



Universiteit
Leiden
The Netherlands

Formation and photostability of N-heterocycles in space. I. The effect of nitrogen on the photostability of small aromatic molecules

Peeters, Z.; Botta, O.; Charnley, S.B.; Kisiel, Z.; Kuan, Y.-J.; Ehrenfreund, P.

Citation

Peeters, Z., Botta, O., Charnley, S. B., Kisiel, Z., Kuan, Y. -J., & Ehrenfreund, P. (2005). Formation and photostability of N-heterocycles in space. I. The effect of nitrogen on the photostability of small aromatic molecules. *Astronomy And Astrophysics*, 433, 583-590. Retrieved from <https://hdl.handle.net/1887/7454>

Version: Not Applicable (or Unknown)

License:

Downloaded from: <https://hdl.handle.net/1887/7454>

Note: To cite this publication please use the final published version (if applicable).

Formation and photostability of N-heterocycles in space

I. The effect of nitrogen on the photostability of small aromatic molecules

Z. Peeters¹, O. Botta^{1,2}, S. B. Charnley³, Z. Kisiel⁴, Y.-J. Kuan^{5,6}, and P. Ehrenfreund¹

¹ Astrobiology Laboratory, Leiden Institute of Chemistry, PO Box 9502, 2300 RA Leiden, The Netherlands
e-mail: peeters@strw.leidenuniv.nl

² International Space Science Institute, Hallerstrasse 6, 3012 Bern, Switzerland

³ Space Science Division, NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035, USA

⁴ Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

⁵ Department of Earth Sciences, National Taiwan Normal University, 88 Sec. 4 Ting-Chou Road, Taipei 116, Taiwan

⁶ Institute of Astronomy and Astrophysics, Academia Sinica, PO box 23-141, Taipei 106, Taiwan

Received 26 November 2004 / Accepted 14 December 2004

Abstract. Nitrogen-containing cyclic organic molecules (N-heterocycles) play important roles in terrestrial biology, for example as the nucleobases in genetic material. It has previously been shown that nucleobases are unlikely to form and survive in interstellar and circumstellar environments. Also, they were found to be unstable against ultraviolet (UV) radiation. However, nucleobases were detected in carbonaceous meteorites, suggesting their formation and survival is possible outside the Earth. In this study, the nucleobase precursor pyrimidine and the related N-heterocycles pyridine and s-triazine were tested for UV stability. All three N-heterocycles were found to photolyse rapidly and their stability decreased with an increasing number of nitrogen atoms in the ring. The laboratory results were extrapolated to astronomically relevant environments. In the diffuse interstellar medium (ISM) these N-heterocycles in the gas phase would be destroyed in 10–100 years, while in the Solar System at 1 AU distance from the Sun their lifetime would not extend beyond several hours. The only environment where small N-heterocycles could survive, is in dense clouds. Pyridine and pyrimidine, but not s-triazine, could survive the average lifetime of such a cloud. The regions of circumstellar envelopes where dust attenuates the UV flux, may provide a source for the detection of N-heterocycles. We conclude that these results have important consequences for the detectability of N-heterocycles in astronomical environments.

Key words. astrobiology – methods: laboratory – stars: individual: CRL 618

1. Introduction

Nucleobases are nitrogen-containing heterocyclic aromatic compounds (N-heterocycles), found in the genetic material of all living organisms on Earth. They can be divided into two groups according to their molecular structure: the purine derivatives (adenine, guanine, xanthine and hypoxanthine) and the pyrimidine derivatives (cytosine, thymine and uracil). The only source where extraterrestrial nucleobases have been detected so far, is in meteorites (van der Velden & Schwartz 1977; Stoks & Schwartz 1979, 1981). Peeters et al. (2003) discussed possible formation routes for nucleobases in circumstellar environments, followed by an examination of the stability of these molecules against UV radiation. The results showed that adenine and uracil are easily degraded, in a matter of years by the UV field present in the diffuse interstellar medium. Nucleobases are not likely to be formed in dense interstellar regions (Smith et al. 2001).

In the extended gas and dust envelopes of late-type stars, polymerisation of acetylene can produce benzene, larger polycyclic aromatic hydrocarbons (PAHs) and large carbonaceous dust particles (e.g. Cherchneff et al. 1992). N-heterocycles may form as by-products of acetylene polymerisation. Intermediate replacement of C_2H_2 by HCN could lead to direct incorporation of a nitrogen atom into a growing aromatic ring (Ricca et al. 2001), forming pyridine. Due to a small HCN/C_2H_2 ratio in these envelopes, this scenario predicts decreasing abundances of aromatic molecules containing more than one nitrogen atom per ring, such as pyrimidine (two nitrogens) and s-triazine (three nitrogens), see Fig. 1.

Inclusion of nitrogen into the symmetric skeleton of aromatic hydrocarbon compounds induces a permanent dipole moment, which allows the molecule to be observed in a pure rotational spectrum. Pyridine has been the subject of more than 20 published studies on rotational spectroscopy. The millimeter wave rotational spectrum of the parent isotopomer was investigated up to $J = 60$ and 205 GHz by

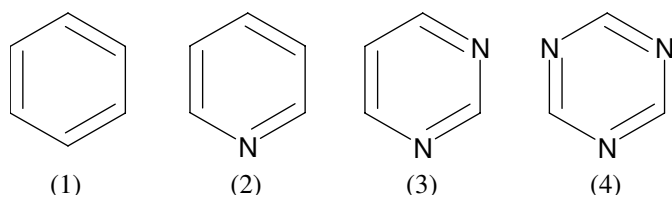


Fig. 1. Four six-membered cyclic aromatic molecules: 1. benzene; 2. pyridine; 3. pyrimidine; and 4. 1,3,5-triazine (or *s*-triazine), having zero, one, two, and three nitrogens per ring, respectively.

Włodarczyk et al. (1988) and accurate spectroscopic constants were reported. The rotational spectrum of pyrimidine has recently been thoroughly reinvestigated with the use of several different spectrometers (Kisiel et al. 1999) and precise spectroscopic constants of the ground state and several excited vibrational states, as well as the molecular geometry have been determined. *s*-Triazine is a symmetric top molecule with zero permanent dipole moment and no results from rotational spectroscopy are available.

Of the four molecules in Fig. 1 only benzene has been detected, by ISO observations in post-asymptotic giant branch (AGB) object CRL 618 (Cernicharo et al. 2001). In parallel with the experimental work reported here and by Peeters et al. (2003), we have undertaken an observational program to search for various N-heterocycles in interstellar and circumstellar environments (Kuan et al. 2003c, 2004). Searches for pyridine towards carbon-rich AGBs did not yield any positive results. The upper limits of total molecular column densities that were derived for pyridine, are $N_{\text{tot}} < 7 \times 10^{12} \text{ cm}^{-2}$ in IRC+10216 and $2 \times 10^{13} \text{ cm}^{-2}$ in CRL 618 (Kuan et al. 2003a, 2004). For nucleic acid building block pyrimidine upper limits of 1.7×10^{14} , 2.4×10^{14} and $3.4 \times 10^{14} \text{ cm}^{-2}$ were found in the objects Sgr B2(N), Orion KL and W51 e1/e2, respectively (Kuan et al. 2003c). Obviously, no searches have been conducted for *s*-triazine.

It is crucial to investigate the photostability of small N-heterocycles in order to understand their role in interstellar and circumstellar gas phase chemistry. Their destruction rates determine the lifetime and abundance of these molecules in interstellar regions and, consequently, their detectability. In the present paper, we measured the UV photostability of the nucleobase precursor molecule pyrimidine, along with the N-heterocycles pyridine and *s*-triazine, to investigate the effect of the number of nitrogen atoms in the ring on the photostability of these molecules. UV photolysis experiments on benzene have been reported by Ruiterkamp et al. (2005) and the results for this hydrocarbon are compared with the results for the nitrogen-containing heterocycles. In the following sections we will describe the photostability experiments and their results, and discuss the implications of these results for astronomical observations of small N-heterocycles in different space environments.

2. Experimental

Matrix isolation spectroscopy and UV destruction of pyridine, pyrimidine and *s*-triazine was performed on a standard matrix

isolation set-up (Peeters et al. 2003, see also Hudgins et al. 1994 for a detailed description of the set-up) with a background pressure of $\sim 10^{-9}$ mbar and a CsI substrate window thermally connected to a closed-cycle helium cryostat, capable of cooling down to 12 K. The substrate window and cryostat can rotate without breaking the vacuum.

For the matrix material 99.999% pure argon (Praxair) was used. Pyridine (99.8%, Fluka) and pyrimidine (99%, Aldrich) were prepared by four freeze-pump-thaw cycles to remove dissolved gases. The hygroscopic *s*-triazine (98%, Merck) was handled exclusively under a nitrogen atmosphere in a glove-box, followed by four freeze-pump-thaw cycles. The vapour of each of these molecules was diluted in argon to a 1:750 ratio, using a glass gas-mixing line with a background pressure of $\sim 10^{-6}$ mbar. The absolute pressures of the gases were measured with a 0.1–200 mbar and a 1–2000 mbar manometer (Leybold). The resulting N-heterocycle/argon-mixtures were deposited onto the 12 K CsI window to a total thickness of $1 \mu\text{m}$, controlled by standard laser interferometry. A $1 \mu\text{m}$ thick sample layer allowed for full penetration of the UV light through the sample.

For the photolysis experiments a microwave-excited hydrogen flow lamp with a flux of $4.6 \times 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$ was used. The UV lamp was calibrated by actinometry as described by Cottin et al. (2003) before and after each series of experiments. UV irradiation was performed in 10 s intervals to a total of 2 min of irradiation (5 s intervals to a total of 1 min irradiation for *s*-triazine) followed by 1 min intervals until the sample was completely destroyed. Photodestruction of the N-heterocycles was monitored with in situ Fourier-transform infra-red (FT-IR) spectroscopy using an Excalibur FTS-4000 spectrometer (BioRad) in the range $4000\text{--}500 \text{ cm}^{-1}$ at 1 cm^{-1} resolution. In these experiments, the combination of an accurate gas mixing ratio, a laser-interferometry controlled sample thickness, and a calibrated lamp flux allowed for accurate and reproducible photodestruction rate measurements, which will be shown in the next section.

3. Results

The three N-heterocycles pyridine, pyrimidine and *s*-triazine were analysed using FT-IR spectroscopy. The resulting spectra are shown in Fig. 2. The spectra were compared with the results obtained by Destexhe et al. (1994) for pyridine and pyrimidine, and Morrison et al. (1997) for *s*-triazine to confirm the obtained spectra and perform band assignments, see Table 1.

The UV photolysis of the heterocyclic molecules was measured by recording the infra-red spectrum after short periods of exposure to UV radiation. In Fig. 2 the spectra after 10 s and 1 and 10 min of photolysis are shown for each N-heterocyclic molecule. The diminishing of the peaks in Fig. 2 after UV irradiation shows that all three molecules were destroyed by the UV. The rate of destruction was calculated by plotting the natural log of the normalised integrated peak areas against time and fitting the data points with a linear regression line. Only the first 120 s of photolysis time (the first 35 s for *s*-triazine) were considered, because at longer photolysis times the destruction rate showed a deviation from first order behaviour.

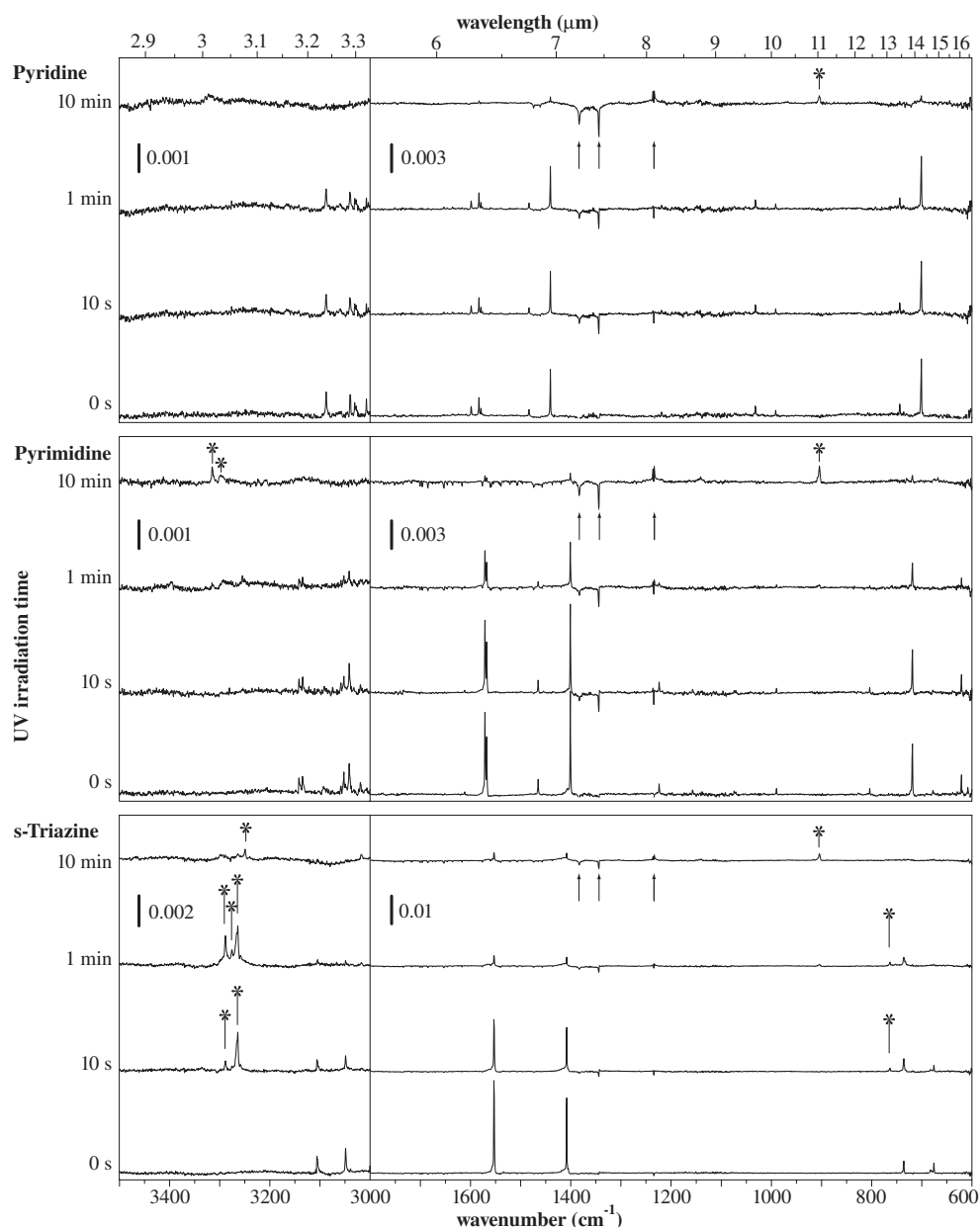


Fig. 2. The FT-IR spectra of pyridine, pyrimidine and s-triazine (top to bottom) isolated in an argon matrix at 12 K in the ranges 3500–3000 cm^{-1} (left panels) and 1800–600 cm^{-1} (right panels) with a resolution of 1 cm^{-1} . The matrix isolated molecules were irradiated with UV for 10 s, 1 and 10 min. The vertical scale bars indicate the infra-red absorption in absorption units. Band assignments are presented in Table 1. New bands appearing after photolysis are designated by asterisks (*). Photoproduct assignments are given in Table 3. Features at 1383, 1344 and 1234 cm^{-1} , designated with arrows, are due to contamination in the system. These contaminations were accumulated outside the argon matrix and did not interfere with the photolysis reactions.

Table 1. The wavenumbers ($\tilde{\nu}$ in cm^{-1}) of the most prominent peaks of the heterocycles with their assignments, used to monitor the UV photodestruction. ν denotes a stretching mode, β is a bending mode and τ refers to a torsion mode. Taken from *a* Destexhe et al. (1994) and *b* Morrison et al. (1997).

Pyridine ^a		Pyrimidine ^a		s-Triazine ^b	
$\tilde{\nu}$ (cm^{-1})	mode description	$\tilde{\nu}$ (cm^{-1})	mode description	$\tilde{\nu}$ (cm^{-1})	mode description
702	τ -ring	621	β -ring	680	β -ring
1031	β -ring	719	τ -ring	738	ν -ring
1441	ν CC, β CH	1400	β CH, ν CN	1416	ν CH
1582	ν CC	1571	ν CN, ν CC	1552	β N out-of-plane
3008	ν CH	3042	ν CH		

Table 2. The UV destruction cross-sections (σ_{uv}) and half-lives in the experimental set-up in the laboratory and in the diffuse interstellar environment (DISM), dense clouds (DC) and the Solar System at 1 AU from the Sun (SoSy). Also included in this table is the cyclic hydrogen-bonded trimer of HCN, which is the first photoproduct of s-triazine. Upon continued irradiation, c-(HCN)₃ is also photolysed, see Fig. 4.

	σ_{uv} (cm ² molecule ⁻¹)	Half-life			
		lab (s)	DISM (yr)	DC (Myr)	SoSy (min)
Pyridine	1.2×10^{-17}	123	18	1.8	32
Pyrimidine	2.7×10^{-17}	56	8.1	0.81	14
s-Triazine	8.7×10^{-17}	17	2.5	0.25	4.4
c-(HCN) ₃	2.6×10^{-17}	57	8.3	0.83	15

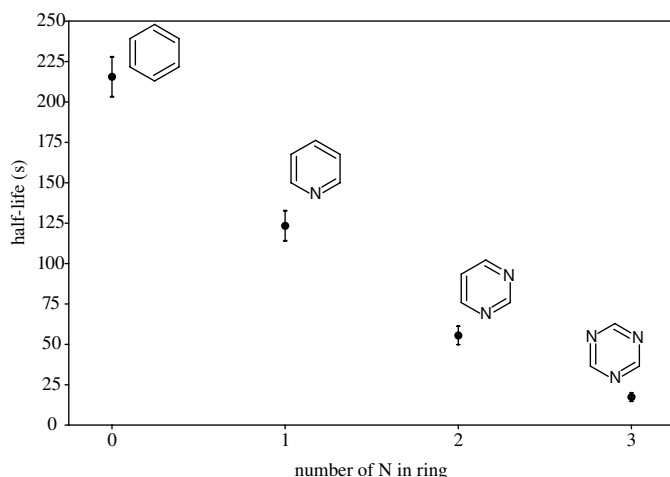


Fig. 3. The half-lives of the three N-heterocycles plotted against the number of nitrogen atoms in the ring. Also included in this graph is the half-life of benzene, taken from Ruiterkamp et al. (2005). This plot shows that the photostability of small heterocyclic molecules decreases when an increasing number of nitrogen atoms is incorporated in the ring. The error bars indicate the standard deviation of the linear fit used in the calculation of the half-lives of those molecules.

From the slopes of the linear fits, the destruction cross-sections and half-lives were calculated, which are compiled into Table 2. Half-lives were calculated from the laboratory data and extrapolated to the diffuse ISM, a dense cloud and the Solar System environment at 1 AU from the Sun, using the appropriate UV fluxes: 1×10^8 photons cm⁻² s⁻¹ for the diffuse ISM (Mathis et al. 1983), 1×10^3 photons cm⁻² s⁻¹ for a dense cloud (Prasad & Tarafdar 1983) and 3×10^{13} photons cm⁻² s⁻¹ for the solar UV flux >6 eV at 1 AU distance from the Sun. The resulting half-lives for those astronomical environments were added to Table 2. Finally, the half-lives for the N-heterocycles were compared to benzene (Ruiterkamp et al. 2005) and plotted against the number of nitrogen atoms in the ring, resulting in Fig. 3.

The photodissociation of s-triazine in an argon matrix has been previously described by Satoshi et al. (1997). New bands appearing after 10 s of UV irradiation, were found at 3264.0, 2098.5, 763.7 and 732.9 cm⁻¹. These bands matched with the results of Satoshi et al. (1997) and are assigned to the C-H stretching mode, the C-N stretching mode, the in-plane bending mode and the out-of-plane bending mode of a hydrogen-bonded cyclic HCN trimer (c-(HCN)₃), respectively. The bands of c-(HCN)₃ reached a maximum after 30 s of irradiation. At longer periods of irradiation, the c-(HCN)₃ bands

Table 3. Wavenumbers (in cm⁻¹) of the photoproducts that appeared after UV irradiation of pyridine, pyrimidine or s-triazine. The band assignments were taken from *a* Milligan & Jacox (1973); *b* Ruiterkamp et al. (2005); *c* Satoshi et al. (1997); and *d* Stroh & Winnewisser (1989). The bands for HCN and C₂H₂ in the pyrimidine photoproducts are shifted with respect to the bands given in the references, so a complex between HCN and C₂H₂ is inferred (see text).

Irradiation time	Wavenumber (cm ⁻¹)	Band assignment
pyridine		
10 min	904.1	[HAr ₂] ⁺ <i>a</i>
pyrimidine		
10 min	904.1	[HAr ₂] ⁺ <i>a</i>
	3297.8	C ₂ H ₂ <i>b</i> (complexed with HCN)
	3314.7	HCN <i>c</i> (complexed with C ₂ H ₂)
s-triazine		
10 s	3288.6	–
	3264.0	c-(HCN) ₃ C-H stretch <i>c</i>
	2098.5	c-(HCN) ₃ C-N stretch <i>c</i>
	763.7	c-(HCN) ₃ in-plane bend <i>c</i>
	732.9	c-(HCN) ₃ out-of-plane bend <i>c</i>
1 min	3288.6	–
	3275.6	–
	3264.0	c-(HCN) ₃ C-H stretch <i>c</i>
	3258.2	–
	2098.5	c-(HCN) ₃ C-N stretch <i>c</i>
	763.7	c-(HCN) ₃ in-plane bend <i>c</i>
	732.9	c-(HCN) ₃ out-of-plane bend <i>c</i>
10 min	3249.1	–
	2295.8	CNCN pseudo-symm. stretch <i>d</i>
	2054.2	CNCN pseudo-asyymm. stretch <i>d</i>
	904.1	[HAr ₂] ⁺ <i>a</i>

disappeared again, while new bands appeared at 2295.8 and 2054.2 cm⁻¹. Using the results from Stroh & Winnewisser (1989) these two bands could be assigned to the pseudo-symmetric stretching mode and pseudo-asymmetric stretching mode of CNCN. Other bands that appeared during photolysis of s-triazine, but that could not be assigned, were found at 3288.6, 3275.6, 3258.2 and 3249.1 cm⁻¹. All bands and their assignments are shown in Table 3.

The change of the relative abundances of s-triazine and its photoproducts during irradiation – as measured by the integrated peak areas, relative to the highest value per peak – is shown in Fig. 4. The relative abundances in Fig. 4 were determined from the peaks at 1552 cm⁻¹ for s-triazine, 3264 cm⁻¹ for c-(HCN)₃ and 2295 cm⁻¹ for CNCN. From the results

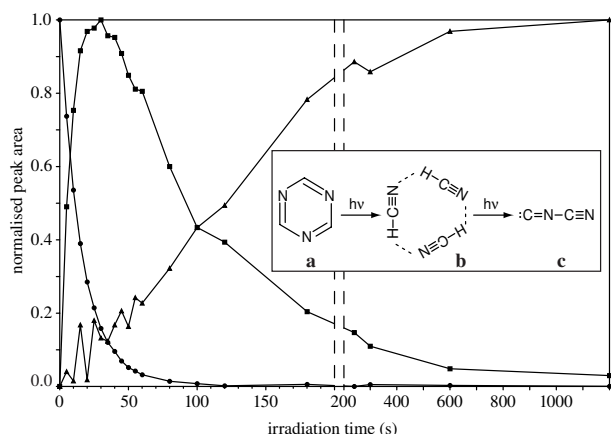


Fig. 4. The relative column densities of s-triazine and its photoproducts during photolysis. Shown in the graph are s-triazine (graph: ●, inset: **a** – measured by the 1552 cm^{-1} transition), c-(HCN) $_3$ (graph: ■, inset: **b** – from the 3264 cm^{-1} vibration) and CNCN (graph: ▲, inset: **c** – from the peak at 2295 cm^{-1}). Inset: the suggested photolysis reaction pathway for s-triazine upon irradiation with UV.

described above, the following s-triazine photolysis pathway is suggested: $\text{C}_3\text{H}_3\text{N}_3 \rightarrow \text{c}-(\text{HCN})_3 \rightarrow \text{CNCN}$, see also the inset in Fig. 4. After 30 s of irradiation only ~10% of the initial amount of s-triazine was remaining. Assuming the suggested photolysis pathway, 90% of the s-triazine was converted into c-(HCN) $_3$ in the first 30 s. After this period c-(HCN) $_3$ degraded with only little replenishment by further degradation of s-triazine. From the c-(HCN) $_3$ peaks in the infra-red spectra between 30 and 100 s of irradiation, the UV destruction cross-section and half-lives for c-(HCN) $_3$ could be calculated in the same way as for pyridine, pyrimidine and s-triazine. The results were added to Table 2.

In the photolysis experiments of pyrimidine only two new bands were found after 10 min of irradiation with UV. These bands were located at 3297.8 and 3314.7 cm^{-1} . Since s-triazine has been shown to photolyse into three HCN molecules (Satoshi et al. 1997) and benzene into acetylene molecules (Ruiterkamp et al. 2005), it can be expected that pyrimidine would degrade into two HCN molecules and one acetylene molecule. These photoproducts are likely to form a complex in some way, since they are enclosed by an argon matrix. The peaks for the HCN monomer in an argon matrix are found at 3306 and 3202 cm^{-1} , while for a linear dimer of HCN these peaks shift to 3304 and 3210 cm^{-1} (Satoshi et al. 1997). For acetylene isolated in an argon matrix a peak is found at 3253 cm^{-1} while a peak at 3284 cm^{-1} might be assigned to a complex of multiple acetylene molecules (Ruiterkamp et al. 2005). Using these data, the new peak at 3297.8 cm^{-1} is tentatively assigned to an acetylene mode and the peak at 3314.7 cm^{-1} to an HCN mode in a complex between acetylene and HCN.

The only new band appearing in the infra-red spectra of pyridine after UV photolysis, is found at 904.1 cm^{-1} . This band is found in every experiment, including pyrimidine and s-triazine and is assigned to a proton-argon complex, $[\text{HAr}_2]^+$ (Milligan & Jacox 1973). All photoproduct bands and their assignments are listed in Table 3.

4. Discussion

4.1. N-heterocycles in dense interstellar and circumstellar regions

Of the 137 interstellar molecules identified to date (see www.astrochemistry.net), only six molecules contain 10 or more atoms, the largest being the linear carbon-chain molecule HC $_{11}\text{N}$. Several small ring molecules have been observed in the interstellar medium (e.g. Dickens et al. 1997; Nummelin et al. 1998). Organic ring molecules containing nitrogen atoms, c-C $_2\text{H}_3\text{N}$ (2H-azirine, Charnley et al. 2001) and c-C $_2\text{H}_5\text{N}$ (aziridine, Kuan et al. 2003b; Dickens et al. 2001; Charnley et al. 2001), have so far only been detected tentatively. Detections of large organic molecules are very difficult, due to the intrinsic weakness of their spectral lines as a result of low abundances and large partition functions. The chance of detection is further lowered for ring molecules as rings have even larger partition functions. The anticipated detectability would be even less for N-bearing heterocycles due to their expected low abundances compared to large organics containing only C, O and H. Yet another challenge for detecting these N-heterocycles could come from the contamination of the already weak target spectral lines by emission from the many interlopers from other (simpler) molecular species, present in the chemically active molecular cloud cores or circumstellar envelopes, the favourable sites for conducting astronomical searches of large organic molecules.

Upon irradiation of N-heterocycles with UV, these molecules are destroyed as can be seen by the extinction of their peaks in the infra-red spectra in Fig. 2. The UV destruction cross-section and half-lives in Table 2 show that this destruction proceeds rapidly under laboratory conditions. When these laboratory results are extrapolated to astrophysical conditions, pyridine, pyrimidine and s-triazine are expected to have very short lifetimes in the diffuse interstellar and Solar System environments. Only in dense interstellar clouds, where these molecules are shielded from the interstellar UV field, would pyridine and pyrimidine be able to survive the average life-span of such a cloud ($\sim 10^6$ years, Elmegreen 2000; Hartmann et al. 2001). s-Triazine, with a half-life of 250 000 years in a dense cloud environment, would have only 6% of its initial amount remaining at the end of the cloud's lifetime. The c-(HCN) $_3$ complex that forms upon photolysis of s-triazine, however, has a half-life that is comparable to the half-life of pyrimidine and might survive the lifetime of a dense cloud.

Around 20 molecules have been detected in CRL 618. According to models by Herpin & Cernicharo (2000) and Woods et al. (2002) benzene and, possibly, N-heterocycles are formed in the circumstellar envelope of CRL 618. The physical structure of this circumstellar envelope is very complex. The strong UV field from the central star has produced a compact H II region that is confined by a dense circumstellar disk (Cernicharo 2004). The benzene absorption arises from the innermost regions of the dense circumstellar disk, where dust absorption attenuates the strong stellar UV flux. Models reported by Woods et al. (2002) indicate that when the extinction decreases to ~ 10 mag at a distance of $\sim 10^{16}\text{ cm}$ from the central

star, the abundances of molecules such as benzene rapidly drop, indicating destruction by interstellar UV photons. In such environments N-heterocycles would be rapidly destroyed as well.

The experiments described in this paper are performed employing the low temperature matrix isolation technique, while the results are extrapolated to the gas phase in different interstellar and circumstellar environments. Although the argon matrix provides a good spectroscopic comparison to the gas phase, there are some small differences between argon matrix and gas phase in terms of photochemistry. In the matrix, energy absorbed by the molecule can be dissipated in the matrix, thereby lowering the chance of photodestruction. Also, after photolysis photoproducts remain in close contact with each other in the matrix, because they are enclosed by solid argon. These two factors will increase the real gas phase destruction rate (lower the gas phase half-life) and the matrix isolated destruction cross-sections presented in this paper can be regarded as lower limits (upper limits for the half-lives). Ruiterkamp et al. (2005) showed a factor 10 difference between gas phase and low temperature matrix isolation data for benzene.

4.2. Possible formation of N-heterocycles in space

The formation of benzene in interstellar environments could proceed via gas phase reactions or gas-grain chemistry. However, in most reaction schemes it is unclear how nitrogen atoms are incorporated into forming rings. Irradiation of icy grain analogues in the laboratory often leads to complex new molecules (Bernstein et al. 1995, 1999; Moore & Hudson 1999). The low photostability of small N-heterocycles like pyridine and pyrimidine, however, may argue against the production by photochemistry on icy grains. In order to understand gas phase reactions leading to N-heterocycles, the combination of observations, theoretical models and laboratory data on the formation of benzene can provide useful information.

Woods et al. (2002) have shown that circumstellar ion-molecule chemistry, based on the findings of McEwan et al. (1999), could in fact produce benzene in the abundance observed in CRL 618. In this scenario, the reaction sequence is initiated by HCO^+ reacting with C_2H_2 . A very high ionization rate (about ~ 100 times the canonical interstellar value due to cosmic ray particles) is required to produce $c\text{-C}_6\text{H}_6$ efficiently. Woods et al. (2002) attributed soft X-rays or shock waves as the source of enhanced ionization. In situ erosion of carbon dust to PAHs and simpler molecules, either by sputtering in shocks or by photolysis (Wooden et al. 2004), could provide a viable source of benzene to compete with its photodestruction in the diffuse ISM.

N-heterocycles are not formed as efficiently as benzene in circumstellar environments, as was discussed in Sect. 1. A low formation rate combined with a low stability against UV radiation, makes the detection of N-heterocycles in circumstellar environments difficult. Nevertheless, sources with higher $\text{HCN}/\text{C}_2\text{H}_2$ ratios in the dust formation zone could have higher production rates of N-heterocycles and thus serve as better targets than CRL 618 to search for these molecules. For example, the $\text{HCN}/\text{C}_2\text{H}_2$ ratio in CRL 618 is observed to be about 0.16

(Woods et al. 2002), whereas the estimated $\text{HCN}/\text{C}_2\text{H}_2$ ratio around the carbon-rich AGB star IRC+10216 is about 0.6 (Cherchneff et al. 1993). This elevated $\text{HCN}/\text{C}_2\text{H}_2$ ratio, along with a much slower outflow velocity and lower UV flux, suggests that the circumstellar envelope of IRC+10216 would be a better source for finding N-heterocycles.

The high photodestruction rates make it unlikely that small N-heterocycles could have survived the conditions during Solar System formation, unless they were well protected against radiation in the disk mid-plane at all times.

4.3. N-heterocycles in meteorites

CI and CM-type carbonaceous meteorites are considered to be the most pristine samples of the early Solar System with respect to their elementary composition. However, both meteorite classes show mineralogical evidence for alteration by liquid water percolating through the parent body, evidence mainly in the form of hydrated minerals like clays, carbonates, sulphates and phyllosilicates (Endress & Bischoff 1996). Interstellar organic matter that was trapped in the meteorite parent body during the formation of the Solar System would thus have undergone subsequent reactions in the aqueous solution to form secondary products (Zolensky & McSween 1988). Whereas early quantitative treatment of this model points to temperature estimates of less than 20°C for CM and $100\text{--}150^\circ\text{C}$ for CI carbonaceous chondrites (Clayton & Mayeda 1984), refinements of the models reduced the temperature for the CIs to $\sim 50^\circ\text{C}$ (Leshin et al. 1997). A pH in the range of 6 to 8 has been suggested for the aqueous phase of CM chondrites (DuFresne & Anders 1962).

It is generally accepted that the amino acids found in carbonaceous meteorites, are produced during the phase of aqueous alteration in the parent body. These compounds can be synthesized from interstellar precursor molecules such as HCN, ammonia and carbonyl compounds, including formaldehyde, acetaldehyde and acetone. This formation route, the so-called Strecker-cyanohydrin reaction, can take place inside the meteorite parent body during aqueous alteration (Cronin & Chang 1993). These conditions could also be favourable for the formation of purines and pyrimidines.

The first synthetic step towards the abiotic synthesis of purines could be HCN polymerisation, which would lead to the formation of the HCN-tetramer diaminomaleonitrile (DAMN) as an intermediate. This compound, which is obtained in yields of 0.3 to 0.5% in aqueous 0.1–1.0 M HCN solutions, is also a possible intermediate for the formation of certain amino acids (Ferris & Hagan 1984). The formation of DAMN requires basic pH values (9.2 in the laboratory experiment), while the liquid inside the meteorite parent bodies is thought to be buffered to pH 6 (slightly acidic) by the mineral composition present in the meteorite (DuFresne & Anders 1962).

Several possible pathways exist for the reaction of DAMN with other compounds such as ammonia and/or formamide to lead to the formation of adenine, the simplest purine. The reaction of DAMN with urea leads to the formation of guanine and xanthine in yields of 5–10%. Another prebiotic pathway for the

formation of the adenine derivative 8-hydroxymethyladenine (HMA) as well as traces of adenine from HCN and formaldehyde, was experimentally demonstrated by Schwartz & Bakker (1989). Finally, it has been demonstrated recently that guanine can be produced from ammonium cyanide polymerisations (Levy et al. 1999).

The abiotic synthesis of pyrimidines is more difficult to achieve. The first proposal for the formation of a pyrimidine from a cyano-compound was the synthesis of cytosine from cyanoacetylene and cyanate, both possibly prebiotic compounds, followed by hydrolysis, leading to uracil (Ferris et al. 1968). Starting from DAMN, a variety of pathways for the formation of pyrimidine derivatives, for example the reaction of DAMN with guanidine that yields 5-hydroxyuracil, were proposed by Ferris et al. (1978). Only uracil was detected in carbonaceous chondrites (Stoks & Schwartz 1979), a fact that may reflect the apparent difficulty in the abiotic synthesis of these compounds.

In summary, carbonaceous chondrites appear to contain several classes of N-heterocyclic compounds, including purines, pyrimidines, quinolines/isoquinolines and pyridines. Stable isotope data of these compounds, which would be very helpful in determining their extraterrestrial origin, have yet to be reported.

5. Conclusion

Pyrimidine is a precursor of the biologically important nucleobases. Together with two other nitrogen-containing heterocyclic molecules pyridine and s-triazine, the UV destruction rate was determined using low temperature matrix isolation in solid argon. We found that these molecules were rapidly destroyed when photolysed with UV radiation and that the stability decreased with an increasing number of nitrogen atoms in the ring. When scaled to the UV fluxes of astronomically relevant environments, these molecules would be destroyed fast in the UV dominated regions of circumstellar envelopes and diffuse interstellar clouds. Only in dense clouds could pyridine and pyrimidine, but not s-triazine, survive the average lifetime of the cloud. From these results, combined with the weak spectral lines and low abundances of these N-heterocycles, we expect a low probability for the detection for these molecules. The most promising search site for N-heterocycles would be targets with a high HCN/C₂H₂ ratio, such as the AGB star IRC+10216. However, N-heterocyclic compounds have been detected in carbonaceous meteorites. The low probability for these compounds to survive in the gas phase in the interstellar medium and during planetary system formation, as strongly indicated by the results of this study, suggest that these N-heterocycles were probably synthesised on the meteorite parent bodies.

Acknowledgements. The authors wish to thank T. Millar, P. Woods and E. Herbst for discussions. P.E. and Z.P. are supported by grant NWO-VI 016.023.003, Y.J.K. is supported by grant NSC 93-2112-M-003, and S.B.C. is supported by NASA's

Exobiology program through NASA Ames Cooperative Agreement No. NCC2-1412 to the SETI Institute. O.B. was an ESA post-doctoral fellow.

References

- Bernstein, M., Sandford, S., Allamandola, L., Chang, S., & Scharberg, M. 1995, *ApJ*, 454, 327
- Bernstein, M., Sandford, S., Allamandola, L., et al. 1999, *Science*, 283, 1135
- Cernicharo, J. 2004, *ApJ*, 608, L41
- Cernicharo, J., Heras, A., Tielens, A., et al. 2001, *ApJ*, 546, L123
- Charnley, S., Ehrenfreund, P., & Kuan, Y.-J. 2001, *Spectrochim. Acta A*, 57, 685
- Cherchneff, I., Barker, J., & Tielens, A. 1992, *ApJ*, 401, 269
- Cherchneff, I., Glassgold, A., & Mamon, G. 1993, *ApJ*, 410, 188
- Clayton, R., & Mayeda, T. 1984, *Earth Planet. Sci. Lett.*, 67, 151
- Cottin, H., Moore, M., & Bénilan, Y. 2003, *ApJ*, 590, 874
- Cronin, J., & Chang, S. 1993, in *The chemistry of life's origin*, ed. J. Greenberg, C. Mendoza-Gomez, & V. Pirronello (The Netherlands: Kluwer Academic Publishers), 209
- Destexhe, A., Smets, J., Adamowicz, L., & Maes, G. 1994, *J. Phys. Chem*, 98, 1506
- Dickens, J., Irvine, W., Nummelin, A., et al. 2001, *Spectrochim. Acta A*, 51, 643
- Dickens, J., Irvine, W., Ohishi, M., et al. 1997, *ApJ*, 489, 753
- DuFresne, E., & Anders, E. 1962, *Geochim. Cosmochim. Acta*, 26, 1085
- Elmegreen, B. 2000, *ApJ*, 530, 277
- Endress, M., & Bischoff, A. 1996, *Geochim. Cosmochim. Acta*, 60, 489
- Ferris, J., & Hagan, W. 1984, *Tetrahedron*, 40, 1093
- Ferris, J., Joshi, P., Edelson, E., & Lawless, J. 1978, *J. Mol. Evol.*, 11, 293
- Ferris, J., Sanchez, R., & Orgel, L. 1968, *J. Mol. Biol.*, 33, 693
- Hartmann, L., Ballesteros-Paredes, J., & Bergin, E. 2001, *ApJ*, 562, 852
- Herpin, F., & Cernicharo, J. 2000, *ApJ*, 530, L129
- Hudgins, D., Sandford, S., & Allamandola, L. 1994, *J. Phys. Chem.*, 98, 4243
- Kisiel, Z., Pszczolkowski, L., Lopez, J., et al. 1999, *J. Mol. Spectrosc.*, 195, 332
- Kuan, Y.-J., Huang, H.-C., Butner, H., et al. 2004, *Astrobiology*, 4, 268
- Kuan, Y.-J., Huang, H.-C., Charnley, S., et al. 2003a, in *25th IAU GA, Joint Discussion 14*, Sydney, Australia, 14, 44
- Kuan, Y.-J., Huang, H.-C., Charnley, S., et al. 2003b, in *Proceedings of the XIIth Rencontres de Blois on Frontiers of Life*, ed. L. Celnikier, & J. Tran Thanh Van (Vietnam: The Gioi), 257
- Kuan, Y.-J., Yan, C.-H., Charnley, S., et al. 2003c, *MNRAS*, 345, 650
- Leshin, L., Rubin, A., & McKeegan, K. 1997, *Geochim. Cosmochim. Acta*, 61, 835
- Levy, M., Miller, S., & Oró, J. 1999, *J. Mol. Evol.*, 49, 165
- Mathis, J., Mezger, P., & Panagia, N. 1983, *A&A*, 128, 212
- McEwan, M., Scott, G., Adams, N., et al. 1999, *ApJ*, 513, 287
- Milligan, D., & Jacox, M. 1973, *J. Mol. Spectrosc.*, 46, 460
- Moore, M., & Hudson, R. 1999, *Icarus*, 140, 451
- Morrison, C., Smart, B., Rankin, D., et al. 1997, *J. Phys. Chem. A*, 101, 10029
- Nummelin, A., Dickens, J., Bergman, P., et al. 1998, *A&A*, 337, 275
- Peeters, Z., Botta, O., Charnley, S., Ruiterkamp, R., & Ehrenfreund, P. 2003, *ApJ*, 593, L129
- Prasad, S., & Tarafdar, S. 1983, *ApJ*, 267, 603

- Ricca, A., Bauschlicher, C., & Bakes, E. 2001, *Icarus*, 154, 516
- Ruiterkamp, R., Peeters, Z., Moore, M., Hudson, R., & Ehrenfreund, P. 2005, *A&A*, in revision
- Satoshi, K., Takayanagi, M., & Nakata, M. 1997, *J. Mol. Struct.*, 413, 365
- Schwartz, A., & Bakker, C. 1989, *Science*, 245, 1102
- Smith, I., Talbi, D., & Herbst, E. 2001, *A&A*, 369, 611
- Stoks, P., & Schwartz, A. 1979, *Nature*, 282, 709
- Stoks, P., & Schwartz, A. 1981, in *Origin of Life*, ed. Y. Wolman (Dordrecht The Netherlands: Reidel Publishing), 59
- Stroh, F., & Winnewisser, M. 1989, *Chem. Phys. L*, 155, 21
- van der Velden, W., & Schwartz, A. 1977, *Geochim. Cosmochim. Acta*, 41, 961
- Wlodarczak, G., Martinache, L., Emaison, J., & van Eijck, B. 1988, *J. Mol. Spectrosc.*, 127, 200
- Wooden, D., Charnley, S., & Ehrenfreund, P. 2004, in *COMETS II*, ed. M. Festou, H. Keller, & H. Weaver (Tucson: Univ. of Arizona)
- Woods, P., Millar, T., Zijlstra, A., & Herbst, E. 2002, *ApJ*, 574, L167
- Zolensky, M., & McSween, H. 1988, in *Meteorites and the early Solar System*, ed. J. Kerridge, & M. Matthews (Tucson, AZ, USA: University of Arizona Press), 114