A Computational Study of the Reaction N(^{2}D) + C_6H_6 : Implications for the Upper Atmosphere of Titan

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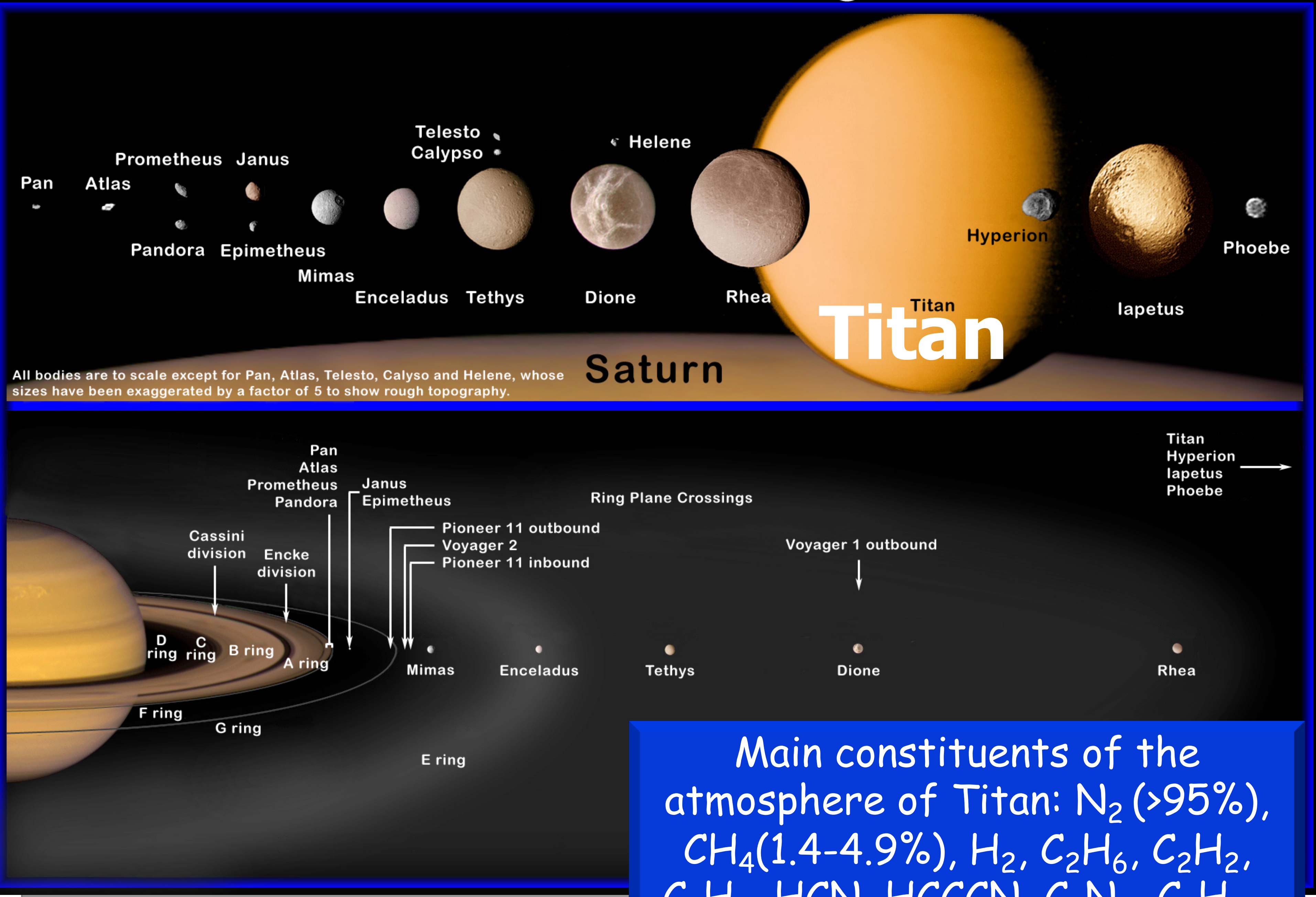
Saturn's Satellites and Ring Structure



All bodies are to scale except for Pan, Atlas, Telesto, Calyso and Helene, whose sizes have been exaggerated by a factor of 5 to show rough topography.

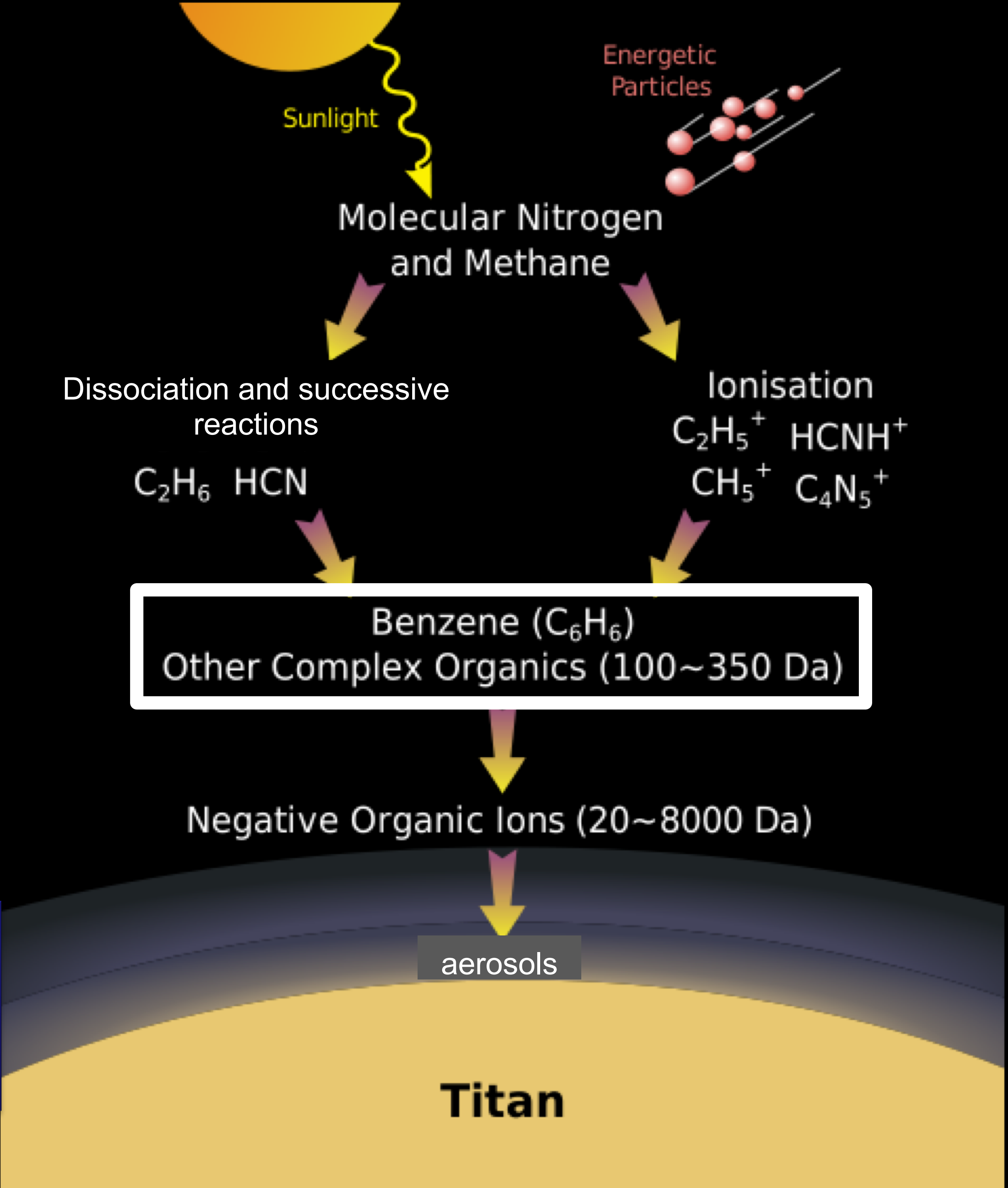
Main constituents of the atmosphere of Titan: N_2 (>95%), CH_4(1.4-4.9%), H_2, C_2H_6, C_2H_2, C_2H_4, HCN, HCCCN, C_2N_2, C_6H_6...

Global chemical scheme

EUV and energetic particles induce the formation of active forms of nitrogen ($N^{\cdot}$, N^*, N_2^*, N^+, N_2^+)

UV photons induce dissociation and ionization of methane

A very active chemistry begins, leading up to N-bearing macro-molecules and their ions.



Molecular Nitrogen and Methane

Dissociation and successive reactions

C_2H_6 HCN

Ionisation

$C_2H_5^+$ $HCNH^+$

CH_5^+ $C_4N_5^+$

Benzene (C_6H_6)
Other Complex Organics (100~350 Da)

Negative Organic Ions (20~8000 Da)

aerosols

Titan

Nitrogen fixation by photochemistry in the atmosphere of Titan

Molecular nitrogen, the main component of the atmosphere of Titan, is characterized by a strong bond and is difficult to chemically fix in compounds.

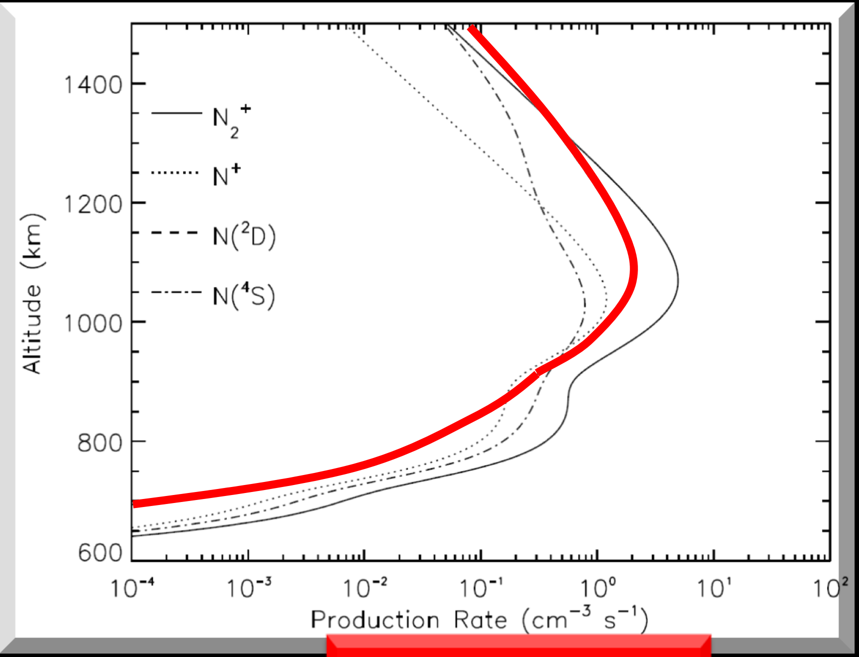
The observation of nitriles in trace amounts indicates that some forms of active nitrogen are produced by several processes (e.g. EUV absorption, electron impact) ➲ N, N_2^+, N^+

EUV ($60<\lambda<82$ nm) & electron impact induced dissociation, dissociative ionization and N_2^+ dissociative recombination produce $N(^4S)$ and $N(^2D)$ states in similar amounts. The excited ^2D state is metastable with a very long radiative lifetime (~ 48 h).

The generation of atomic nitrogen in the first electronically excited state, ^2D, is extremely relevant in assessing the role of neutral nitrogen chemistry in the atmosphere of Titan because $N(^4S)$ atoms exhibit very low reactivity with closed-shell molecules and the probability of collision with an open-shell radical is small.

The excited ^2D state is metastable with a very long radiative lifetime (~ 48 h) and a very high energy content (230 kJ/mol). In the upper atmosphere of Titan EUV & electron impact induced dissociation, dissociative ionization and N_2^+ dissociative recombination produce $N(^4S)$ and $N(^2D)$ states in similar amounts.

$N(^2D)$ production rate with altitude



Lavvas *et al.*, 2011

We have already investigated (2009-12) the reactions of $N(^2D)$ with the aliphatic hydrocarbons abundant in Titan, e.g., CH_4, C_2H_6, C_2H_4

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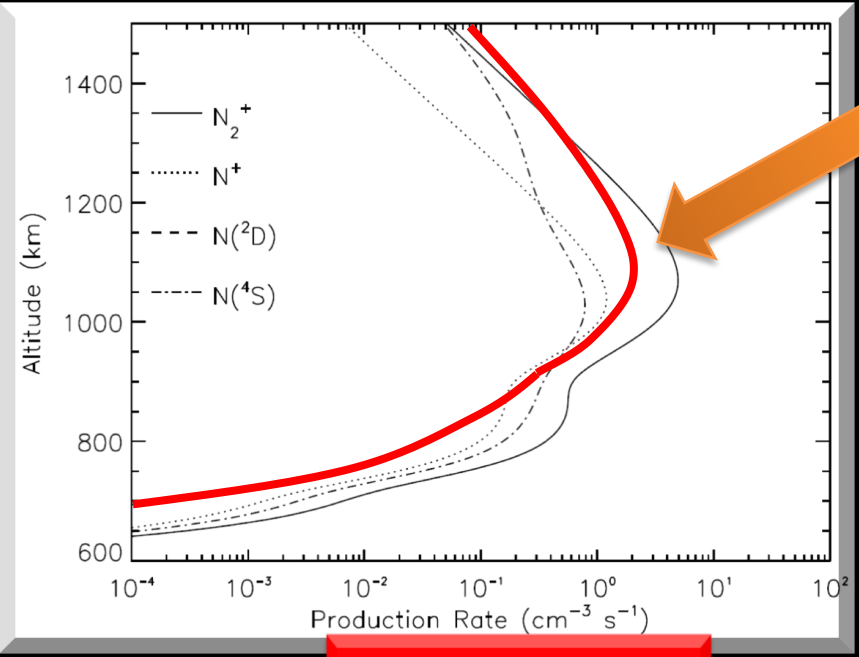
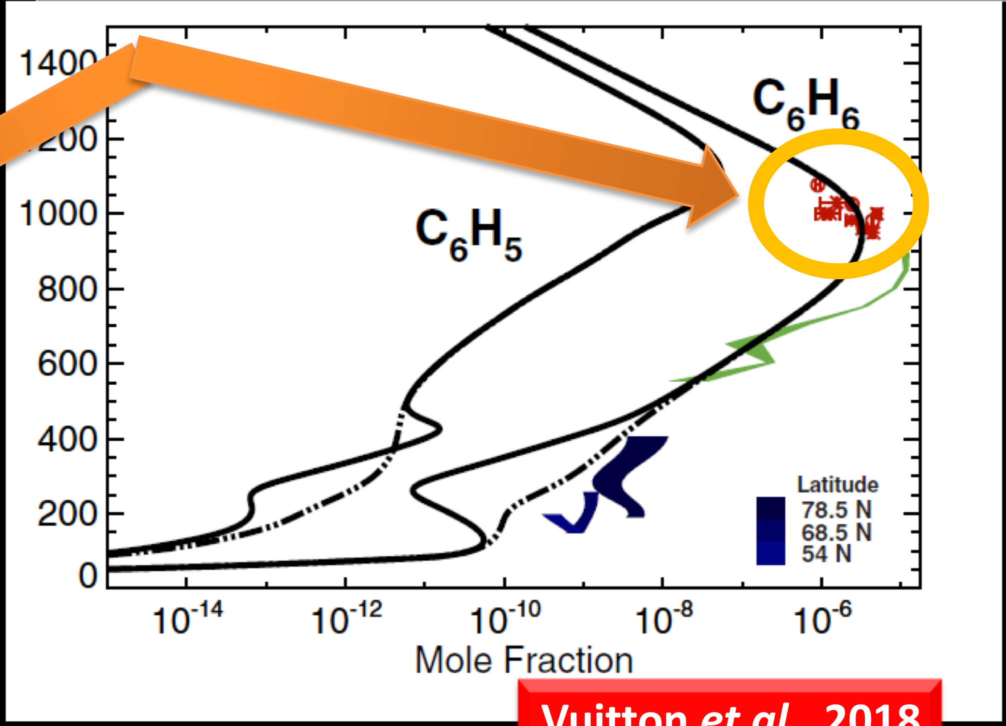
$N(^2D)$ production rate with altitude

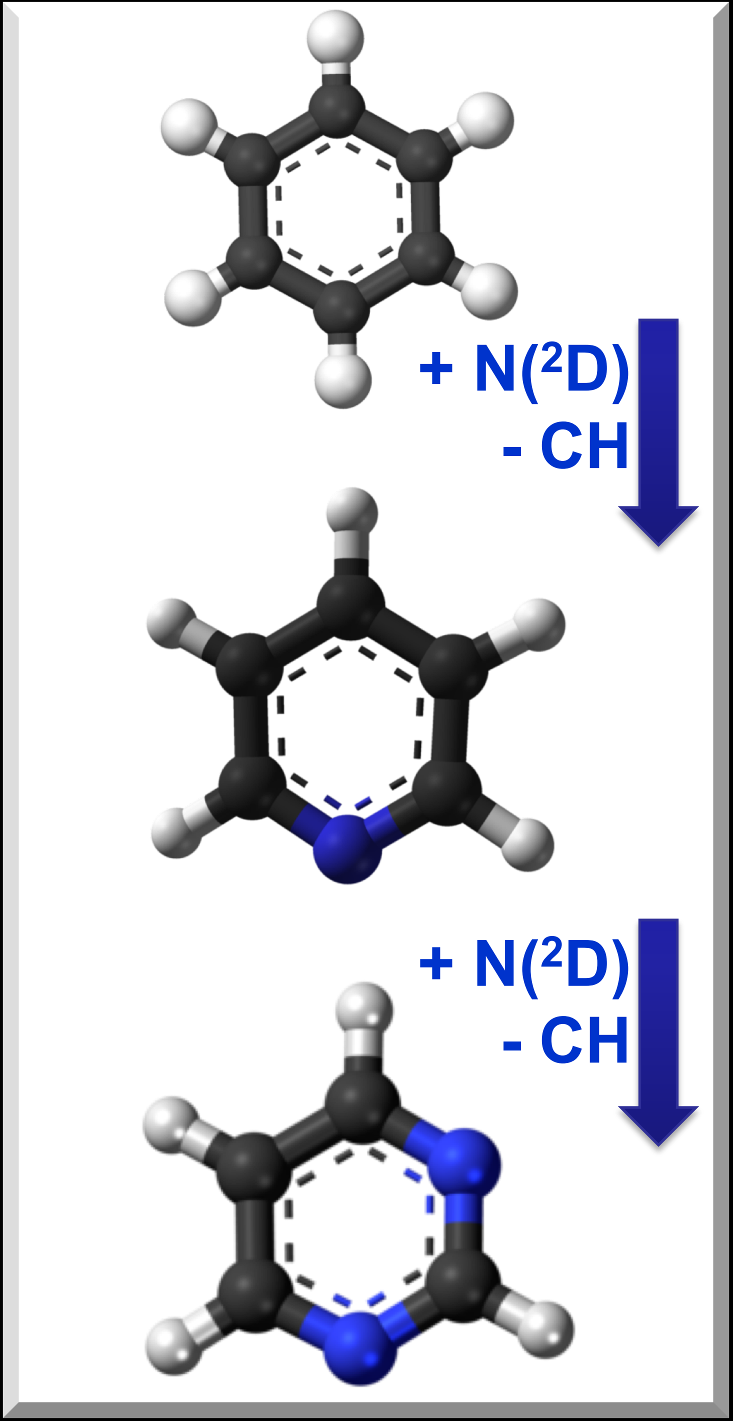


Lavvas *et al.*, 2011

Benzene mole fractions as a function of the altitude

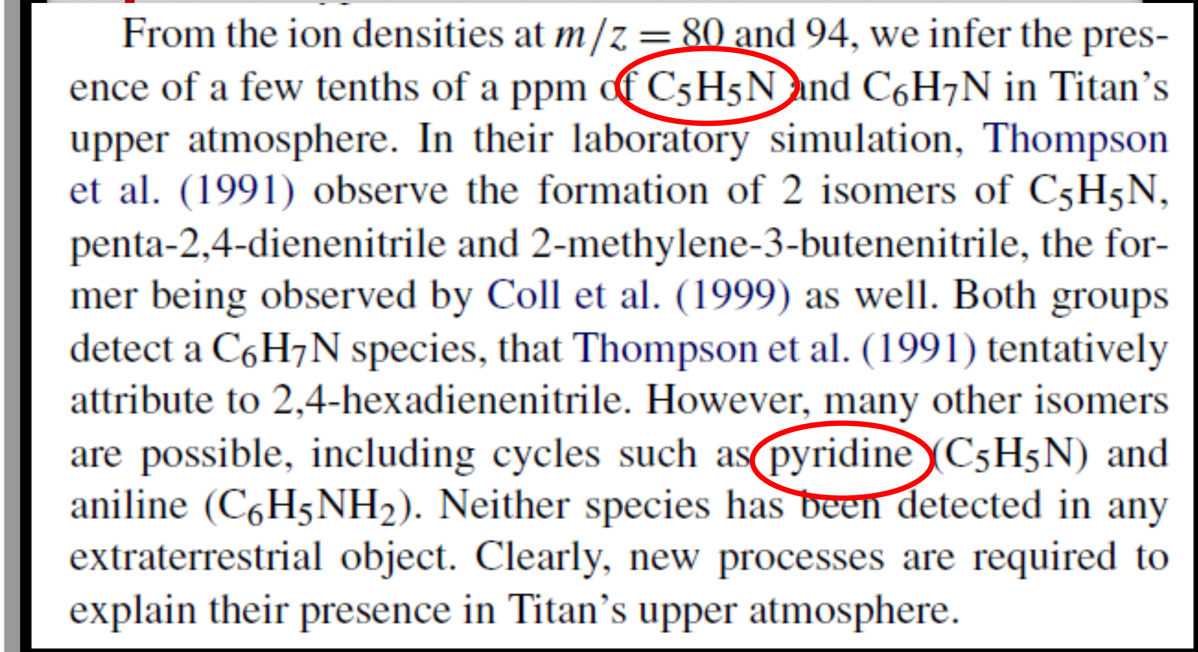


Vuitton *et al.*, 2018



benzene: widely detected (even as ice flakes in the stratosphere)

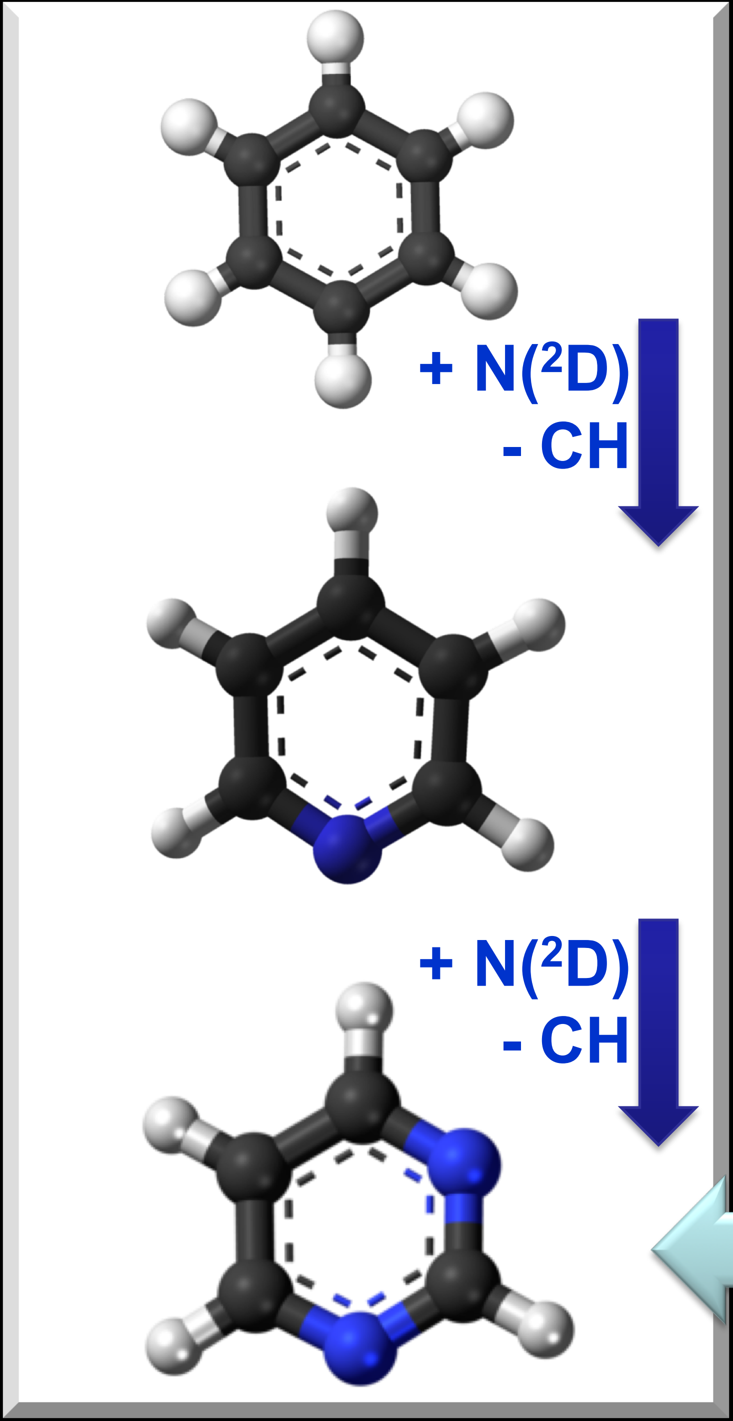
possible detection of pyridine by the Ion Neutral Mass Spectrometer onboard Cassini



From the ion densities at $m/z = 80$ and 94, we infer the presence of a few tenths of a ppm of C_5H_5N and C_6H_7N in Titan's upper atmosphere. In their laboratory simulation, Thompson et al. (1991) observe the formation of 2 isomers of C_5H_5N, penta-2,4-dienenitrile and 2-methylene-3-butenenitrile, the former being observed by Coll et al. (1999) as well. Both groups detect a C_6H_7N species, that Thompson et al. (1991) tentatively attribute to 2,4-hexadienenitrile. However, many other isomers are possible, including cycles such as pyridine (C_5H_5N) and aniline ($C_6H_5NH_2$). Neither species has been detected in any extraterrestrial object. Clearly, new processes are required to explain their presence in Titan's upper atmosphere.

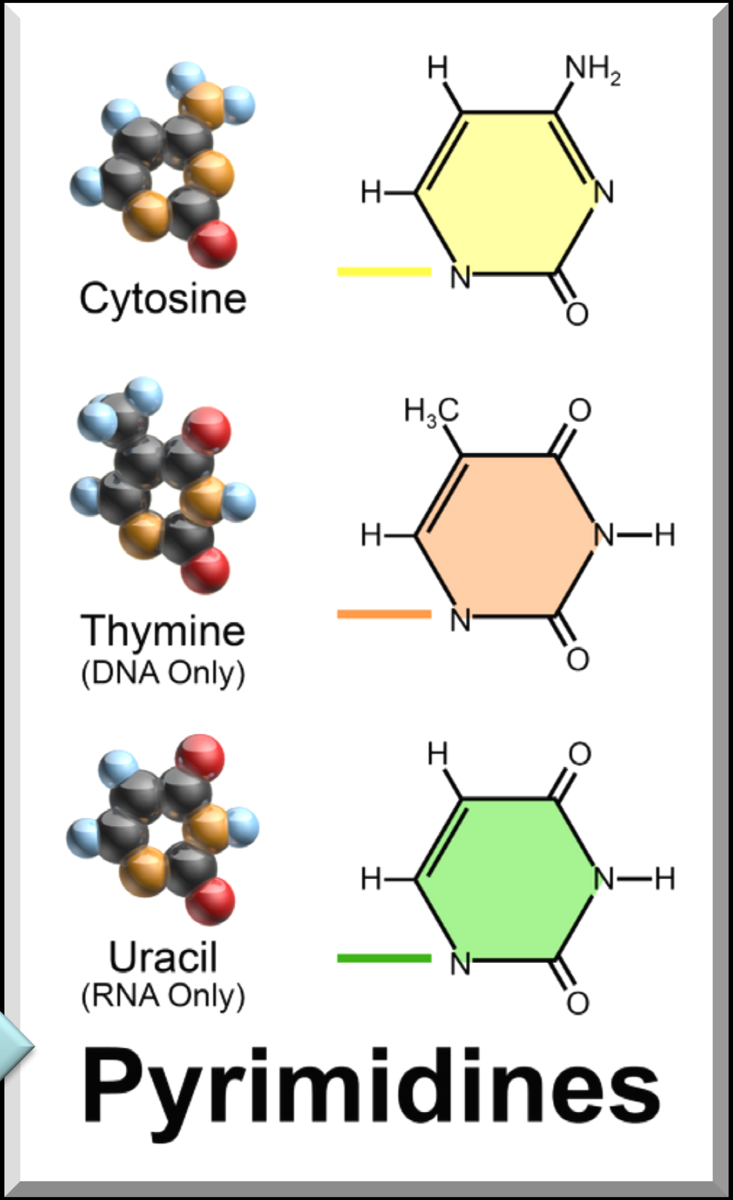
V. Vuitton, R. V. Yelle, M. J. McEwan, *Icarus* 191 (2007) 722-742

Implications for prebiotic chemistry



+ N(^{2}D)
- CH

+ N(^{2}D)
- CH



Pyrimidines

Methods

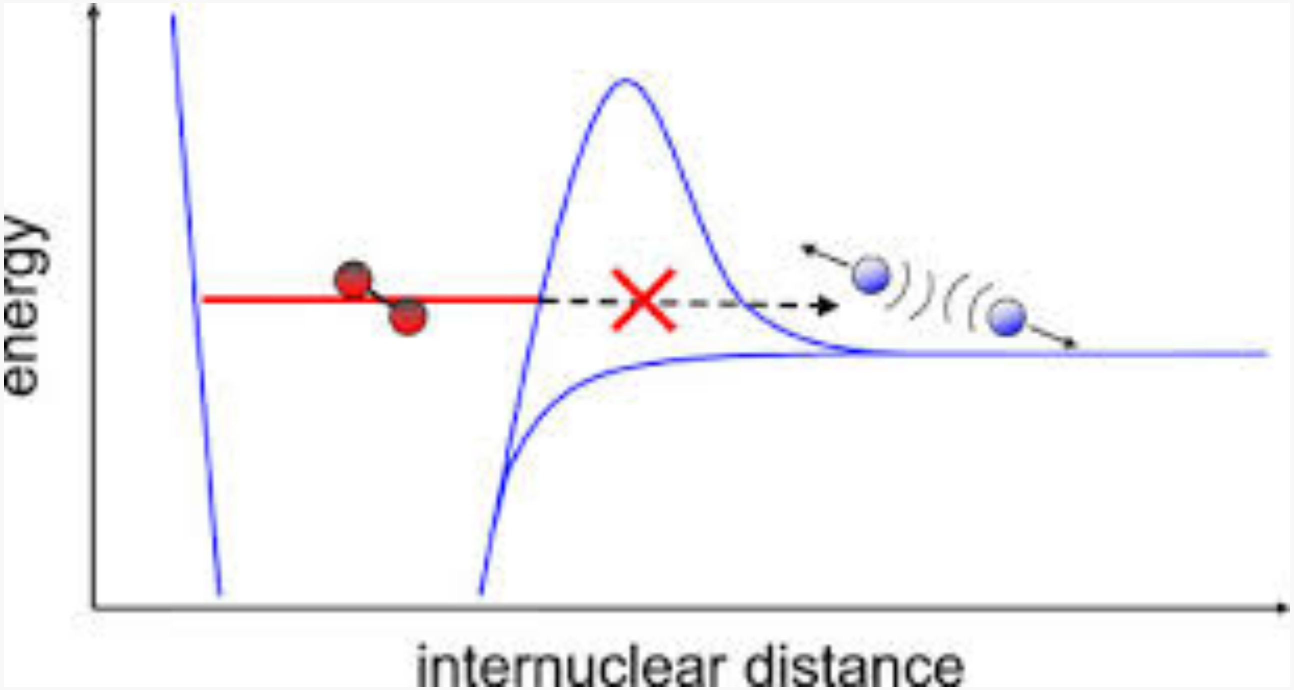
- Electronic structure calculations of the relevant potential energy surface

- Microcanonical kinetics calculations

    - Capture theory
    - Rice-Ramsperger-Kassel-Marcus (RRKM) calculations
    - Master equation resolution

- Derivation of temperature-dependent rate coefficients through Boltzmann averaging

The capture model



For the initial exothermic step the capture model is used. The essential assumption is that a successful capture has occurred if the centrifugal barrier can be overcome.

The RRKM scheme

Instead, the RRKM (Rice-Ramsperger-Kassel-Marcus) scheme is used for unimolecular intermediate steps. In the RRKM scheme for a unimolecular reaction, two assumptions are made:

- The available energy is distributed statistically among all available degrees of freedom

- The reaction proceeds through a **transition state** (no-recrossing assumption).

The RRKM scheme

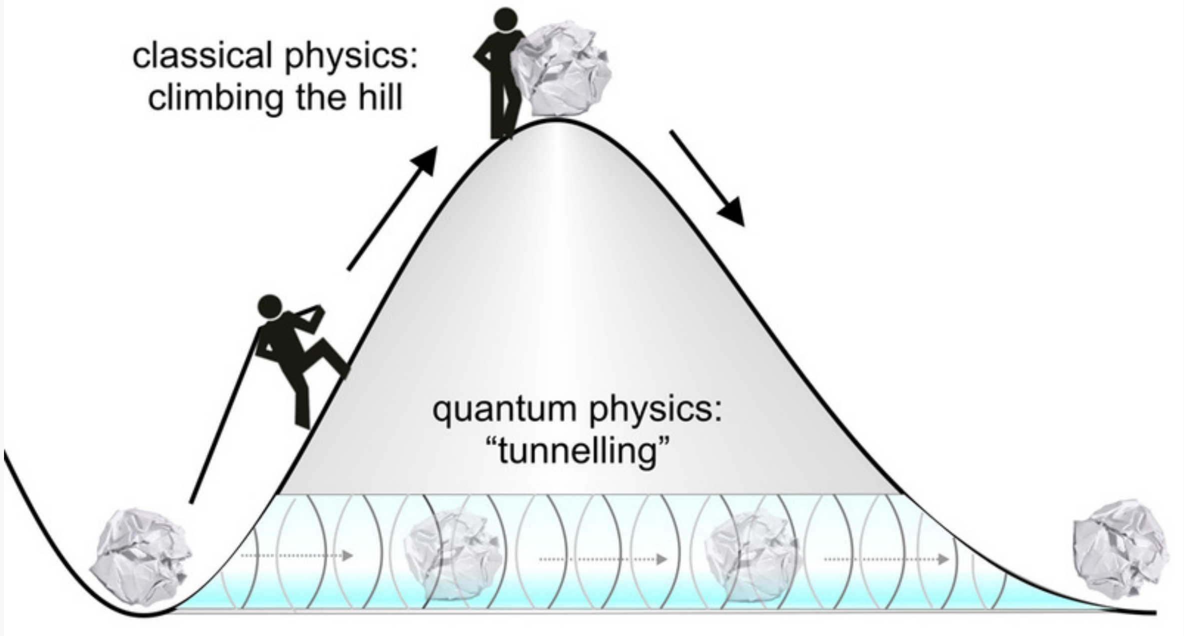
Within these two assumptions, the unimolecular rate constant is given by the formula

$$k(E) = \frac{N(E)}{h\,\rho(E)}$$

where $N(E)$ is the number of states in the transition state configuration below the energy E, $\rho(E)$ is the reactant density of states at the same energy and h is Planck's constant.

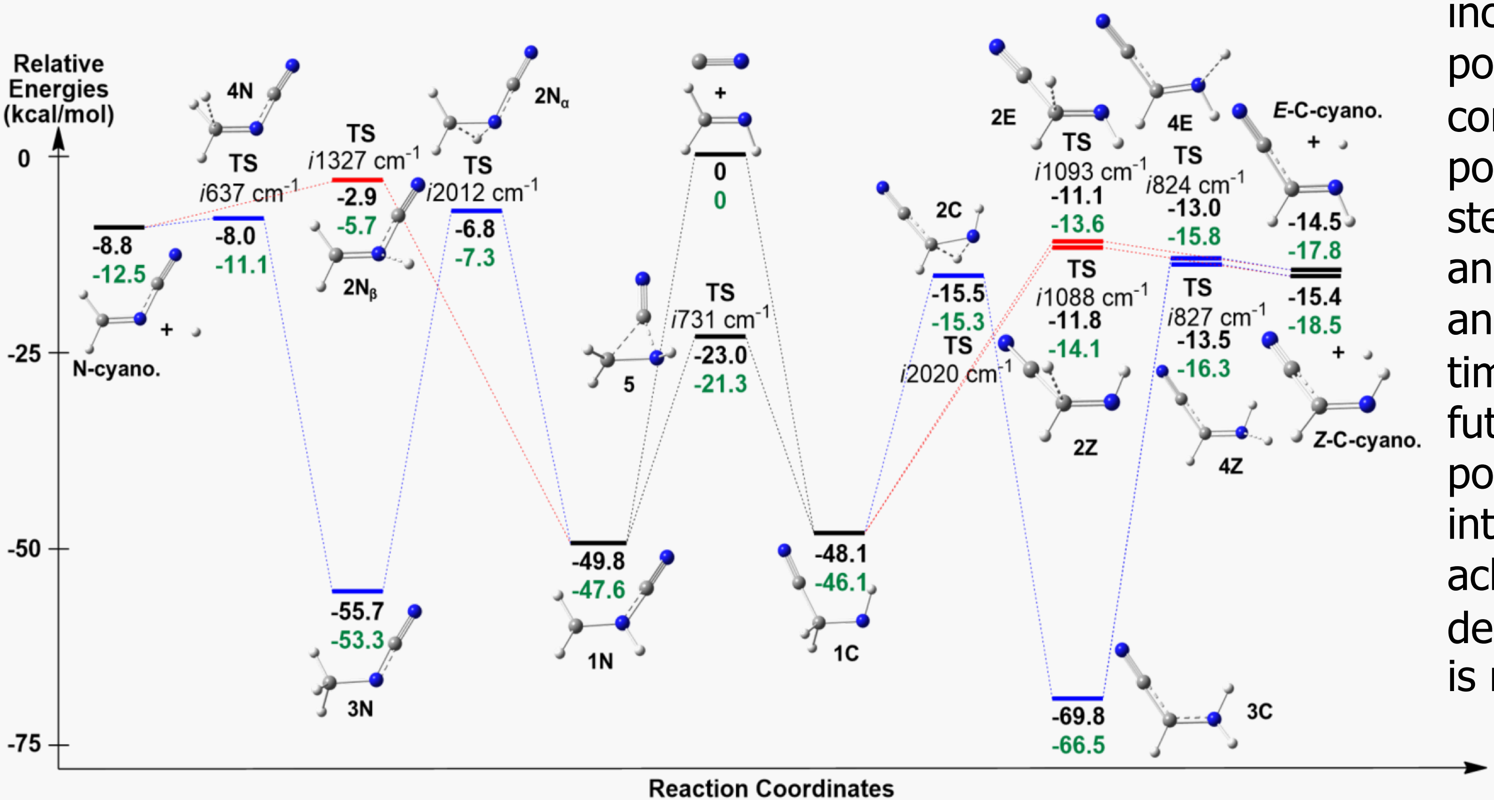
And how about tunnelling?

We use the imaginary frequency of the transition state to **simulate** the height and width of the barrier to be crossed as an **Eckart barrier**.



The master equation

If our system includes more than one intermediates, then we must calculate (based on the initial abundances) the branching ratio between the various product channels.



This means including all possible rate constants for all possible reaction steps (forwards and backwards) and extrapolating time to the infinite future (where all possible intermediates have achieved their destiny and there is no turning back).

Boltzmann averaging

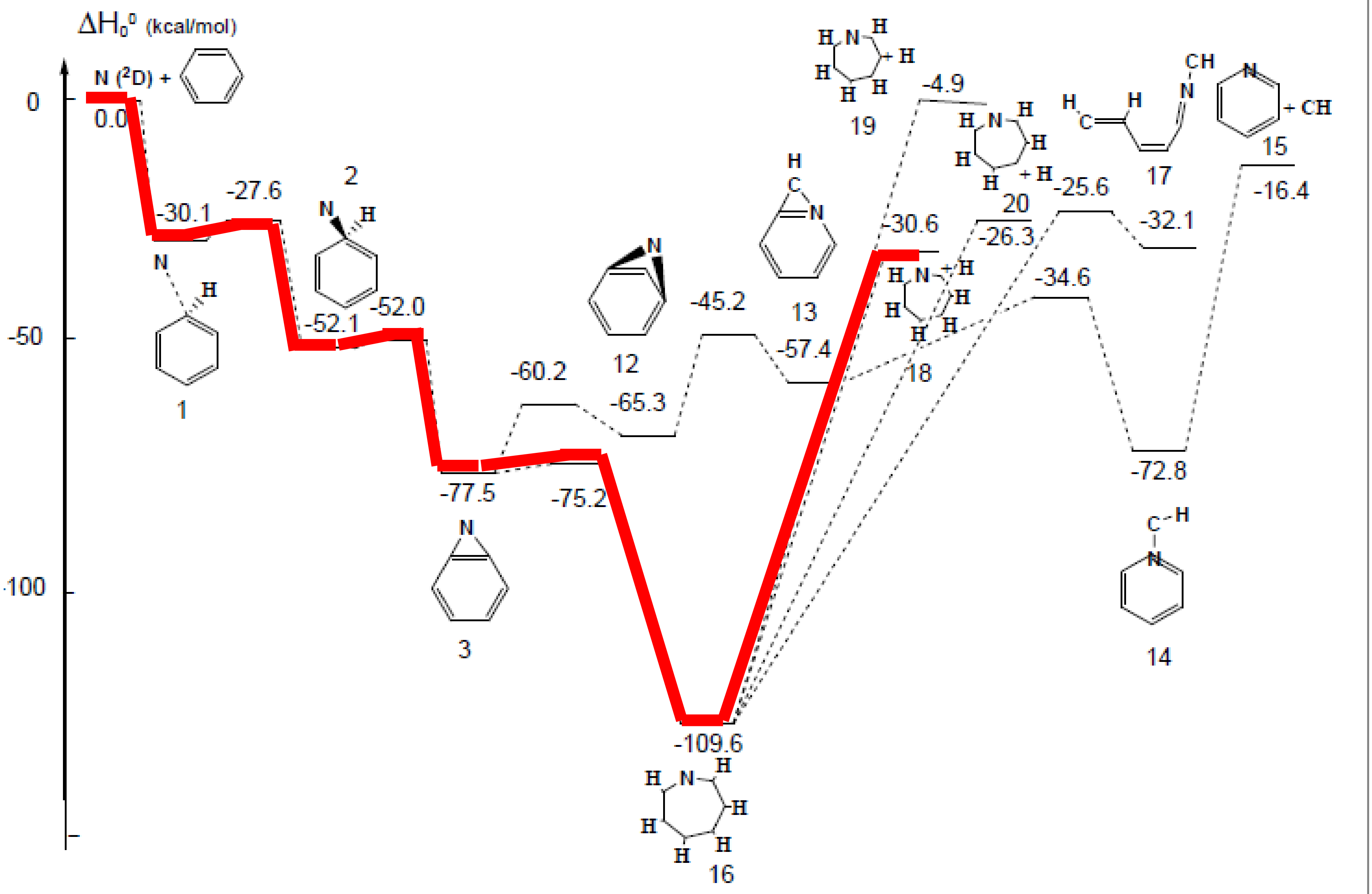
Having obtained rate constants for a sufficient range of energies, we proceed with *Boltzmann averaging* to convert energy to temperature information

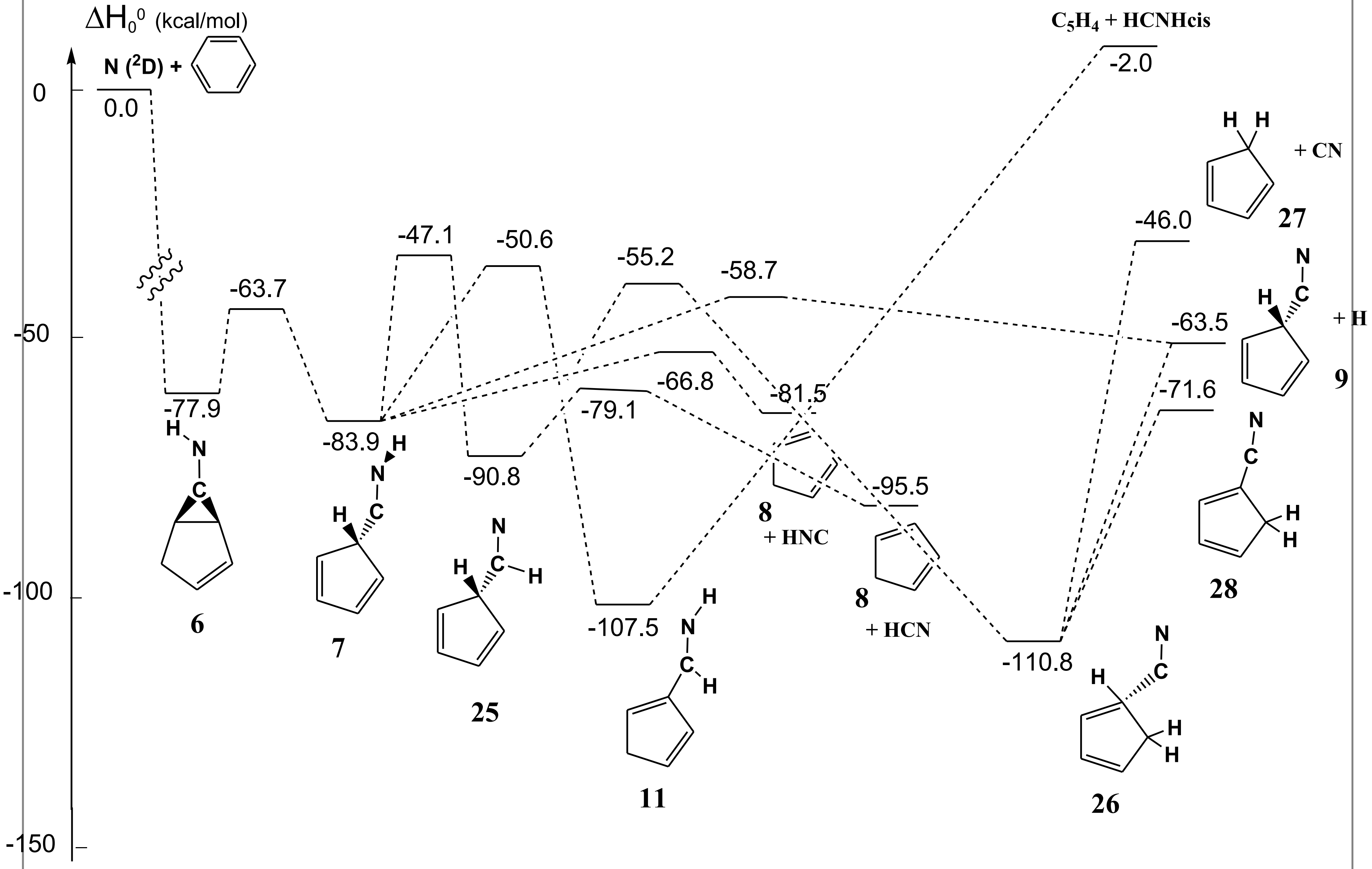
$$k_c(T) = \frac{1}{q(T)} \int k_m(E) \times \rho(E) \times e^{-E/k_B T} dE$$

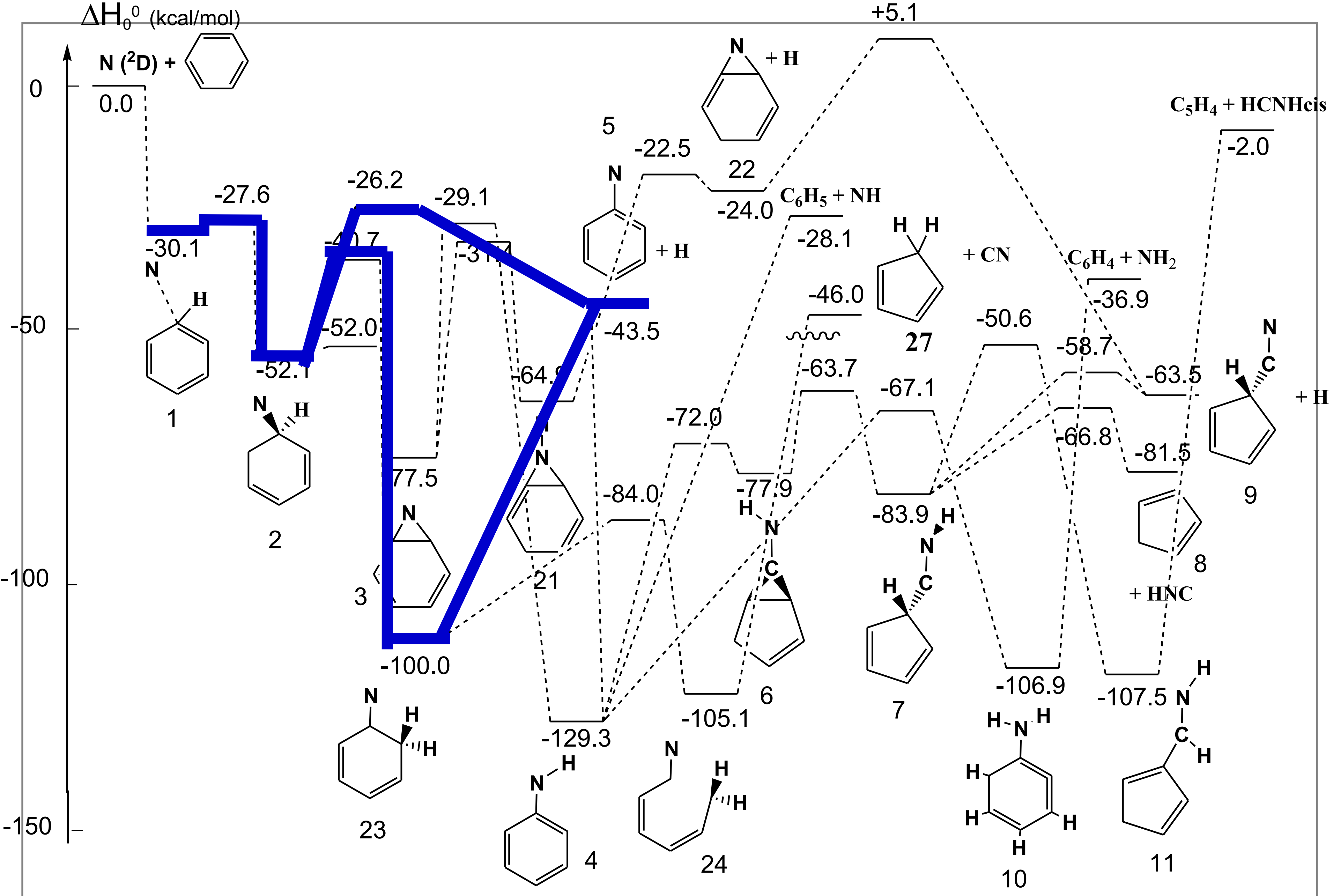
where *q(T)* is the reactant partition function at temperature *T* and *ρ(E)* is the reactant density of states at the energy *E*.

N(^{2}D) + C_6H_6 : Computational details

- Electronic structure calculations have been performed on the N(^{2}D) + C_6H_6 system using DFT calculations and employing the B3LYP functional in conjunction with the m-aug-cc-pVTZ basis set. Coupled cluster calculations have also been (just!) effected, which will permit higher accuracy.
- Energies, vibrational frequencies and rotational constants of all intermediates and transition states have been determined.


ΔH0⁰ (kcal/mol)
0
-50
-100
N (²D) +
0.0
-30.1
-27.6
1
2
-52.1
-52.0
-77.5
3
-75.2
-60.2
-65.3
12
-45.2
13
-57.4
-109.6
16
19
-4.9
+ H
20
-30.6
-26.3
18
-25.6
17
-32.1
-34.6
-72.8
14
15
+ CH
-16.4


ΔH$_0^0$ (kcal/mol)
0
-50
-100
-150
N (^{2}D) +
0.0
-77.9
6
-63.7
-83.9
7
-47.1
-90.8
25
-50.6
-55.2
-107.5
11
-66.8
-79.1
-58.7
-81.5
8
+ HNC
-95.5
8
+ HCN
-110.8
26
C$_5$H$_4$ + HCNHcis
-2.0
+ CN
27
-46.0
-63.5
+ H
9
-71.6
28
H
N
C


ΔH_0^0 (kcal/mol)
0
-50
-100
-150
N (^{2}D) +
0.0
-30.1
-27.6
-52.1
-26.2
-40.7
-29.1
-31.4
-52.0
-77.5
-100.0
-64.9
-43.5
-129.3
-22.5
-24.0
+5.1
+ H
-84.0
-72.0
-77.9
-105.1
C_6H_5 + NH
-28.1
-46.0
-63.7
-67.1
-83.9
+ CN
27
-50.6
-106.9
C_6H_4 + NH_2
-36.9
-58.7
-66.8
-63.5
-81.5
-107.5
C_5H_4 + HCNHcis
-2.0
+ HNC
+ H
N
H
C
1
2
3
4
5
6
7
8
9
10
11
21
22
23
24

Reaction mechanism and rates

- After the initial attack on the C_6H_6 ring, the N atom is attached to a C atom through a σ-bond. Subsequently there is a choice:

1. A C-C-N ring can be formed. After this, there can be a ring opening to form an overall seven-membered ring (six carbon atoms and one nitrogen atom) with a subsequent H expulsion. From the relative barrier heights, it can be understood why this is the major fate of the initial intermediate.

2. An H atom can be expelled to form phenylnitrene. Before the H atom expulsion, there is the possibility of a 1,2 H-migration.

Reaction mechanism and rates

- As it turns out, the formation of a seven-membered ring product is by far the dominant one. In fact, the formation of the ortho-product (n. 18 in the scheme) has a yield of 86-87% for all temperatures up to 300K.

- The corresponding para-product (n. 20 in the scheme) is the second most favoured one, with a yield of 7-8%.

- Finally, the formation of phenylnitrene (with or without an initial H atom migration) accounts only for 4-5% of the products.

CONCLUSIONS

- The predominant scenario is the formation of a seven-membered ring product (six carbon atoms and one nitrogen atom).

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- A minor product is phenylnitrene, formed by the expulsion of an H atom while the N atom is still σ-bonded to benzene.

CONCLUSIONS

- The predominant scenario is the formation of a seven-membered ring product (six carbon atoms and one nitrogen atom).
- A minor product is phenylnitrene, formed by the expulsion of an H atom while the N atom is still σ-bonded to benzene.
- Even though pyridine appears in the overall reaction scheme, its formation rate is far too low to be of any importance.

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