The pursuit of formamide
Observations & experiments

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LERMA - Rendez-vous pôle 3 - Molécules dans l'Univers
Tour 32 - salle 304 - Université Pierre et Marie Curie
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Why NH$_2$CHO?

- It contains C, H, O, and N, the four most important elements for biological systems.
- It contains a peptide bond, crucial to form chains of amino acids.
It was recently proposed as a precursor of both metabolic and genetic material, thus providing a unified framework in the quest for the origin of life on Earth.

Saladino et al. 2012, 2015

Key biochemical molecule!
First detection in 1971 in Sgr B2, followed by subsequent detections in other high-mass star-forming regions

Initially associated with hot gas

Detected in comet Hale-Bopp in 2000

It represents an important fragment of the prebiotic chemistry puzzle
Survey by Lópeza-Sepulcre et al. 2015
@ \lambda=1, 2, 3 \text{ mm w/ IRAM 30-m telescope}

- Low-mass pre-stellar
- Low-mass protostellar
- Hot corino
- Intermediate-mass
- Outflow shock
NH$_2$CHO in space

HNCO and NH$_2$CHO chemically related?

Necessity of experiments to find an answer...

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Surface reaction: HNCO + H/D

Hydrogenation of isocyanid acid...
Will it lead to formamide?

HNCO + 2H → NH₂CHO ?
Hydrogenation at low temperatures does not always lead to saturation: the case of HNCO

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**ABSTRACT**

**Context.** It is generally agreed that hydrogenation reactions dominate chemistry on grain surfaces in cold, dense molecular cores, saturating the molecules present in ice mantles.

**Aims.** We present a study of the low temperature reactivity of solid phase isocyanic acid (HNCO) with hydrogen atoms, with the aim of elucidating its reaction network.

**Methods.** Fourier transform infrared spectroscopy and mass spectrometry were employed to follow the evolution of pure HNCO ice during bombardment with H atoms. Both multilayer and monolayer regimes were investigated.

**Results.** The hydrogenation of HNCO does not produce detectable amounts of formamide (NH\textsubscript{2}CHO) as the major product. Experiments using deuterium reveal that deuteration of solid HNCO occurs rapidly, probably via cyclic reaction paths regenerating HNCO. Chemical desorption during these reaction cycles leads to loss of HNCO from the surface.

**Conclusions.** It is unlikely that significant quantities of NH\textsubscript{2}CHO form from HNCO. In dense regions, however, deuteration of HNCO will occur. HNCO and DNCO will be introduced into the gas phase, even at low temperatures, as a result of chemical desorption.
The making of HNCO

\[
\text{Acide Cyanurique} \quad \xrightarrow{650 \, ^\circ C \quad 10^{-3} \, \text{mbar}} \quad 3 \, \text{H} - \text{N}=\text{C}=\text{O} \\
\text{Acide Isocyanique}
\]
The making of HNCO

Figure 2.2. Montage de la pyrolyse de l'acide cyanurique
The making of HNCO
RING set-up @PIIM, Marseille

Used to perform multilayer/bulk ice experiments

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Experiments @PIIM, Marseille

HNCO ice @17K bombarded with H or D atoms

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Experiments @PIIM, Marseille

HNCO ice @ 17K bombarded with H or D atoms

NH₂CHO not produced in detectable quantities
Experiments @ PIIM, Marseille

H bombardment of NH$_2$CHO:

NH$_2$CHO + 2H $\rightarrow$ NH$_2$CH$_2$COH (amminomethanol) ?

- a) Pure NH$_2$CHO
- b) NH$_2$CHO + H
- c) b) - a)

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H bombardment of NH2CHO:

NH₂CHO + 2H --> NH₂CH₂COH (amminomethanol) ?

c) b) - a)

b) NH₂CHO + H

a) Pure NH₂CHO
H bombardment of NH2CHO:

NH₂CHO + 2H --> NH₂CH₂COH (amminomethanol) ?

NH₂CH₂COH is not formed via this route

c) b) - a)

b) NH₂CHO + H
a) Pure NH₂CHO
FORMOLISM set-up @LERMA-Cergy

Used to perform monolayer & sub-monolayer experiments
Surface reaction: HNCO + H/D

a) HNCO (m/z=43)

b) HNCO + H (m/z=43)
Surface reaction: HNCO + H/D

a) HNCO (m/z=43)
b) HNCO + D (m/z=43)
c) HNCO (m/z=44)
d) DNCO
Surface reaction: HNCO + H/D

- a) HNCO (m/z=43)
- c) HNCO + D (m/z=43)
- d) HNCO + D (m/z=44) DNCO

No signal at m/z=47 (NHDCDO)
Surface reaction: HNCO + (high dose) H/D

- a) 1 ML HNCO (m/z=43)
- b) 1 ML HNCO + 25 ML D (m/z=43)
- c) 1 ML HNCO + 25 ML D (m/z=44)

Yet, no NHDCDODO
Surface reaction: HNCO + H/D

Proposed reaction scheme:

The expected hydrogenation of HNCO to NH$_2$CHO does not readily occur and thus has a very high barrier.

Astrophysical implications

Our results **contradict** theoretical studies which propose that subsequent hydrogenation of HNCO leads to NH$_2$CHO

Formation in gas phase remains unlikely, **grain surface chemistry** should still be the dominant mechanism to form NH$_2$CHO

NH$_2$CHO can form by recombination between the radicals NH$_2$ and HCO after **energetic processing** (e.g., UV photons)

Our results suggest that **thermal reactions**, such as the reaction with NH$_3$ and H$_2$O, should dominate HNCO chemistry on grains

NH$_2$CHO **does not react** with hydrogen to produce amminomethanol