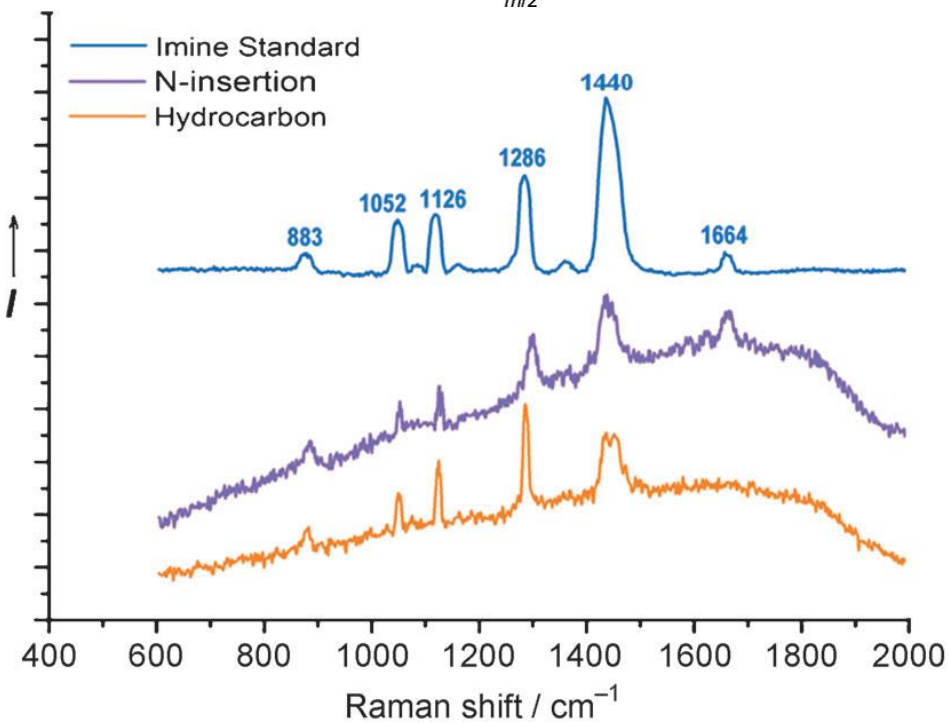
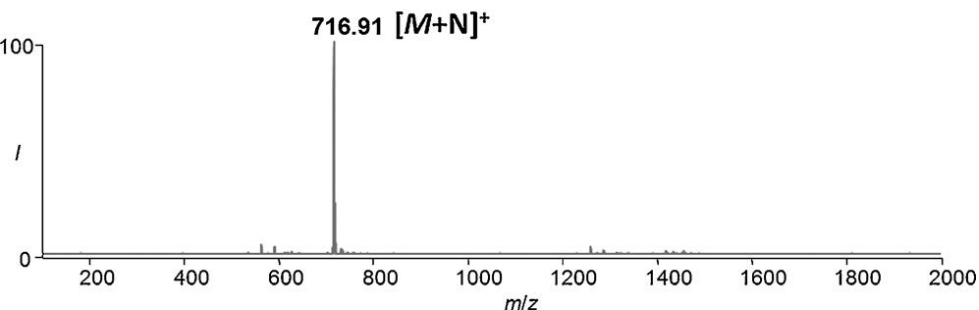
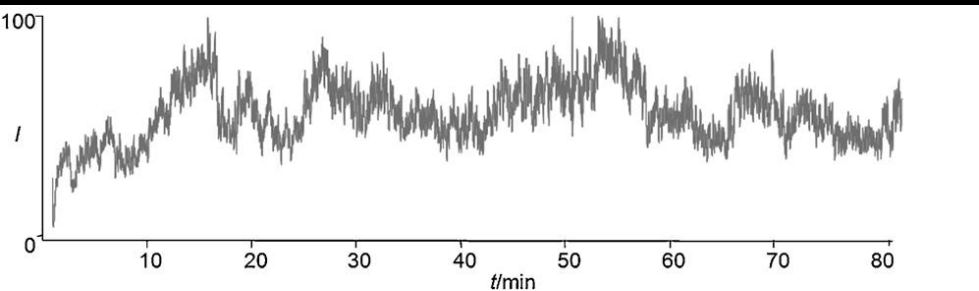
5m, 0.53mm ID, 0.10 μ m MXT®-1HT Sim Dist (cat.# 70100)
 0.2 μ L Polywax® 1000 standard (cat.# 36227)
 Solvent: carbon disulfide
 Oven temp.: 40°C to 430°C @ 10°C/min. (hold 30 min.)
 Injector: on-column (track oven)
 Carrier gas: helium (constant pressure)
 Head pressure: 1.0psi
 Linear velocity: 60cm/sec.
 Flow rate: 7.8mL/min.
 Det.: FID @ 430°C
 Make-up gas flow: 40cc/min.

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Isotopic distribution for the C₁₁₀ peaks compared to calculated isotopic distribution of C₁₁₀H₂₂₂N

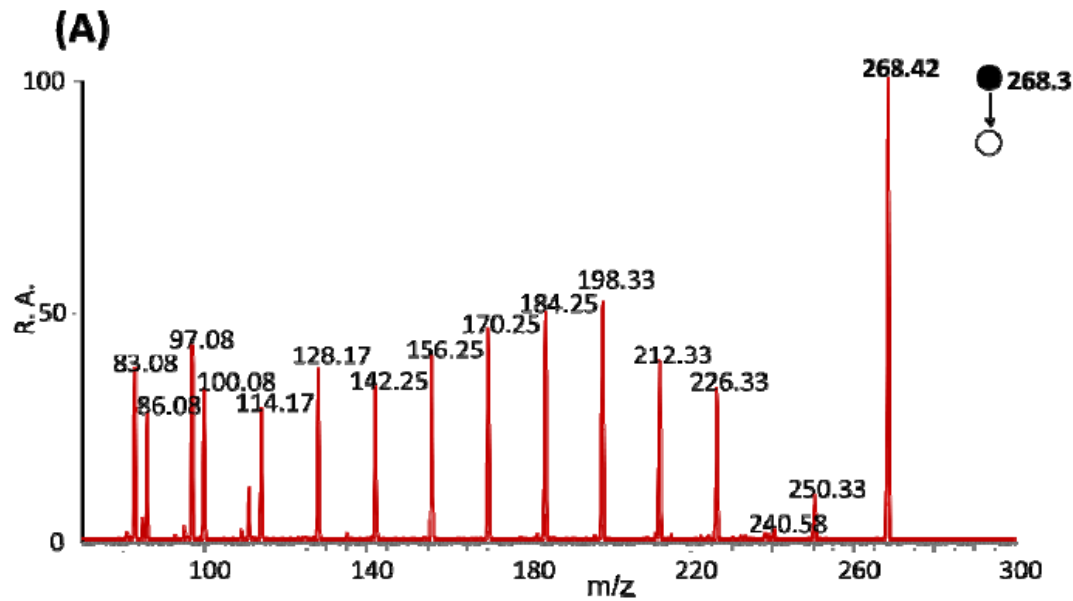


The $[M+N]^+$ ion signal lasted several hours using 10 mg alkane with no appreciable loss of intensity.

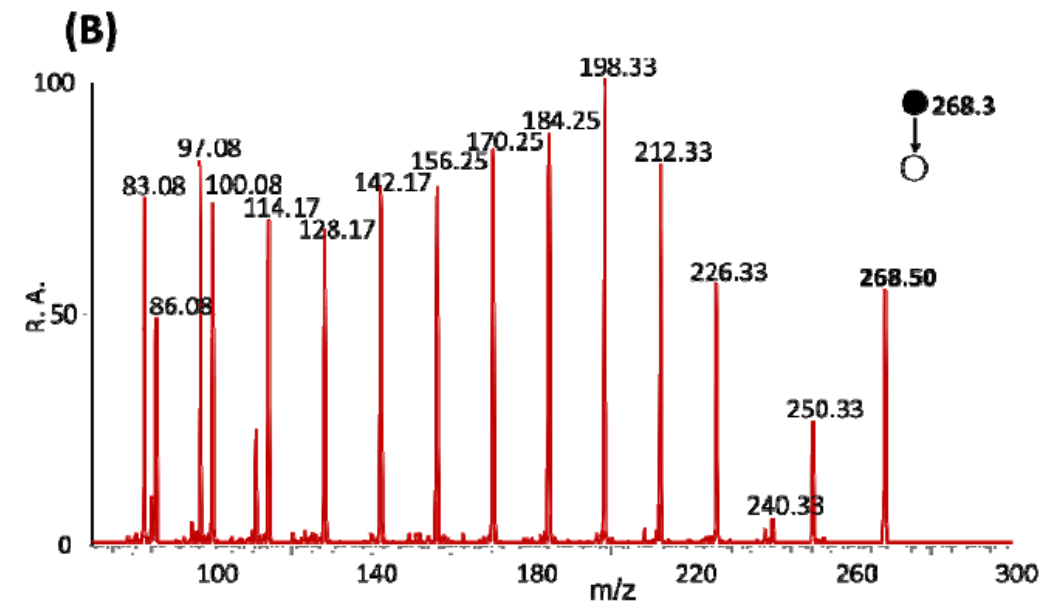
The mass spectrum is dominated by the $[M+N]^+$ ion.

Raman analysis of the collected sample showed a distinctive absorption band around 1664 cm^{-1} .

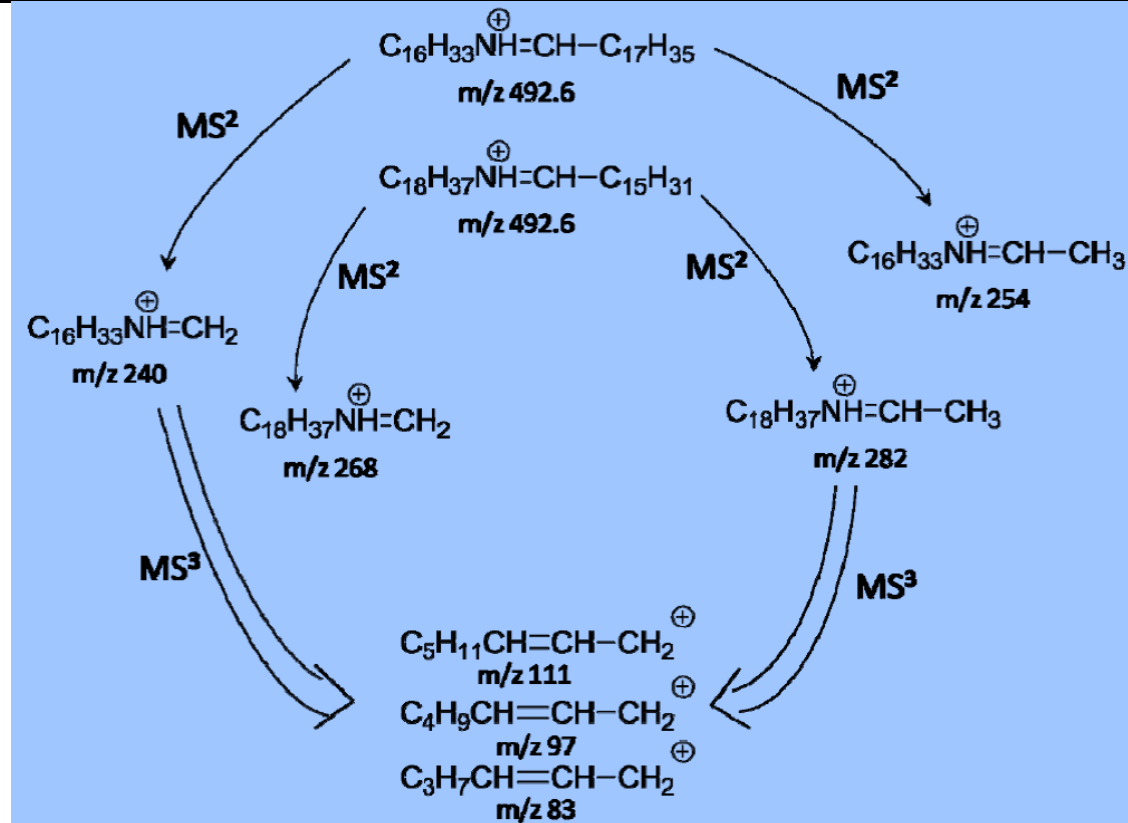
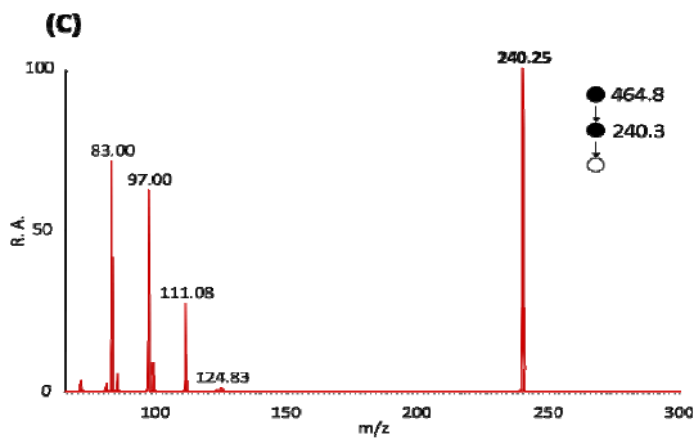
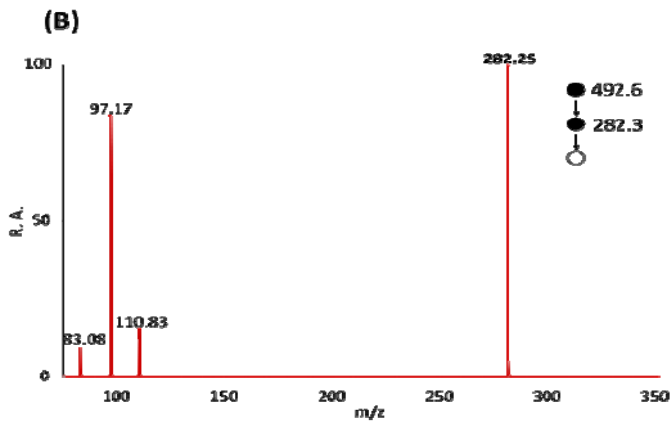
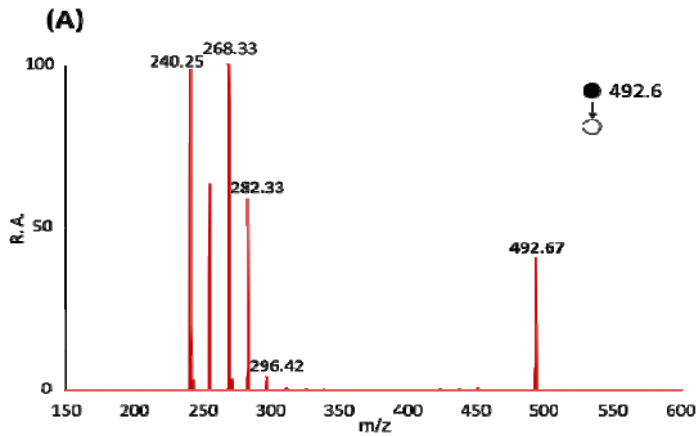
A characteristic Raman-active band for neutral imines.



On-line analysis



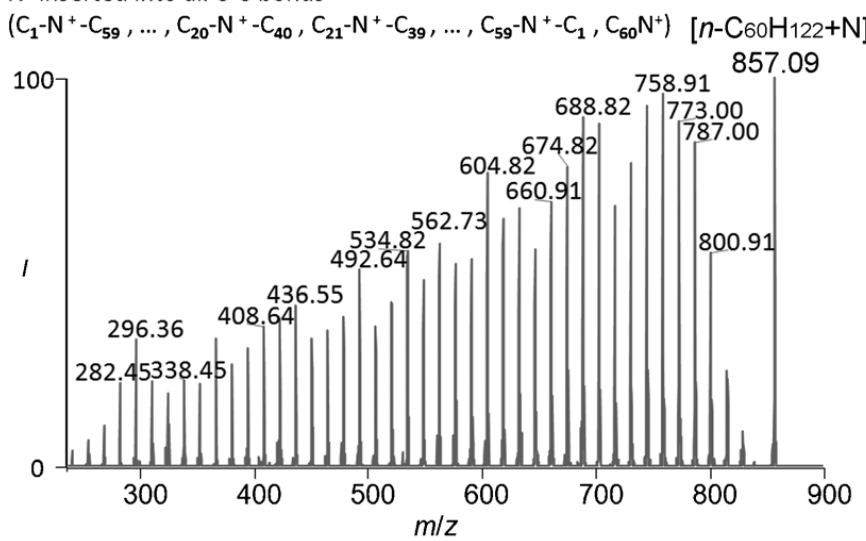
Mass spectrum from the rinsed sample



MS/MS study from two isomeric product gave homologous peaks .

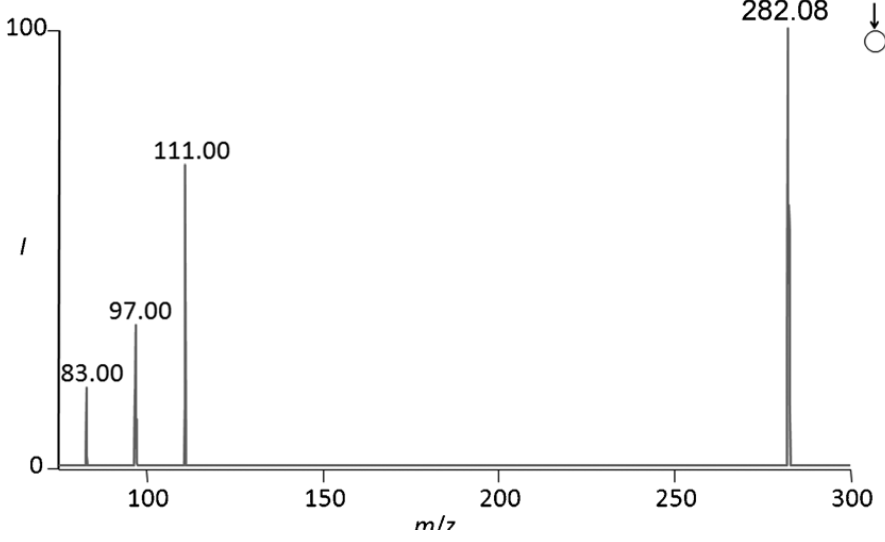
a) \bullet 857.09
 \circ

N^+ inserted into all C-C bonds
 $(C_1-N^+-C_{59}, \dots, C_{20}-N^+-C_{40}, C_{21}-N^+-C_{39}, \dots, C_{59}-N^+-C_1, C_{60}N^+)$ $[n-C_{60}H_{122}+N]^+$



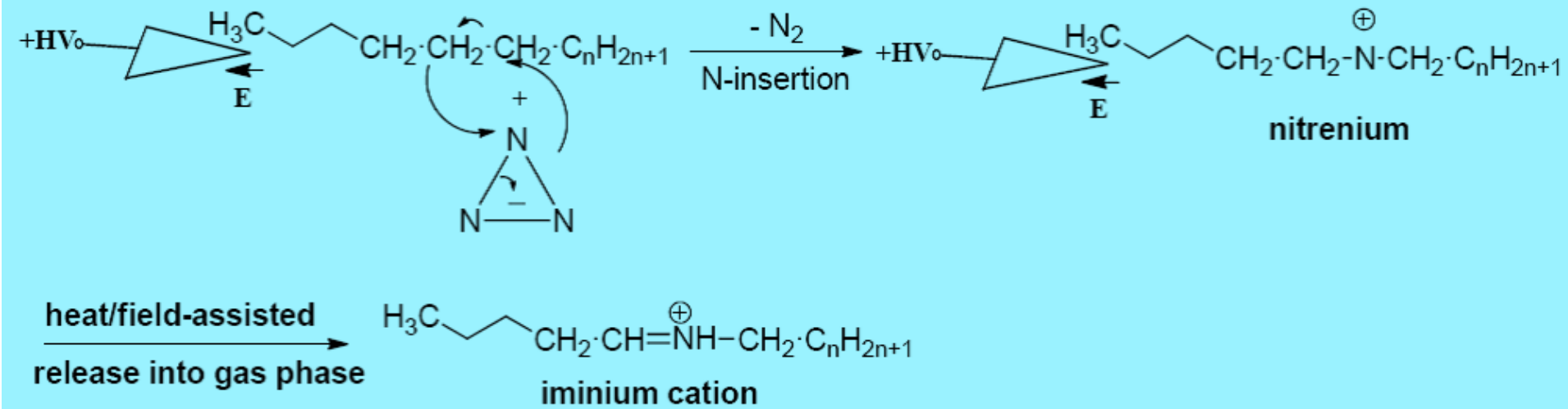
a) Continuous distribution of alkene elimination fragments observed on dissociation of the N-insertion product of $n-C_{60}H_{122}$. b) Further fragmentation of a typical product ion, m/z 282.2, observed as the MS^3 spectrum.

b) \bullet 857.0
 \bullet 282.2
 \circ

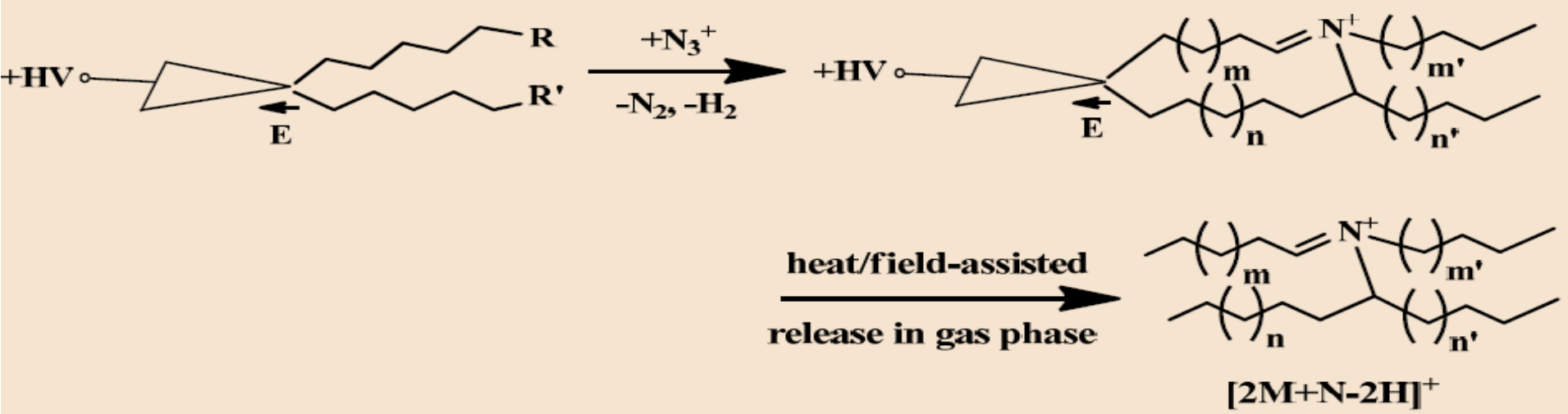


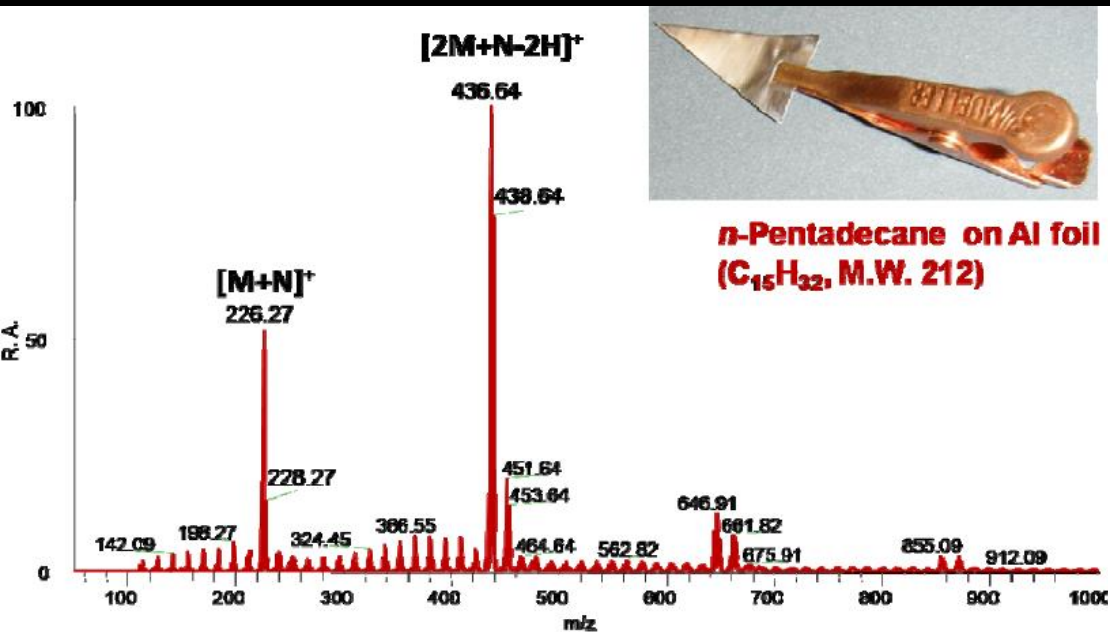
Nitrogen is inserted nonspecifically into the C-C backbone of alkanes to form the continuous distribution of homologous iminium ions

Tentative mechanism of nitrogen insertion into alkanes on paper



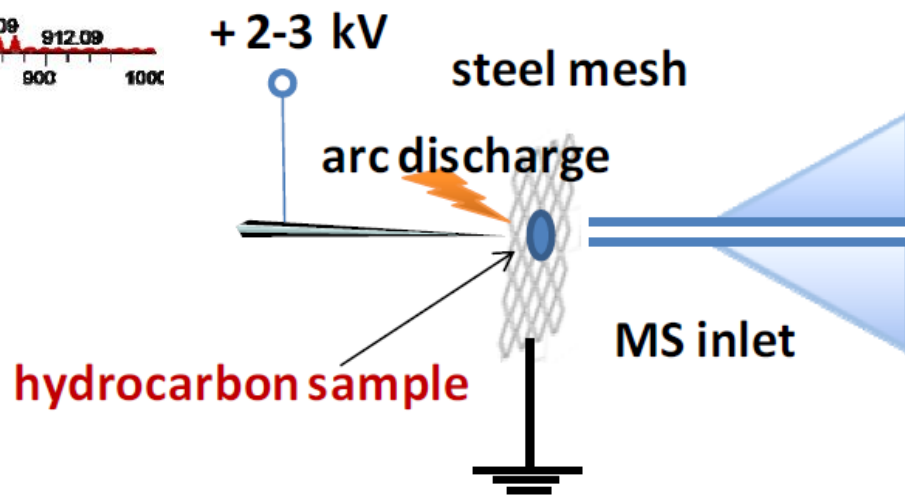
Tentative mechanism of dimeric ion formation





n-Pentadecane on Al foil
(C₁₅H₃₂, M.W. 212)

They have done the same experiment with Al foil and steel also



N₂ atmosphere, 50-250 °C

Direct insertion of nitrogen into C-C bonds of saturated alkanes to form iminium salts without involving metal species.

Based on all this evidence, it is concluded that nitrogen is inserted nonspecifically into the C–C backbone of alkanes to form the continuous distribution of homologous iminium ions.

Alkanes are field-activated while physisorbed to the paper where they are strongly polarized by the strong terminal electric fields. This explains the field assistance for the reaction.

These experiments also offer a new strategy for mass spectrometric analysis of petroleum products.

Thank you ...

