Methyl isocyanate CH$_3$NCO: An important missing organic in current astrochemical networks

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Abstract

Methyl isocyanate (CH$_3$NCO) is one of the important complex organic molecules detected on the comet 67P/Churyumov-Gerasimenko by Rosetta’s Philae lander. It was also detected in hot cores around high-mass protostars along with a recent detection in the solar-type protostar IRAS 16293-2422. We propose here a gas-grain chemical model to form CH$_3$NCO after reviewing various formation pathways with quantum chemical computations. We have used NAUTILUS 3-phase gas-grain chemical model to compare observed abundances in the IRAS 16293-2422. Our chemical model clearly indicates the ice phase origin of CH$_3$NCO.

Key words: Astrochemistry, ISM: molecules, ISM: abundances, ISM: evolution, methods: statistical

1 INTRODUCTION

Comets are considered to be the repository of the most pristine material from the origin of the solar system in the form of ice, dust, silicate and refractory organic material (Mumma & Charnley 2011). It is believed that some of the water and organic material found on Earth may have been delivered by comets (Hartogh et al. 2011). In the Solar System, when a comet passes close to the Sun, it warms and begin to evaporate its surface and evolve gases. This process, called outgassing, produces a coma of gas and dust that has been extensively observed (Crovisier 2006). More than 20 organic molecules have been identified in the coma of comets via ground and space-based observations (Biver et al. 2014; Crovisier et al. 2004). The chemical composition of comets clearly indicates that these objects are populated with many organic compounds that are commonly detected in the ISM. Biver et al. (2015) have found a good correlation between the type of species detected in the coma of comets and those of warm molecular clouds.

Recently, the spacecraff Rosetta has detected many complex organic molecules (COMs) (such as ethanol (CH$_3$CHO), formamide (NH$_2$CHO), methyl isocyanate (CH$_3$NCO), ethylamine (C$_2$H$_5$NH$_2$) and many more) on the material of the comet 67P/Churyumov-Gerasimenko by the COSAC experiment (Goessmann et al. 2015) and even simplest amino acid glycine accompanied by methylamine and ethylamine in the coma measured by the ROSINA (Altwegg et al. 2016). CH$_3$NCO is one of those organics that could play a role in the synthesis of amino acid chains called peptides (Pascal et al. 2005). It was first detected in Sgr B2 by Halfen et al. (2015) and later in Orion KL by Cernicharo et al. (2016). Recently, it was also detected in the solar-type protostar IRAS 16293-2422 by Martin-Domenech et al. (2017) and Ligterink et al. (2017).

However, it is not well understood how CH$_3$NCO is formed in the ISM. Recently, Martín-Doménech et al. (2017) has included the chemistry proposed by Halfen et al. (2015) and suggested that the production of CH$_3$NCO could occur mostly via the gas-phase chemistry after the evaporation of HNCO from grain surface. Belloche et al. (2017) has considered a grain surface production of CH$_3$NCO in their model via the radical-addition reaction between CH$_3$ and OCN. Another study by Ligterink et al. (2017) claimed that CH$_3$NCO can be formed in the solid state by VUV irradiation of CH$_3$:HNCO mixtures through CH$_3$ and NCO recombinations. This motivated us to revisit the chemistry of CH$_3$NCO in the ISM.

This paper reports the first public gas-grain chemical network for CH$_3$NCO followed by astrochemical modelling of low mass protostar IRAS 16293. The chemistry is presented in Section 2. The chemical model is described in Section 3 while the results are discussed in the last Section.
2 REVIEW OF THE INTERSTELLAR CHEMISTRY OF CH$_3$NCO

Despite an intensive search, we did not find any reaction producing efficiently CH$_3$NCO in the gas phase. Halonen et al. (2015) proposed the following gas phase formation route:

\[
\begin{align*}
\text{HNCO} + \text{CH}_3 & \rightarrow \text{CH}_3\text{NCO} + \text{H} \\
\text{HNCO} + \text{CH}_3^+ & \rightarrow \text{CH}_3\text{NCOH}^+ + \text{H}_2 \\
\text{CH}_3\text{NCOH}^+ + e^- & \rightarrow \text{CH}_3\text{NCO} + \text{H}
\end{align*}
\]

But we have found that reaction 1 is endothermic by 77 kJ/mol and shows a Transition State (TS) located 83 kJ/mol above the entrance level (see Table 4 in the online supplementary material) and thus cannot play any role in gas phase neither on grain surface at low temperature. Reaction 2 has been studied experimentally by Wight & Beauchamp (1980) and they observed proton transfer process which forms H$_2$NCO$^+$ and CH$_3$, instead of CH$_3$NCOH$^+$ and H$_2$. Reaction 3 has then no impact on the CH$_3$NCO formation. An alternative could have been the CH$_3$HNC + OH $\rightarrow$ H + CH$_3$NCO reaction, which is exothermic by 107 kJ/mol, and may not show any barrier. However, CH$_3$NC has a low abundance in molecular clouds (Cernicharo et al. 1988; Gratier et al. 2013). So the reaction CH$_3$NC + OH $\rightarrow$ H + CH$_3$NCO will involve very low fluxes and we can thus neglect this reaction.

The detection of CH$_3$NCO being limited to warm sources (hot cores and hot corinos) suggests a formation of this molecule on grains rather than in the gas phase (Cernicharo et al. 2016). We have found four potential grain surface reactions which may produce CH$_3$NCO efficiently. The first one is the s-CH$_3$ + s-OCN $\rightarrow$ s-CH$_3$NCO reaction (here ‘s’ is to represent species on the surface). As it is a reaction between two radicals *CH$_3$ + *OCN, this reaction is barrier-less and leads to CH$_3$NCO which arises from the pairing up of electrons on the two reactants radicals.

The second one is the CH$_3$ + OCN $\rightarrow$ CH$_3$NCO + e$^-$ reaction which is exothermic by 30 kJ/mol at M06-2X/AVTZ level in the gas phase. The M06-2X highly nonlocal functional is developed by Zhao & Truhlar (2008) and is well suited for structures and energetics of the transition states. OCN$^-$ is widely observed on interstellar ice (van Broekhuizen et al. 2005) and CH$_3$ is supposed to be relatively abundant on ice and relatively mobile (Wakelam et al. 2017), then this reaction may play a role in the CH$_3$NCO formation. However, the adsorption energy of OCN$^-$ on ice is large due to dipole-ion interaction, and even if free electron is also strongly bound to ice (Kamimura et al. 2006; de Koning et al. 2016), this reaction may be endothermic on ice. By comparison, the H + OCN$^-$ $\rightarrow$ HNCO + e$^-$ reaction is more exothermic (by 107 kJ/mol in the gas phase) which should prevent OCN$^-$ detection on ice if this reaction was also exothermic on ice due to the importance of H reaction on ice. Then free electron should be less bounded on ice than OCN$^-$, as a result CH$_3$ + OCN $\rightarrow$ CH$_3$NCO + e$^-$ reaction is likely endothermic on ice and is neglected here.

Another reaction is induced through the HCN...CO reaction. As introduced in Ruaud et al. (2015), the proximity of HCN and CO in the van der Waals complex favors the reaction between excited H$_2$CN$^*$ (formed through s-HCN + s-H reaction) and CO (see Table 3 in the online supplementary material and Figure 1 for the energy profile diagram of the H + HCN...CO reaction). Then considering the large amount of CO and HCN, this reaction may be important. We then characterise the H + HCN and H$_2$CN + CO reactions to estimate the importance of these reactions to CH$_3$NCO formation on ice. The H + HCN $\rightarrow$ H$_2$CN shows a notable barrier (computed to be equal to 15.4 kJ/mol (Jiang & Guo 2013), 28.3 kJ/mol at M06-2X/AVTZ level (this work, see Table 2 in the online supplementary material) and 36.4 kJ/mol at CCSD(T)/6-311++G level (Sumathi & Nguyen 1998)). Despite this barrier, this reaction is enhanced on ice due to tunneling (Ruaud et al. 2016), leading to the formation of excited H$_2$CN$^*$. As the amount of energy in H$_2$CN$^*$ is equal to 105.3 kJ/mol (initially with a very narrow distribution), there is a competition between relaxation and reactivity for all the HCN linked to CO as the transition state for the H$_2$CN + CO $\rightarrow$ H$_2$CNCO is located 44.1 kJ/mol above the H$_2$CN + CO level, so 61.2 kJ/mol below the energy of the H$_2$CN$^*$ formed through the H + HCN reaction. As the energy distribution of the H$_2$CN$^*$ is initially very narrow, a notable part of the H$_2$CN$^*$ will react with CO. It should be noted that this mechanism of reaction induced through van der Waals complex will also lead to HNCO formation through N$_2$CO + H $\rightarrow$ HNCO reaction, mechanism which should be very efficient in that case.

The fourth reaction which can produce CH$_3$NCO is the s-N + s-CH$_3$CO reaction. The first step, leading to s-CH$_3$C(N)O in a triplet state, is barrierless characteristic of a radical-radical reaction. The s-CH$_3$C(N)O can evolve toward s-CH$_3$ + s-OCN on the triplet surface, isomerize into s-CH$_3$NCO on the triplet surface or being converted into s-CH$_3$C(N)O in a singlet state (which can also isomerize into s-CH$_3$NCO (or s-CH$_3$OCN) on the singlet surface). Considering the exothermicity of the various step (see Table 6 in the online supplementary material), the formation of s-CH$_3$NCO is without doubt the most favorable exit channel, either through adduct isomerization or through the recombination of s-CH$_3$ + s-OCN. Very minor CH$_3$OCN may also be produced, and some s-CH$_3$C(N)O may also be stabilized as the TS for dissociation or isomerization are notably
above the CH3C(N)O energy, s-CH3C(N)O will react with s-H leading ultimately to CH3C(O)NH2 which are however not considered here.

All the introduced and reviewed reactions discussed here are presented in Table 1.

3 ASTROCHEMICAL MODELLING

3.1 The NAUTILUS chemical model

To investigate the chemistry of CH3NCO in ISM, we have used the state-of-the-art chemical code NAUTILUS described in Ruaud et al. (2016). NAUTILUS computes the chemical composition as a function of time in the gas-phase, and at the surface of dust grains. Here, surface chemistry is solved using the rate equation approximation and assuming a different chemical behaviour between the surface of the mantle and the bulk (i.e. a three-phase model). The equations and the chemical processes included in the model are described in Ruaud et al. (2016). NAUTILUS includes physisorption of gas-phase species on grain surfaces, diffusion of species at the surface of the grains resulting in chemical reactions and several desorption mechanisms. Desorption can be due to the temperature (thermal desorption), cosmic-ray heating (cosmic-ray induced desorption, Hasegawa & Herbst (1993)), UV photon impact (photodesorption) and chemical (Garrod et al. 2007).

3.2 Modification of the network

Our gas phase chemistry is based on the public chemical network kida.uva.2014 (Wakelam et al. 2015a) with the updates on chemistry of HNCO (and their isomers) from the KIDA database and chemistry of CH3NCO discussed in Section 2 and listed in Table 1 in this work. The surface network is based on the one of Garrod et al. (2007) with several additional processes from Ruaud et al. (2015) and Table 1 in this work. The entire network considered here is available on the KIDA website.

3.3 Physical models

To simulate the chemistry of CH3NCO in the ISM, we have considered two different physical models which are representative of : (i) dense core and (ii) solar-type protostar (representative of IRAS 16293). For dense core, NAUTILUS is used with homogeneous conditions and integrated over 10^7 years. The initial elemental abundances are same as in Hincelin et al. (2011) with depleted value of fluorine abundance of 6.68 × 10^{-9} from Neufeld et al. (2005) and we have used a standard C/O ratio of 0.7 (Wakelam et al. (2015b); Majumdar et al. (2016)). The model was run with constant dust and gas temperature of 10 K, a total proton density of 2 × 10^4 cm^{-3}, a cosmic-ray ionization rate of 1.3 × 10^{-17} s^{-1}, and a visual extinction of 30.

For low mass protostar IRAS 16293, we have used the same physical structure as in Wakelam et al. (2014) and Majumdar et al. (2016) and that was computed using the radiation hydrodynamical (RHD) model from Masunaga & Inutsuka (2000). Here the model initially starts from a dense molecular cloud core with a central density n(H2) ∼ 3 × 10^4 cm^{-3} and the core is extended up to r = 4 × 10^5 AU with a total mass of 3.852 M⊙. The prestellar core evolves to the protostellar core in 2.5 × 10^5 yr. When the protostar is formed, the model again follows the evolution for 9.3 × 10^4 yr, during which the protostar grows by mass accretion from the envelope.

4 RESULTS AND DISCUSSIONS

4.1 Chemistry in dark cloud

Figure 1 shows the time evolution of the abundances of HNCO and CH3NCO under typical dark cloud conditions. Here, we have shown the chemical evolution of CH3NCO together with HNCO since in the past HNCO was assumed to be the main precursor for CH3NCO formation by Martín-Doménech et al. (2017) and Halfen et al. (2015). But this is not the case from our revised chemistry.

Recently, Ruaud et al. (2016) suggested a best fit chemical age for TMC-1 (CP) to be a few 10^5 years. At this time, 70% of the observed species in TMC-1 (CP) are reproduced by the model within a factor of 10. At 2 × 10^5 year, abundance of gas phase HNCO predicted by our model is 3 × 10^{-10} with respect to nH. This is in good agreement with with the observed abundance of 2 × 10^{-10} in TMC-1 (CP) (Agúndez & Wakelam 2013). At this age, HNCO is formed mainly from the barrier-less surface reaction s-N + s-HCO and the gas phase dissociative recombination reaction of HNCOH+.

In our model, CH3NCO is formed efficiently only in the surface via the reactions of s-H + s-H2CNCO and

1 http://kida.obs-u-bordeaux1.fr/
s-N + s-CH₂CO since the main gas phase formation route CH₃ + HNCO has a large activation barrier of 8040 K. s-H₂CNCO is formed from the reaction between van der Waals complex s-HC₅N...CO and highly mobile s-H atoms. Here, s-HC₅N...CO is considered to be formed when gas phase HCN land on the proximity of s-CO on the grain surfaces (Ruaud et al. 2015). s-CH₃CO forms mainly via the reaction s-H + s-H₂CCO. The peak gas phase abundance of CH₃NCO from our model is of the order of ~10⁻³² with respect to n_H whereas ice phase abundance is 7 × 10⁻¹⁰ around few 10⁵ years. This shows that CH₃NCO is frozen in the ices around TMC-1 (CP) (also have lower rotational dipole moment compared to HNCO) and thus not free to rotate. Hence, CH₃NCO is not detectable via its millimeter wavelength rotational spectra around TMC-1 (CP).

### 4.2 Chemistry in low mass protostar

In order to validate our chemistry, we present the computed abundances of CH₃NCO, in the gas phase and at the surface of the grains in the protostellar envelope as a function of radius to the central protostar and compare with the observation of CH₃NCO in IRAS 16293. The abundance profiles of CH₃NCO can be discussed by considering two different regions. The first region is defined by radii larger than 200 AU where the temperature is below 50 K. In this region, most of the CH₃NCO in the grains is inherited from the cold
core phase. The second region is defined by radii smaller than 100 AU where the temperature reaches above 100 K and the gas phase abundance of CH$_3$NCO increases sharply. The CH$_3$NCO abundance on grains has an inverse profile showing that at low temperature, the CH$_3$NCO molecules are formed on the grains and are thermally desorbed in the inner part of the envelope.

Martín-Doménèch et al. (2017) has determined an upper limit of $1.4 \times 10^{-10}$ (with respect to molecular H$_2$) for CH$_3$NCO in the envelope of IRAS 16293 B at about 60 AU from the central protostar. Another study by Ligerink et al. (2017) has also determined an upper limit of $3.3 \times 10^{-10}$ (with respect to molecular H$_2$) for CH$_3$NCO in the same source IRAS 16293 B. Our model is in agreement with these upper limits at this radius ($2 \times 10^{-10}$). At 60 AU, the gas phase CH$_3$NCO/HNCO abundance ratio from our model is $2 \times 10^{-2}$ which is also reasonably close to the ratio $8 \times 10^{-2}$ measured by Martín-Doménèch et al. (2017) and Ligerink et al. (2017). The ice phase CH$_3$NCO/HNCO ratio from our model in the outer part of the envelope (>$1000$ AU) where possible comets should be formed is of the order of 3.7. This is very close to the CH$_3$NCO/HNCO-4.33 ratio initially measured by the Philae lander on the comet 67P/Churyumov-Gerasimenko (Goessmann et al. 2015). This observation is, however, now questioned (can only be considered as an upper limit) by the recent measurement from the Double Focusing Mass Spectrometer (DFMS) of the ROSINA experiment (Altwegg et al. 2017).

5 CONCLUSION AND PERSPECTIVES

In this letter, we have provided new insights concerning the chemistry of CH$_3$NCO in the ISM. Our computation allowed us to confirm the hypothesis made by Cernicharo et al. (2016) about its grain surface origin. Moreover, we tested the impact of these new kinetic data on the prediction of CH$_3$NCO abundance in the low mass protostar IRAS 16293-2422 and on the CH$_3$NCO/HNCO abundance ratio observed by the Philae lander on the comet 67P/Churyumov-Gerasimenko. However, the study of the CH$_3$NCO/HNCO abundance ratio in high mass protostars with proper chemodynamical model is out of the scope of the current letter, but could be done in the near future by comparing with the observations in SgrB2 (N) (Halfen et al. 2015; Belloche et al. (2017)) and in Orion KL (Cernicharo et al. 2016).

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Appendix:
A large part of the reactions treated in this study have unknown reaction rates (without experimental measurements and/or theoretical calculations to rely upon) in the temperature range of interest (T in the 10-50 K range) but also unknown exothermicity. To make a reasonable estimate of their reaction rates at low temperature, we performed quantum chemical calculations. For our calculations, we have used DFT method using the M06-2X functional with the cc-pVTZ basis set. This highly nonlocal functional developed by Zhao and Truhlar 2008 is well suited for structures and energetics of the transition states.

Table 1: Relative energies at the M06-2X/aug-cc-pVTZ level (in kJ/mol at 0 K including ZPE) with respect to the HCN + CO energy, geometries and frequencies (in cm$^{-1}$, unscaled) of the various stationary points. The absolute energies at the M06-2X/aug-cc-pVTZ level including ZPE in hartree are also given in column 1.

| Species (Energy, hartree) | Relative energies (kJ/mol) | Geometries (Position of the atoms in Cartesian coordinates) | Harmonic Frequencies (cm$^{-1}$) |
|--------------------------|----------------------------|------------------------------------------------------------|---------------------------------|
| HCN (-93.407418)         | 0                          | C 0.000000 0.000000 -0.494880  | 789, 789, 2248, 3448          |
|                          |                            | H 0.000000 0.000000 -1.560893  |                                |
|                          |                            | N 0.000000 0.000000 0.647167  |                                |
| CO (-113.315083)         |                            | C 0.000000 0.000000 -0.640800  | 2260                           |
|                          |                            | O 0.000000 0.000000 0.480600  |                                |
| HCN…CO (-206.722951)     | -1.2                      | C -2.315172 0.203401 0.000202  | 22, 61, 67, 78, 791, 804, 2254, 2261, 3453 |
|                          |                            | H -3.165133 0.847465 0.000675  |                                |
|                          |                            | N -1.404659 -0.485993 -0.000321 |                                |
|                          |                            | O 2.154516 -0.324565 0.000274  |                                |
|                          |                            | C 1.608775 0.655100 -0.000305  |                                |
Table 2: Relative energies at the M06-2X/aug-cc-pVTZ level (in kJ/mol at 0 K including ZPE) with respect to the H + HCN energy, geometries and frequencies (in cm⁻¹, unscaled) of the various stationary points. The absolute energies at the M06-2X/aug-cc-pVTZ level including ZPE in hartree are also given in column 1.

| Species          | Relative energies (kJ/mol) | Geometries (Position of the atoms in Cartesian coordinates) | Harmonic Frequencies (cm⁻¹) |
|------------------|---------------------------|-------------------------------------------------------------|-----------------------------|
| H (-0.4982065)   | 0                         | C 0.000000 0.000000 -0.494880                               | 789, 789, 2248, 3448        |
| HCN (-93.407418) |                           | H 0.000000 0.000000 -1.560893                               |                             |
|                  |                           | N 0.000000 0.000000 0.647167                               |                             |
| TS (-93.894842)  | 28.3                      | N 0.097054 -0.717467 0.000000                               | 505, 779, 921, 2134, 3388, |
|                  |                           | C 0.097054 0.436285 0.000000                               | 8891*                       |
|                  |                           | H 0.394533 1.463794 0.000000                               |                             |
|                  |                           | H -1.656237 0.940767 0.000000                               |                             |
| H₂CN (-93.945717)| -105.3                    | C 0.000000 0.000000 -0.501313                               | 948, 1012, 1384, 1749,     |
|                  |                           | N 0.000000 0.000000 0.735111                                 | 3005, 3072                  |
|                  |                           | H 0.000000 0.937025 -1.068947                               |                             |
|                  |                           | H 0.000000 -0.937025 -1.068947                              |                             |

*: imaginary frequency
Table 3: Relative energies at the M06-2X/aug-cc-pVTZ level (in kJ/mol at 0 K including ZPE) with respect to the H$_2$CN + CO energy, geometries and frequencies (in cm$^{-1}$, unscaled) of the various stationary points. The absolute energies at the M06-2X/aug-cc-pVTZ level including ZPE in hartree are also given in column 1.

| Species       | Relative energies (kJ/mol) | Geometries (Position of the atoms in Cartesian coordinates) | Harmonic Frequencies (cm$^{-1}$) |
|---------------|---------------------------|---------------------------------------------------------------|----------------------------------|
| H$_2$CN (-93.945717) | C 0.000000 0.000000 -0.501313  
N 0.000000 0.000000 0.735111  
H 0.000000 0.937025 -1.068947  
H 0.000000 -0.937025 -1.068947 | 948, 1012, 1384, 1749, 3005, 3072 |                                 |
| CO (-113.315083)   | C 0.000000 0.000000 -0.640800  
O 0.000000 0.000000 0.480600 | 2260 |                                 |
| TS (-207.244021)   | C 1.719507 0.198906 0.000021  
H 2.715274 -0.248015 0.000178  
H 1.639585 1.285638 -0.000032  
N 0.731882 -0.567158 -0.000051  
O -1.840088 -0.111857 0.000040  
C -0.845729 0.438984 -0.000040 | 99, 294, 442, 5459, 1062, 1082, 1415, 1722, 461i* |                                 |
| CH$_2$NCO (-207.290007) | C -1.778814 0.139360 0.000083  
H -1.993176 1.195587 -0.000180  
H -2.555836 -0.603926 0.000319  
N -0.496439 -0.287279 -0.000136  
C 0.672696 -0.037344 -0.000042  
O 1.832599 0.100900 0.000071 | 134, 261, 417, 544, 629, 974, 1133, 1490, 1557, 2410, 3175, 3309 |                                 |

*: imaginary frequency
Table 4: Relative energies at the M06-2X/aug-cc-pVTZ level (in kJ/mol at 0 K including ZPE) with respect to the CH$_3$ + HNCO energy, geometries and frequencies (in cm$^{-1}$, unscaled) of the various stationary points. The absolute energies at the M06-2X/aug-cc-pVTZ level including ZPE in hartree are also given in column 1.

| Species (Energy, hartree) | Relative energies (kJ/mol) | Geometries (Position of the atoms in Cartesian coordinates) | Harmonic Frequencies (cm$^{-1}$) |
|--------------------------|----------------------------|-------------------------------------------------------------|---------------------------------|
| CH$_3$ (-39.795501)      |                            | C 0.000000 0.000000 0.000000 | 524, 1416, 1416, 3133, 3310, 3310 |
|                          |                            | H 0.000000 1.076523 0.000000 |                                  |
|                          |                            | H 0.932296 -0.538261 0.000000 |                                  |
|                          |                            | H -0.932296 -0.538261 0.000000 |                                  |
| HNCO (-168.665769)       |                            | N 1.154466 -0.122413 0.000026 | 567, 660, 787, 1371, 2369, 3698  |
|                          |                            | C -0.045063 0.016768 -0.000079 |                                  |
|                          |                            | O -1.204109 0.015868 0.000031 |                                  |
|                          |                            | H 1.821983 0.629339 0.000041  |                                  |
| TS (-208.429659)         | 83.0                       | C -0.920547 0.289264 0.000721 | 101, 159, 252, 551, 591, 669, 674, 969, 1003, 1241, 1432, 1441, 2197, 3109, 3262, 3277, 3704, 747i* |
|                          |                            | O -1.786482 -0.500823 -0.000027 |                                  |
|                          |                            | N 0.248291 0.696949 -0.001215 |                                  |
|                          |                            | H 0.499206 1.668765 0.005455  |                                  |
|                          |                            | C 1.895977 -0.433809 0.000426 |                                  |
|                          |                            | H 1.460329 -1.413255 -0.130380 |                                  |
|                          |                            | H 2.432240 -0.036324 -0.848907 |                                  |
|                          |                            | H 2.309463 -0.223972 0.975670  |                                  |

*: imaginary frequency
Table 5: Relative energies at the M06-2X/aug-cc-pVTZ level (in kJ/mol at 0 K including ZPE) with respect to the N + CH₃CO energy, geometries and frequencies (in cm⁻¹, unscaled) of the various stationary points. The absolute energies at the M06-2X/aug-cc-pVTZ level including ZPE in hartree are also given in column 1.

| Species                                | Relative energies (kJ/mol) | Geometries (Position of the atoms in Cartesian coordinates) | Harmonic Frequencies (cm⁻¹) |
|-----------------------------------------|---------------------------|-------------------------------------------------------------|----------------------------|
| N(S) (-54.58746)                        |                           |                                                             |                            |
| CH₃CO(1'A) (-153.127903)               | 0                         | C 0.388178 0.005985 0.047915  
O 0.332327 -0.003169 0.973347  
C -0.033493 0.000250 -1.417739  
H -0.490106 -0.873754 -1.877220  
H -0.470486 0.882909 -1.879688  
H 1.049276 -0.012223 1.552598  | 62, 469, 867, 958, 1051,  
1355, 1460, 1460, 1989,  
3050, 3149, 3151 |
| CH₃C(N)O(1'A) (-207.821775)            | -279                      | O -0.867949 -1.010897 -0.000001  
C 1.345357 -0.042331 -0.000012  
H 1.717670 0.484667 -0.878557  
H 1.696968 -1.069968 -0.001305  
C -0.156245 -0.028182 0.000018  
N -0.760476 1.230407 -0.000001  | 85, 380, 518, 522, 844,  
942, 1023, 1234, 1389,  
1467, 1470, 1692, 3063,  
3132, 3176 |
| CH₃C(N)O(1'A) (-207.815884)            | -264                      | O -0.961115 -0.798213 -0.000009  
C 1.473599 -0.015759 -0.000021  
H 1.777168 -0.577365 -0.882612  
H 1.774500 -0.575912 0.883383  
C 0.013128 0.099415 0.000068  
N -0.960123 0.867106 -0.000002  | 141, 361, 434, 544, 913,  
981, 1056, 1255, 1404,  
1466, 1478, 1944, 3076,  
3154, 3173 |
| TS(1'A) (CH₃ + NCO) (-207.774031)      | -154                      | O -0.651718 -1.175499 0.000121  
C 1.572500 0.110376 0.000042  
H 1.600004 1.188300 -0.099523  
H 1.804223 -0.305225 0.969591  
H 1.844574 -0.474905 -0.865333  
C -0.503234 0.013874 -0.001984  
N -0.921522 1.178618 0.000519  | 127, 265, 443, 509, 653,  
673, 992, 1252, 1412,  
1432, 1814, 3105, 3263,  
3293, 503i* |
| TS(1'A) (CH₃OCN → CH₃NCO) (-207.783064) | -178                      | O -0.285154 1.199652 -0.001644  
C -1.114689 -0.748877 0.001882  
H -0.711470 -1.598000 -0.526160  
H -1.174977 -0.822782 1.076861  
H -1.875839 -0.171890 -0.495240  
C 0.555497 0.280798 -0.009050  
N 1.342667 -0.599438 0.000101  | 135, 454, 535, 606, 848,  
912, 1218, 1297, 1432,  
1468, 2092, 3151, 3318,  
3328, 860i* |
| CH₃NCO(1'A) (-207.933895)              | -574                      |                                                             | 56, 151, 622, 659, 895,  
1132, 1160, 1459, 1498,  
1509, 1605, 1698 |
| Structure | Coordinates | Normal Modes |
|-----------|-------------|--------------|
| CH\textsubscript{3}OCN(1A) | (-207.891329) | -462 | 1517, 1552, 2415, 3061, 3129, 3154 |
| CH\textsubscript{3} | (-39.795501) | -188 | 154, 235, 551, 644, 938, 1170, 1178, 1252, 1479, 1503, 1503, 2420, 3081, 3166, 3203 |
| NCO | (-167.991408) | 545, 619, 1330, 2053 |

*: imaginary frequency