Electronic supplementary information file for "A Kinetic Study of the $N(^2D) + C_2H_4$ Reaction at Low Temperature."

Table S1 New/updated reactions added to the reaction network

Reaction	α	β	γ	F_0	g	Comments and references
H + CH_2NCH → CH_3 + HCN → CH_3 + HCN	1.0e-10 2.0e-10	0 0	470 0	3 3	300 0	There is a small barrier at the M06-2X/AVYZ level for H addition on CH_2 site leading to CH_3NCH and no barrier for H addition on the carbon atom of the CH group leading to CH_2NCH_2, in good agreement with B3LYP calculations.[27, 30] The TS for CH_3NCH → CH_3 + HCN is located 37.5 kJ/mol above the CH_3 + HCN level (so -200.6 kJ/mol below the H + CH_2NCH entrance channel) and the TS for CH_3NCH → CH_3NC + H is located 12.3 kJ/mol above the CH_3NC + H level (so -124.5 kJ/mol below the H + CH_2NCH entrance channel). The main exit channel of CH_3NCH will then be CH_3 + HCN. CH_2NCH_2 should evolve towards CH_3 + HCN after CH_2NCH_2 → CH_3NCH isomerization through a TS located -47 kJ/mol below the H + CH_2NCH channel.
H + c-CH_2NCH → H + CH_3CN → HCN + CH_3	1.6e-11 8.0e-12	0 0	1600 1400	3 3	600 600	At the M06-2X/AVTZ level we found activation barriers of approximately 2100-2200 K for both H atom additions leading to c-CH_2NHCH and CH_2NCH_2. We use a smaller activation barrier to take into account the tunneling. c-CH_2NHCH should evolve through a complex mechanism with a relatively low TS energy (c-CH_2NHCH → CH_2CHNH → CH_3CNH) to CH_3CN + H [27, 30]. c-CH_2NCH_2 can also evolve to CH_3CN + H through a less favorable pathway as one TS is close to the entrance channel. We neglect this channel as CH_3CN is already produced through the c-CH_2NCHCH pathway, but can also lead easily to the more stable linear CH_2NCH_2 which can evolve to CH_3NCH through a TS just below the entrance level and then to CH_3 + HCN. Some CH_2NCH_2 may be stabilized but for Titan's atmosphere the $N(^2D)$ reactions happen mainly in the upper atmosphere where the pressure is very low, so we can neglect the three body stabilization process. We neglect the H atom addition on CH_2 as it involves a much higher TS (4400K).
C_2H + c-CH_2NCH → C_2H_2 + CH_2CN → C_3H_3 + HCN → CH_3 + HC_3N	5.0e-11 5.0e-11 1.0e-10	0 0 0	0 0 0	3 3 3	0 0 0	We consider that the C_2H addition to the C=N double bond is barrierless, by comparison with the $C_2H + C_2H_4$ reaction, leading to various adducts including the cyclic one, which is calculated to be 289 kJ/mol more stable than the entrance channel. The TS from this cyclic adduct to CH_3 + HC_3N is located -127 kJ/mol below the entrance level and the TS to C_3H_3 + HCN is located -70 kJ/mol below the entrance level, so CH_3 + HC_3N production should be favored. C_2H_2 + CH_2CN production is also likely to be a potential exit channel. For H atom abstraction, we found, at the M06-2X/AVTZ level, a barrier for the abstraction of the hydrogen atom of the CH group (1.5 kJ/mol) and a submerged barrier for H atom abstraction on the CH_2 group (-4.0 kJ/mol). As M06-2X/AVTZ calculations underestimate the barrier for such reactions there are likely to be non-negligible barriers for these processes and we neglect these processes.

$N(^2D) + C_2H_4$ $\rightarrow CH_2NCH + H$	5.7e-11	0	0	1.8	0	See text
$\rightarrow$ c-$CH_2(N)CH$ +H	2.4e-11	0	0	1.8	0	
$N(^2D)$ + c-$CH_2NCH \rightarrow C_2H_2 + H + N_2$	3.0e-11	0	0	3	0	Similar rate to the $N(^2D) + C_2H_4$ reaction We suppose an attack of $N(^2D)$ on the C=N double bond followed by rearrangement.
$\rightarrow$ 2HCN + H	3.0e-11	0	0	3	0	
CN + c-$CH_2NCH \rightarrow$ HCN + CH_2CN	3.0e-10	0	0	3	0	There is likely to be a small barrier for H atom abstraction but not for CN addition on the C=N double bond which should evolve toward HCN + CH_2CN.

Reaction rate are expressed as $k = \alpha\times(T/300)^{\beta}\times\exp(-\gamma/T)$ cm^3 $molecule^{-1}$ s^{-1}
Uncertainties are expressed as $F(T) = F_0 \times\exp(\gamma\times\lvert 1/T-1/300 \rvert)$

Photodissociation cross sections

Photodissociation cross sections of CH_2NCH and c-CH_2NCH are calculated in a similar way to those of van Hemert and van Dishoeck[72] with vertical excitation energies, transition dipole moments and oscillator strengths calculated at the EOM-CCSD(T)/AVTZ level using Gaussian16.[69] The branching ratios of the photodissociations of CH_2NCH and c-CH_2NCH are taken to be equal to 50% towards CH_2 + HCN and 50% towards H + CH_2CN between 100 and 350 nm.

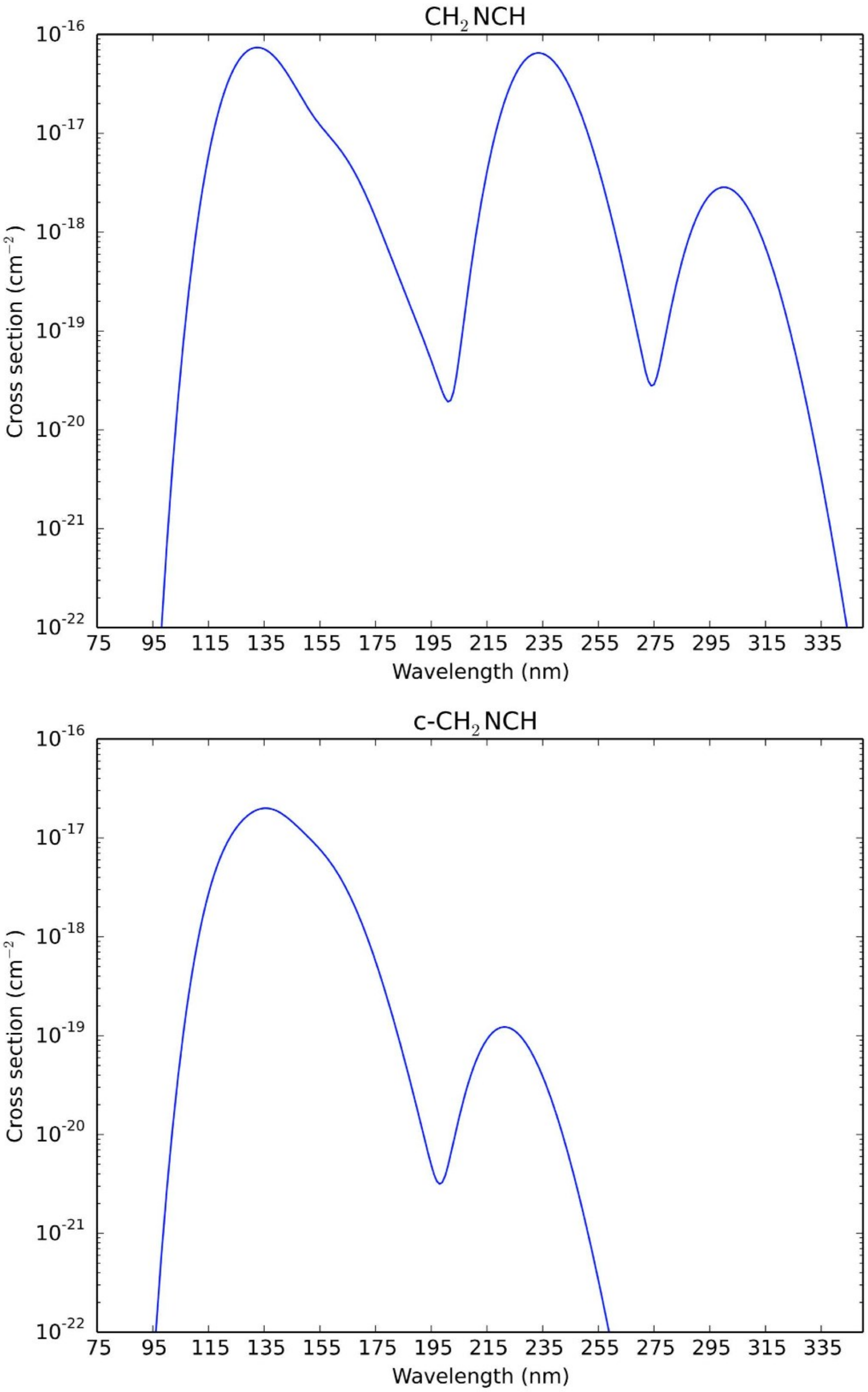

Figure S1 Photodissociation cross sections of CH_2NCH (upper panel) and c-CH_2NCH (lower panel) calculated at the EOM-CCSD(T)/AVTZ level.

Supplementary references

72. M. C. van Hemert and E. F. van Dishoeck, *Chem. Phys.*, 2008, **343**, 292–302.