



Can Cytosine, Uracil, and Thymine Be Formed from HC_3N and H_2NCO^+ in Interstellar Space?

Joong Chul Choe 

Department of Chemistry, Dongguk University-Seoul, Seoul 04620, Republic of Korea; jcchoe@dongguk.edu
Received 2021 February 12; revised 2021 April 15; accepted 2021 April 28; published 2021 June 24

Abstract

Syntheses of cytosine, uracil, and thymine starting from interstellar molecules were examined theoretically. Potential energy surfaces for the formation of protonated cytosine (CyH^+), uracil (UrH^+), and thymine (ThH^+) from cyanoacetylene (HC_3N), protonated isocyanic acid (H_2NCO^+), and one of NH_3 , H_2O , and CH_3OH , respectively, were determined by quantum chemical calculation using the CBS-QB3 method. Barrierless pathways were found for all the three reactions. Investigation of the energetics and kinetics of further possible reactions of CyH^+ , UrH^+ , and ThH^+ led to the conclusion that cytosine, uracil, and thymine could not be formed along the proposed pathways in the interstellar gas phase, whereas their formation might be possible on interstellar icy grain mantles.

Unified Astronomy Thesaurus concepts: [Interstellar medium \(847\)](#); [Interstellar molecules \(849\)](#); [Astrobiology \(74\)](#); [Astrochemistry \(75\)](#)

1. Introduction

Studies of the formation of building blocks of life such as amino acids, sugars, and nucleobases from molecules detected in the interstellar medium (ISM) provide valuable clues to the origin of life. Not detecting these building blocks in interstellar space does not rule out their formation in extraterrestrial environments. Some amino acids, sugars, nucleobases, and their precursors have been discovered in carbonaceous meteorites that have fallen to Earth (Stoks & Schwartz 1979; Sephton 2002; Martins et al. 2008; Pearce & Pudritz 2015), providing strong evidence for their prebiotic syntheses in the ISM. Adenine, guanine, cytosine, and uracil are four nucleobases that make up RNA. Uracil is displaced by thymine in DNA. These five nucleobases are chemically classified into two groups: (1) purines, including adenine and guanine, and (2) pyrimidines, including the other three.

Simulation experiments have been performed to synthesize nucleobases under space conditions. However, they are limited compared to those performed extensively under prebiotic terrestrial conditions (Pearce & Pudritz 2015; Kobayashi 2019). Ultraviolet (UV) photoirradiation of pyrimidine ($\text{C}_4\text{H}_4\text{N}_2$) in interstellar ice analogs containing H_2O , NH_3 , or CH_4 has led to the formation of cytosine, uracil, and/or thymine in studies by Sandford and coworkers (Nuevo et al. 2009, 2012, 2014; Materese et al. 2013). Mechanisms for the formation of uracil and thymine have been suggested in their subsequent theoretical studies (Bera et al. 2010, 2016). Adenine and guanine have been synthesized from the UV photoirradiation of purine ($\text{C}_5\text{H}_4\text{N}_2$) in interstellar ice analogs in experiments performed by the same group (Materese et al. 2017, 2018), for which mechanisms have been suggested (Bera et al. 2017). Recently, UV photoirradiation of the interstellar ice analog containing H_2O , CO , NH_3 , and CH_3OH at 10 K has formed cytosine, uracil, thymine, and adenine (Oba et al. 2019). In another recent UV photoirradiation study using the interstellar ice analog containing H_2O , NH_3 , and CH_3OH , three pyrimidine bases were synthesized (Ruf et al. 2019). All of these studies were performed with interstellar ice analogs.

Theoretical investigations using quantum chemical calculation have been made to reveal the mechanisms of prebiotic nucleobase syntheses from various small molecular systems. We have reported potential energy surfaces (PESs) for the formation of adenine by the pentamerization of HCN, a mechanism that has long been mentioned in the field of prebiotic chemistry, and the formation of the protonated adenine from HCNH^+ and four molecules of HCN (Jung & Choe 2013). Pathways for the formation of guanine and its protonated species starting from 4-aminoimidazole-5-carbonitrile ($\text{C}_4\text{H}_4\text{N}_4$) by adding H_2O and H_3O^+ , respectively, have been proposed (Choe 2018). Wang & Bowie (2012) have proposed mechanisms for the formation of cytosine and uracil from urea and other molecules, together with the formation of thymine from two molecules of isocyanic acid (HNCO) and the propional enolate anion ($\text{CH}_3\text{CHCHO}^-$). We have proposed reaction pathways to form cytosine and uracil from cyanoacetaldehyde (HCOCH_2CN) and guanidine (Choe 2020a) and pathways to form cytosine from urea and cyanoacetylene (HC_3N) or HCOCH_2CN (Choe 2020b). According to these studies, activation energies for bimolecular reactions between neutral molecules are as high as several hundred kJ mol^{-1} . For such a bimolecular reaction to occur thermally at low temperatures within the timescale of the chemical revolution of typical dense interstellar clouds in the gas phase, the activation energy should be zero (Herbst 2001) or at most a few kJ mol^{-1} (Yim & Choe 2012; Jung & Choe 2013; Zamirri et al. 2019). Molecules in dense interstellar clouds can be protonated, ionized, or dissociated to radicals by exposure to energy sources such as cosmic rays, electrons, and UV photons (Sandford et al. 2020). In fact, 31 ionic and 37 radical species are included in 204 molecular species detected in the ISM, reported recently (McGuire 2018). Therefore, consideration of ion–molecule reactions or radical–molecule reactions can be more suitable in studies of prebiotic syntheses of the building blocks of life because their activation energies are much smaller than bimolecular reactions between neutral molecules. Free radicals have been used as reactants for the formation of pyrimidine bases in theoretical investigations by Nguyen and

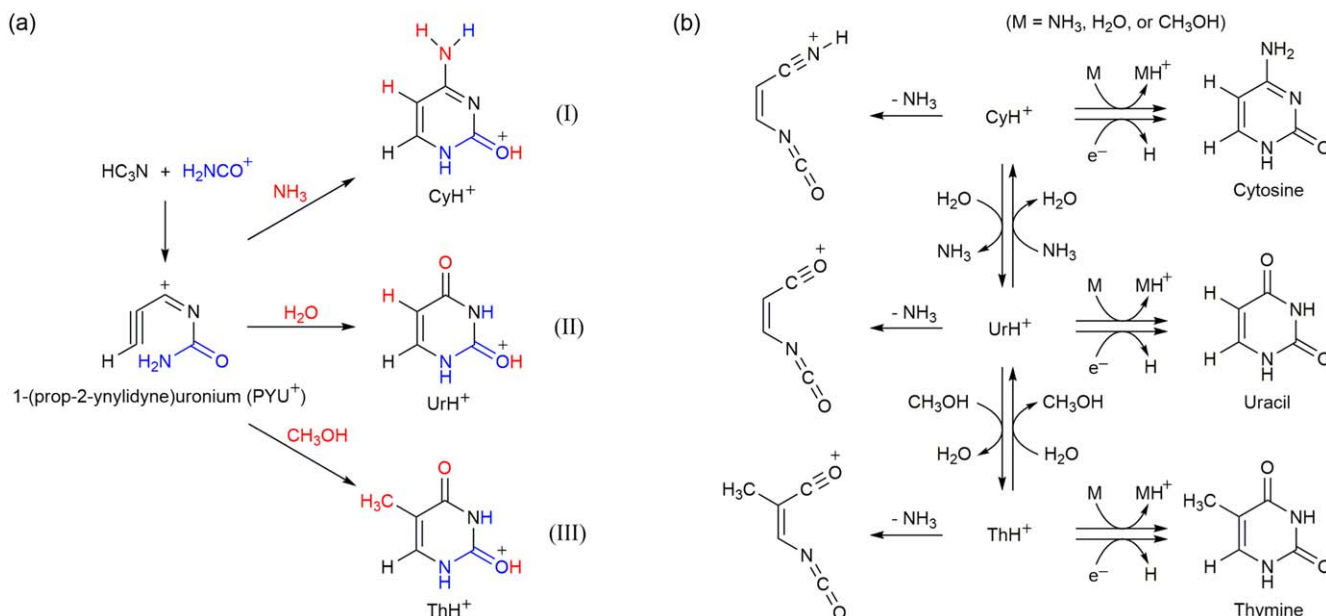


Figure 1. (a) Reactions for the formation of CyH^+ , UrH^+ , and ThH^+ , and (b) further reactions of CyH^+ , UrH^+ , and ThH^+ examined in this study.

coworkers (Jeilani et al. 2013, 2015; Nguyen et al. 2015; Jeilani et al. 2016), Sandford and coworkers (Bera et al. 2010, 2016, 2017), and Kaur & Sharma (2019). Cations or anions have been used as reactants for the formation of nucleobases or their protonated species in our previous studies (Jung & Choe 2013; Choe 2018, 2020a, 2020b), in a study by Gupta et al. (2013b), and in studies by Sandford and coworkers (Bera et al. 2010, 2016, 2017).

It is well known that HC_3N is a good candidate starting material in the formation of cytosine. Cytosine has been synthesized from the reaction of HC_3N with urea or potassium cyanate (KOCN) in an aqueous solution (Sanchez et al. 1966; Ferris et al. 1968). In our recent study, we have proposed theoretical pathways for the formation of cytosine and protonated cytosine (CyH^+) from reactions of urea with HC_3N and HC_3NH^+ , respectively (Choe 2020b). A barrierless pathway has been suggested for the formation of CyH^+ with catalytic H_2O . As a successive study, we paid attention to the reaction of HC_3N and cyanate (NCO^-) as mentioned above. Because NCO^- has not been yet detected in the ISM, isocyanic acid (HNCO) and protonated isocyanic acid (H_2NCO^+) can be good candidates reactant partners of HC_3N . In the nonenergetic environments of interstellar space, e.g., without UV photons, the occurrence of reactions between neutral molecules is hardly possible due to high activation energies, whereas the occurrence of ion–molecule reactions with small or without activation energies is possible. Therefore, in this work we tried to find out reaction pathways to form the three pyrimidine bases thermally from HC_3N and H_2NCO^+ in the presence of NH_3 , H_2O , and CH_3OH . The latter three molecules are among the main components of interstellar icy grain mantles (Boogert et al. 2015), of which analogs have been used in the aforementioned experimental studies for synthesizing pyrimidine bases. HC_3N has been detected widely and abundantly in many different regions of the Milky Way and nearby galaxies, including Sgr B2, L483, and TMC-1 (Turner 1971; Morris et al. 1976; Suzuki et al. 1992; Jiang et al. 2017; Agúndez et al. 2019). H_2NCO^+ has been detected toward Sgr B2 and L483

(Gupta et al. 2013a; Marcelino et al. 2018; Agúndez et al. 2019).

In the first stage of syntheses (Figure 1(a)), HC_3N and H_2NCO^+ can react to form a cationic adduct, 1-(prop-2-ynylidene)uronium (PYU^+), which further reacts with NH_3 , H_2O , and CH_3OH to form CyH^+ and protonated uracil (UrH^+) and thymine (ThH^+), respectively, in the second stage. PESs for these reactions in the gas phase were obtained using quantum chemical calculation. We also investigated possible further reactions of highly excited ionic products formed through reactions I–III (Figure 1(b)) to discuss the possible formation of cytosine, uracil, and thymine in the gas phase or on icy grain surfaces of the ISM.

2. Computational Methods

Molecular orbital quantum chemical calculation was performed with the Gaussian 16 program (Frisch et al. 2016) to construct PESs for examined reactions in the gas phase. Geometries of reactants, intermediates, and products were optimized at the B3LYP level (Becke 1993) of the density functional theory using the 6-311G(d,p) basis set. Transition state (TS) geometries connecting those species were examined and checked by calculating intrinsic reaction coordinates at the B3LYP/6-311G(d,p) level. For better accuracy of energies, the complete basis set (CBS-QB3) model calculation (Montgomery et al. 1999) was performed.

3. Results and Discussion

We present only individual lowest-energy pathways for examined reactions. All energies presented here are CBS-QB3 energies at 0 K, including zero-point vibrational energies (ZPVEs). We considered the reaction of HC_3NH^+ and HNCO instead of the reaction of HC_3N and H_2NCO^+ , the common first stage of reactions I–III (Figure 1(a)). Because the energy of its ionic adduct, $\text{HNC}_3\text{HNHCO}^+$, was 16 kJ mol^{-1} higher than that of $\text{HC}_3\text{NH}^+ + \text{HNCO}$, this route was not examined further. On the other hand, HC_3N and H_2NCO^+ react to form

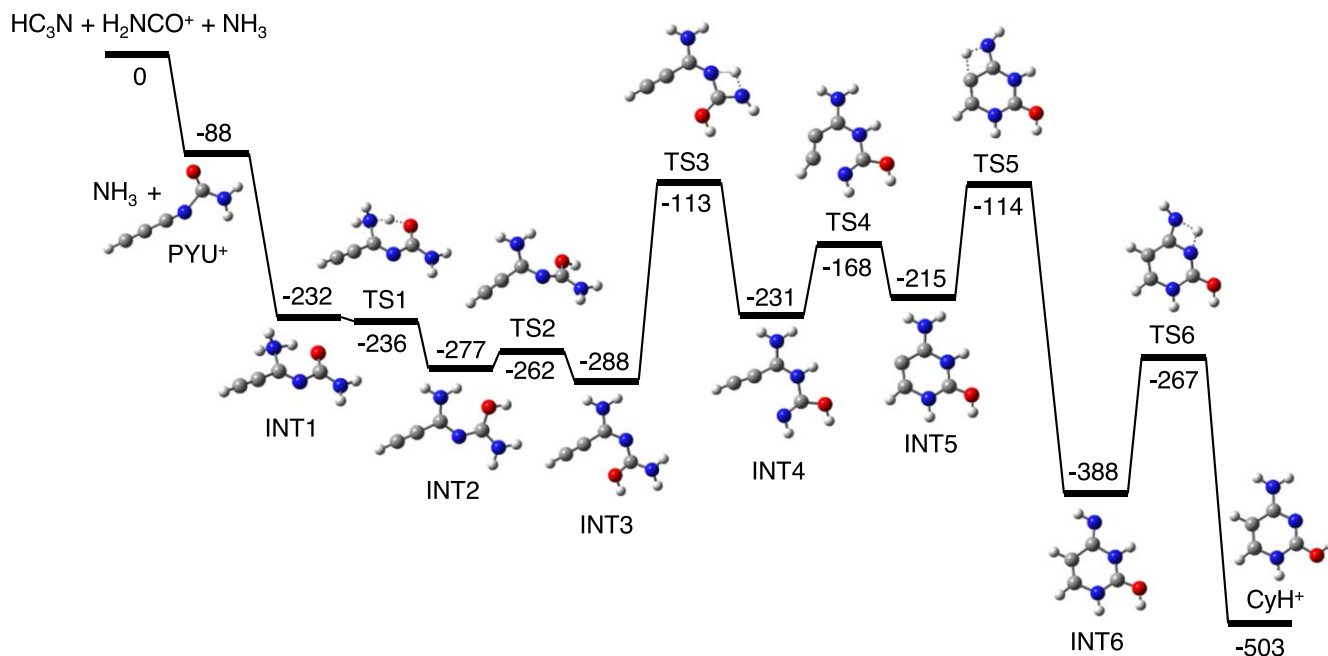


Figure 2. Potential energy kJ mol^{-1} diagram for the formation of CyH^+ from HC_3N , H_2NCO^+ , and NH_3 , derived from CBS-QB3 calculation.

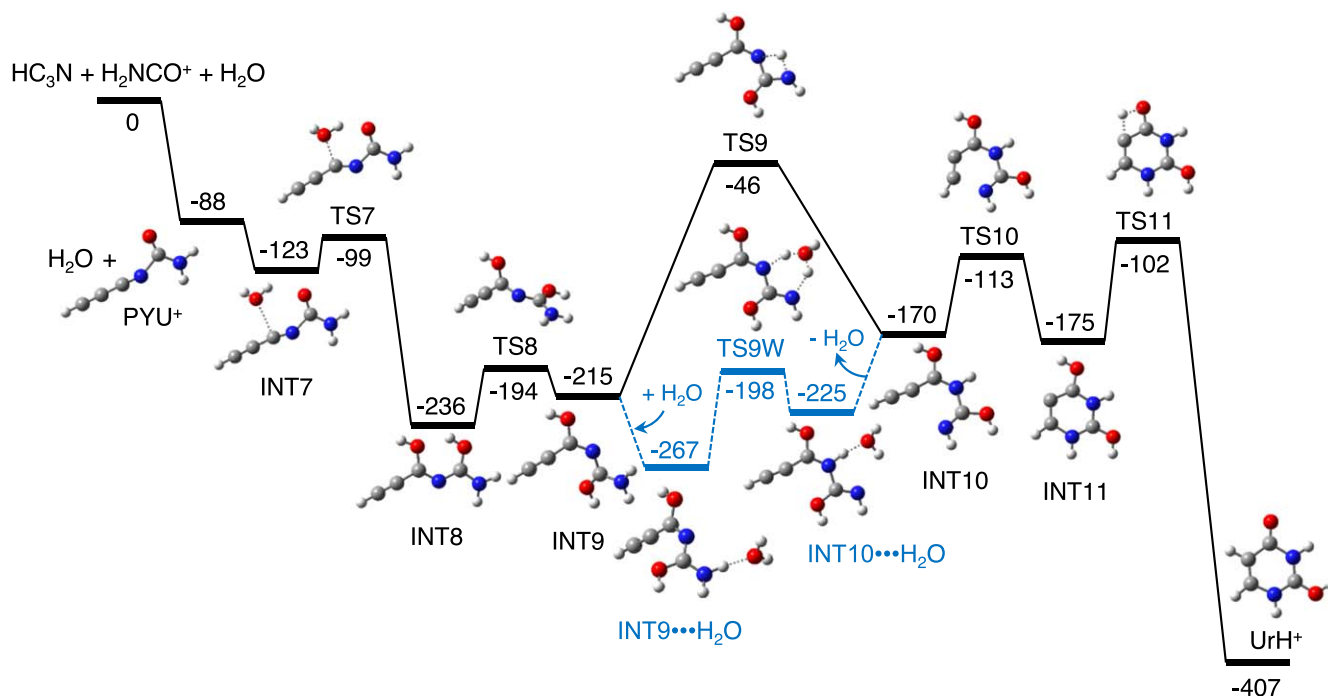


Figure 3. Potential energy kJ mol^{-1} diagram for the formation of UrH^+ from HC_3N , H_2NCO^+ , and H_2O , derived from CBS-QB3 calculation. Energies of TS9W, $\text{INT}\cdots 9\text{H}_2\text{O}$, and $\text{INT}\cdots 10\text{H}_2\text{O}$ are relative to the sum of energy of HC_3N , H_2NCO^+ , and $2\text{H}_2\text{O}$.

an ionic adduct, PYU^+ , lying 88 kJ mol^{-1} lower than reactants as shown in Figure 2.

3.1. Formation of CyH^+ (Reaction I)

After the formation of PYU^+ from HC_3N and H_2NCO^+ , NH_3 is added to PYU^+ to form an intermediate, INT1 , which undergoes a shift of H from the NH_3 moiety to the O atom to form INT2 and a subsequent rotation to INT3 (Figure 2). TS1 lies lower than INT1 because the ZPVE of TS1 is low enough to overcome their potential energy difference than the ZPVE

of INT1 . Reaction $\text{INT1} \rightarrow \text{INT3}$ occurs very rapidly. The next tautomerization to INT4 needs a high activation energy, 175 kJ mol^{-1} , because of the highly unstable four-membered ring TS, TS3 . TS3 lies the highest in the pathway of the second stage, $\text{PYU}^+ + \text{NH}_3 \rightarrow \text{CyH}^+$, but still lower than $\text{PYU}^+ + \text{NH}_3$ by 25 kJ mol^{-1} . Then INT4 undergoes cyclization to INT5 , followed by two further tautomerization steps to finally form CyH^+ . Notably, the second stage occurs without an activation barrier, indicating that reaction I can occur at very low temperatures at around 10 K in dark interstellar clouds.

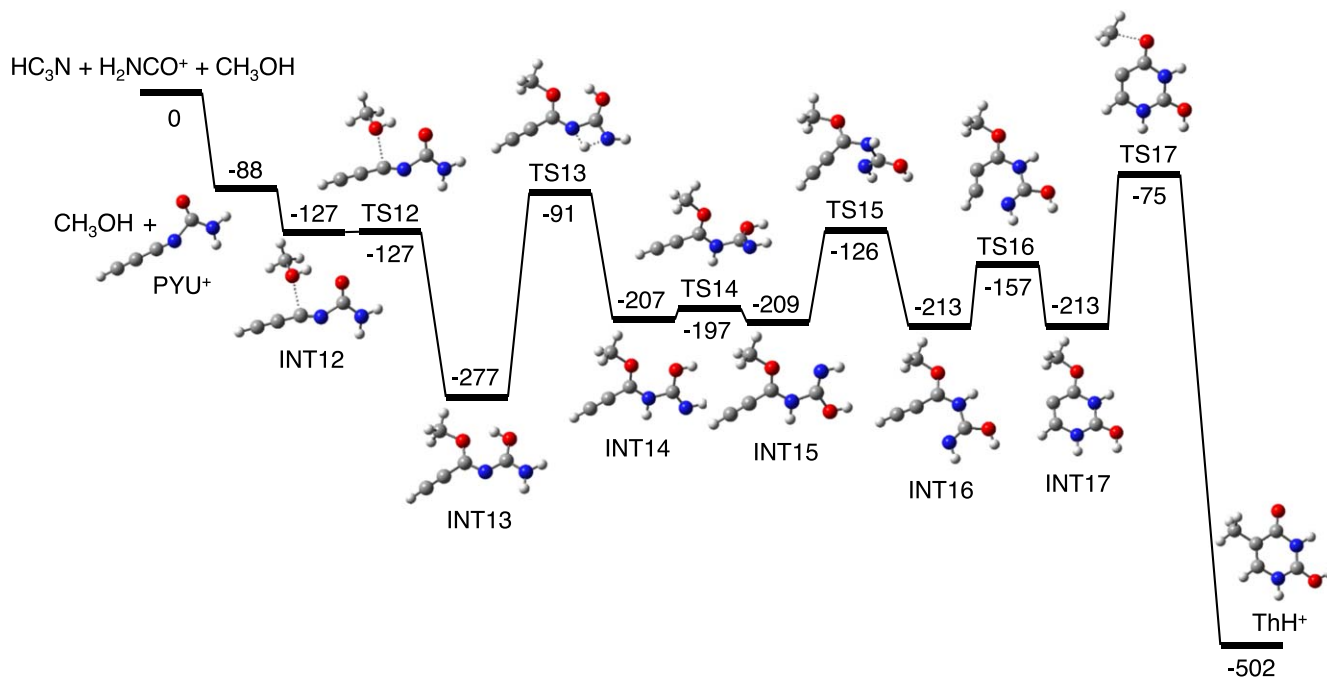


Figure 4. Potential energy kJ mol^{-1} diagram for the formation of ThH^+ from HC_3N , H_2NCO^+ , and CH_3OH , derived from CBS-QB3 calculation.

3.2. Formation of UrH^+ (Reaction II)

INT7 can be formed from the association of PYU^+ and H_2O . Subsequent steps to form UrH^+ are very similar to those of reaction I (Figure 3). After the rapid tautomerization of INT7 to INT9, the consecutive tautomerization to INT10 occurs with a high activation energy of 169 kJ mol^{-1} through a four-membered TS, TS9, that lies the highest in the pathway of the second stage of this reaction, $\text{PYU}^+ + \text{H}_2\text{O} \rightarrow \text{UrH}^+$. INT10 undergoes cyclization to INT11, followed by a H shift to finally form UrH^+ . The overall activation of the second stage is 42 kJ mol^{-1} , unlike the second stage of reaction I where there is no activation barrier. This suggests that occurrence of reaction II in nonenergetic environments in the ISM is possible only when PYU^+ formed at the first stage possesses an energy higher than 42 kJ mol^{-1} . To meet this condition, PYU^+ with an internal energy of 88 kJ mol^{-1} should react with H_2O before losing the energy.

The barrier for a H rearrangement occurring through a four-membered TS is greatly lowered by catalytic H_2O (Wolfe et al. 1995; Wang & Bowie 2012; Choe 2017, 2018, 2020a, 2020b; Lee & Choe 2017). The high barrier for the step $\text{INT9} \rightarrow \text{INT10}$ is significantly lowered when assisted by a molecule of H_2O . After the formation of an adduct $\text{INT} \cdots 9\text{H}_2\text{O}$, a H is shifted to form $\text{INT} \cdots 10\text{H}_2\text{O}$, through a relatively stable six-membered TS, TS9W, followed by the loss of H_2O as shown in Figure 3. Then the second stage can occur thermally without an overall activation energy. When the reaction occurs in an H_2O -rich region such as icy grain mantles, the probability of this happening would increase (Herbst 2017; Zamirri et al. 2019).

3.3. Formation of ThH^+ (Reaction III)

The association of PYU^+ and CH_3OH forms an ionic adduct, INT12, in the first step of the second stage of reaction III (Figure 4). A shift of H from the O atom of the CH_3OH moiety to the other O atom rapidly occurs to form INT13, which then undergoes consecutive tautomerization and rotation steps to

form INT16. Alternatively, INT13 can undergo a rotation first, followed by a tautomerization, similar to the pathways in reactions I and II described above. Its overall activation energy is 6 kJ mol^{-1} higher than that the pathway shown in Figure 4. After subsequent cyclization and a CH_3 shift from O to C atoms, ThH^+ is finally formed. The barrier for the final step $\text{INT17} \rightarrow \text{ThH}^+$ lies the highest in the pathway of the second stage, 13 kJ mol^{-1} higher than $\text{PYU}^+ + \text{CH}_3\text{OH}$. Therefore, thermal occurrence of reaction III at low temperatures is possible when at least 13 kJ mol^{-1} of the energy (88 kJ mol^{-1}) possessed in the first stage is transferred to the second stage.

3.4. Comparison with Previously Proposed Pathways

Previous studies proposing theoretical pathways for thermal reactions for syntheses of pyrimidine bases are limited. Wang & Bowie (2012) have proposed pathways for the formation of three pyrimidine bases with or without the assistance of H_2O : cytosine from urea and C_3NH , HC_3N , or HCOCH_2CN , uracil from urea and CCCO , and thymine from 2HNCO and $\text{CH}_3\text{CHCHO}^-$. Their overall activation Gibbs energies are in the range of $50\text{--}180 \text{ kJ mol}^{-1}$, indicating that the pathways are not adequate for occurrence of the thermal reactions in the ISM. According to our previous study, CyH^+ can be formed without an overall barrier when urea reacts with HC_3NH^+ , whereas the overall activation energy for the formation of cytosine is 127 kJ mol^{-1} when urea reacts with HC_3N (Choe 2020b). Other reported pathways are mainly for syntheses under photoirradiation conditions, in which several radicals are involved as reactants. Nguyen and coworkers have proposed several pathways for syntheses of pyrimidine bases starting from HCN, formamide (NH_2CHO), or urea (Jeilani et al. 2015, 2016; Nguyen et al. 2015). Several reactants such as H, H_2O , NH_2 , NH_3 , CCH , HCCH , NH_2CHO , and/or CH_2CHO are included. Kaur & Sharma (2019) have proposed pathways for the formation of cytosine and uracil from the reaction of urea, NH_2 , and HCOCH_2CN . Their overall activation energies are 66 and 72 kJ mol^{-1} , respectively. Gupta et al. (2013b) have

proposed a barrierless pathway for the formation of cytosine, in which HC_3N , NH , NCO^+ , 3H , and H^+ have been used as reactants or a catalyst. Bera et al. (2016, 2010) have suggested pathways (not full pathways) for the formation of uracil and thymine, starting from pyrimidine by addition of 2OH , $2\text{H}_2\text{O}$, and/or CH_3 , for explanation of their UV photoirradiation experiments. Compared to previously proposed pathways, the present pathways have two advantages; all reactions are barrierless and all reactants have been detected in the ISM. This strongly suggests a possible occurrence of the thermal reactions along the proposed pathways in the ISM. A disadvantage is that each of final products of reactions I–III is a highly excited single species, CyH^+ , UrH^+ , or ThH^+ . In this case, these excited ions can undergo dissociation much faster than reactions forming the corresponding pyrimidine bases.

3.5. Astrophysical Implications

Although all reactions described above are barrierless, their occurrence in the ISM should be carefully evaluated. The rate for the formation of PYU^+ was estimated using the data reported from the detection of HC_3N and H_2NCO^+ toward L483 (Agúndez et al. 2019), a dense core around a Class 0 protostar, as an example to check the possibility of its occurrence in the ISM. The rate equation for the association of HC_3N and H_2NCO^+ to form PYU^+ is given by

$$\frac{dn(\text{PYU}^+)}{dt} = k_a n(\text{HC}_3\text{N}) n(\text{H}_2\text{NCO}^+), \quad (1)$$

where k_a is the rate constant and $n(i)$ is the instantaneous concentration, or volume density, of a species i . k_a was estimated using the Su–Chesnavich expression (Su & Chesnavich 1982; Wakelam et al. 2010) because experimental data are not available. $n(\text{HC}_3\text{N})$ and $n(\text{H}_2\text{NCO}^+)$ detected in L483 are 3×10^{-5} and $2 \times 10^{-8} \text{ cm}^{-3}$, estimated from their reported abundances relative to H_2 , $n(\text{H}_2) = 3 \times 10^{-4} \text{ cm}^{-3}$ (Agúndez et al. 2019). Because $n(\text{HC}_3\text{N}) \gg n(\text{H}_2\text{NCO}^+)$, the above second-order equation becomes a pseudo-first-order equation as $dn(\text{PYU}^+)/dt \approx k'_a n(\text{H}_2\text{NCO}^+)$, where $k'_a = k_a n(\text{HC}_3\text{N})$. k_a estimated from the Su–Chesnavich formula is $2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. The electric dipole moment (3.73 D; Haynes et al. 2017) and calculated polarizability ($4.8 \times 10^{-24} \text{ cm}^3$) of HC_3N were used in the calculation together with the reported kinetic temperature of 10 K. Then, the half-life of H_2NCO^+ , $\tau_{\text{H}_2\text{NCO}^+} = \ln 2/k'_a$, against the formation of PYU^+ is estimated to be $4 \times 10^4 \text{ yr}$. This suggests that the formation of PYU^+ would occur within the timescale of chemical revolution of the typical dense interstellar clouds of 10^6 yr , although $\tau_{\text{H}_2\text{NCO}^+}$ can be longer, due to the competitive association reactions of H_2NCO^+ with other species. $\tau_{\text{H}_2\text{NCO}^+}$ can be much shorter than the estimate if the association with HC_3N occurs in other regions where the abundance of HC_3N is much higher.

PYU^+ formed from HC_3N and H_2NCO^+ , having at least 88 kJ mol^{-1} of internal energy, can redissociate or be stabilized by radiative relaxation. Collisional stabilization in the ISM is not effective due to an extremely low gas density. To compare rates of redissociation and radiative relaxation, the micro-canonical rate constant for $\text{PYU}^+ \rightarrow \text{HC}_3\text{N} + \text{H}_2\text{NCO}^+$ was calculated using the statistical Rice–Ramsperger–Kassel–Marcus (RRKM) theory (Marcus & Rice 1951). The method

Table 1
Dissociation Rate Constants Calculated using the RRKM Formula

Reaction	Internal Energy (kJ mol ⁻¹)	Rate Constants (s ⁻¹)
$\text{PYU}^+ \rightarrow \text{HC}_3\text{N} + \text{H}_2\text{NCO}^+$	88.0 ^a 87.8 ^b	3×10^3 7×10^3
$\text{CyH}^+ \rightarrow \text{HN}=\text{CH}-\text{CH}=\text{NCO}^+ + \text{NH}_3$	415 ^c 503 ^d	9×10^4 1×10^7
$\text{UrH}^+ \rightarrow \text{OC}=\text{CH}-\text{CH}=\text{NCO}^+ + \text{NH}_3$	319 ^c 407 ^d	2×10^5 6×10^7
$\text{ThH}^+ \rightarrow \text{OC}=\text{C}(\text{CH}_3)-\text{CH}=\text{NCO}^+ + \text{NH}_3$	414 ^c 502 ^d	2×10^6 7×10^7

Notes.

^a $T = 10 \text{ K}$.

^b $T = 50 \text{ K}$.

^c Case A.

^d Case B.

has been described elsewhere (Baer & Hase 1996; Yim & Choe 2011; Choe et al. 2017; Choe & Kim 2019). At 10–50 K, energies in the range of $0.2\text{--}1 \text{ kJ mol}^{-1}$ ($5/2RT$) of thermal translational and rotational energies of HC_3N and H_2NCO^+ are transferred to an vibrational internal energy of PYU^+ , which are added to 88 (87.8, more precisely) kJ mol^{-1} of the energy of PYU^+ for redissociation. RRKM rate constants calculated at this energy range were $(3\text{--}7) \times 10^3 \text{ s}^{-1}$ (Table 1). On the other hand, rate constants for typical radiative relaxations of vibrationally excited ions have been found to be lie within the range $10^1\text{--}10^3 \text{ s}^{-1}$ (Herbst 1985; Dunbar et al. 1996; Smith et al. 2001; Wakelam et al. 2010). This indicates that a considerable number of the excited PYU^+ ions would be stabilized by comparing rate constants. At lower temperatures, stabilization would be more effective because rate constants for dissociation and radiative relaxation are expected to show positive and negative dependences on temperature, respectively (Wakelam et al. 2010). The stabilized PYU^+ ions can undergo a further association reaction with NH_3 , H_2O , or CH_3OH . We will call this case A. These association reactions with NH_3 and H_2O , which finally lead to CyH^+ and UrH^+ , respectively, can occur without activation barriers. The latter reaction is barrierless when assisted by a H_2O molecule. On the other hand, the reaction of stabilized PYU^+ ion with CH_3OH to form ThH^+ can hardly occur thermally at low temperatures due to its overall activation energy of 13 kJ mol^{-1} .

Another possibility is when further association reactions of the excited PYU^+ with NH_3 , H_2O , or CH_3OH occur faster than redissociation. This is barely possible in the gas phase of the ISM because bimolecular reactions are much slower than unimolecular redissociations due to an extremely low gas density. If reactions I–III occur after adsorption on icy grain mantles, reactants would be solvated by NH_3 , H_2O , and/or CH_3OH (Herbst 2017; Zamirri et al. 2019). Therefore, INT1, INT7, or INT12 could be formed directly by the association of HC_3N and H_2NCO^+ . In this case, additional association of PYU^+ with NH_3 , H_2O , or CH_3OH is unnecessary. Subsequent steps finally leading to CyH^+ , UrH^+ , and ThH^+ , would occur faster than redissociation or radiative relaxation. We will call this case B.

CyH^+ , UrH^+ , and ThH^+ , formed by reactions I–III, are highly excited because the reactions are exoergic by 503, 407, and 502 kJ mol^{-1} , respectively. To form corresponding

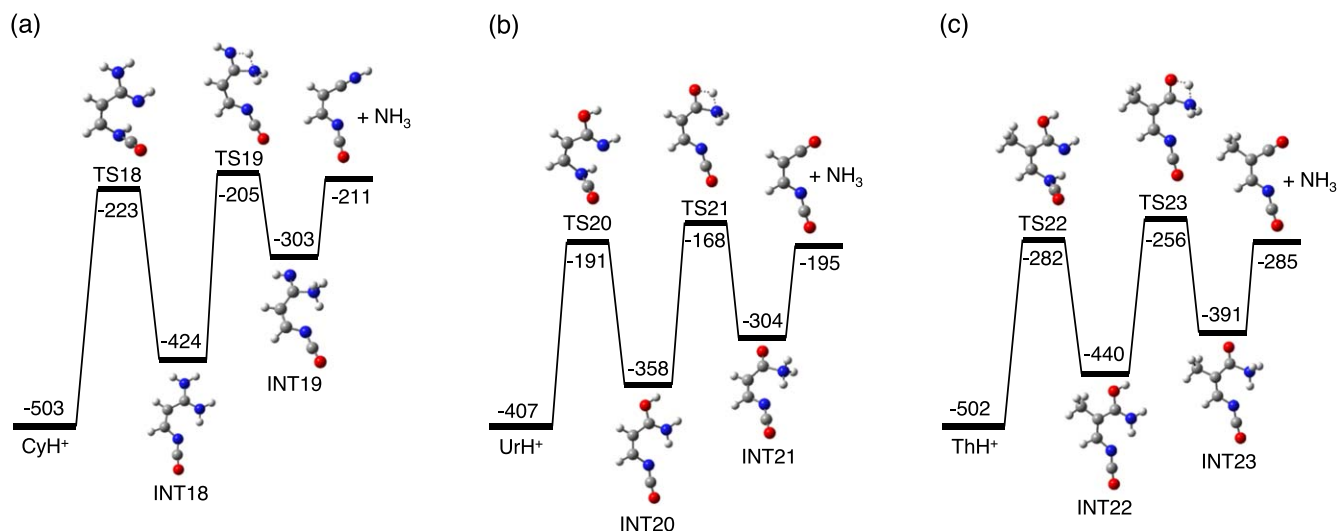


Figure 5. Potential energy kJ mol^{-1} diagram for losses of NH_3 from CyH^+ , UrH^+ , and ThH^+ , derived from CBS-QB3 calculation. Energies of CyH^+ , UrH^+ , and ThH^+ are relative to the sum of the energy of $\text{HC}_3\text{N} + \text{H}_2\text{NCO}^+$ and NH_3 , H_2O , or CH_3OH , respectively.

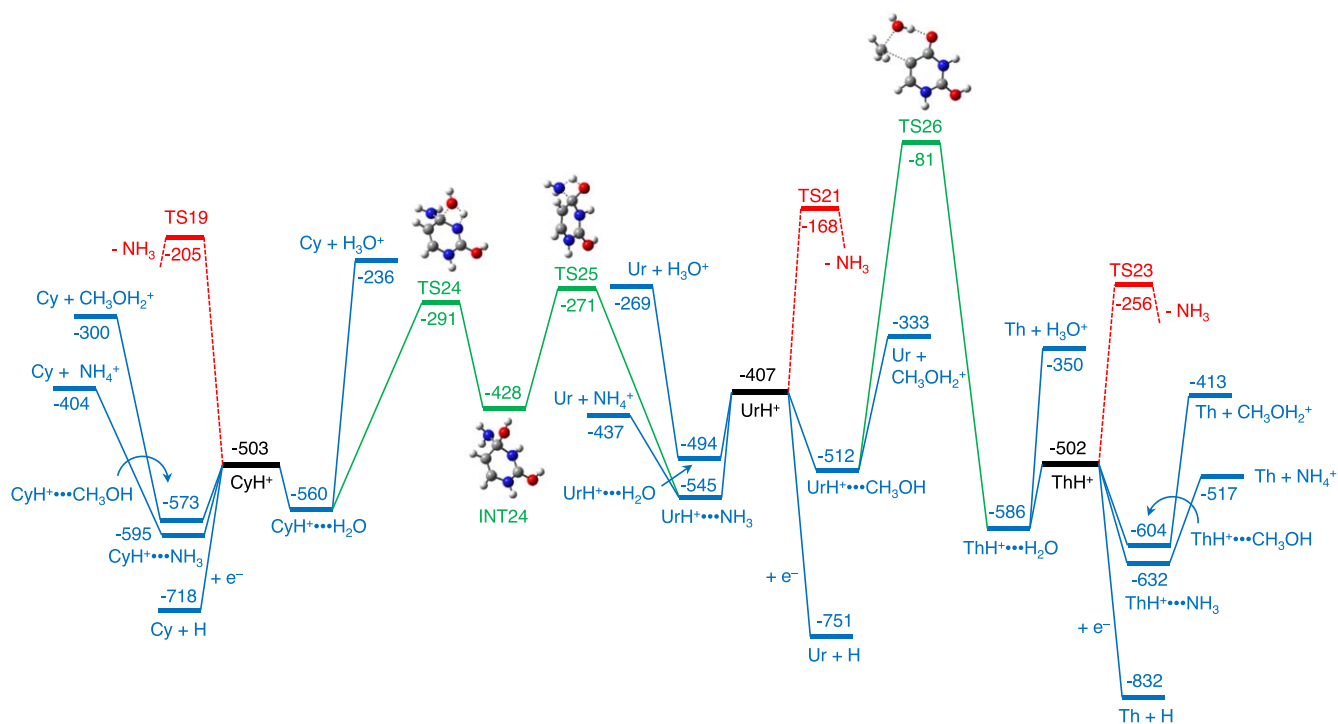


Figure 6. Potential energy kJ mol^{-1} diagram for reactions of CyH^+ , UrH^+ , and ThH^+ , derived from CBS-QB3 calculation. Energies of CyH^+ , UrH^+ , and ThH^+ are relative to the sum of the energy of $\text{HC}_3\text{N} + \text{H}_2\text{NCO}^+$ and NH_3 , H_2O , or CH_3OH , respectively. For bimolecular reactions, the energy of each added reactant is summed to the reference energy. Cy, Ur, and Th stand for cytosine, uracil, and thymine, respectively. The highest barriers for the losses of NH_3 (TS19, TS21, and TS23 shown in Figure 5) are included for comparison.

pyrimidine bases, these ions should be successfully deprotonated while overcoming other competitive processes. These excited ions can undergo further ion–molecule reactions including a dissociative recombination with electron or other molecules, radiative relaxation, or dissociation. Such possible reactions are summarized in Figure 1(b). Their calculated PESs are shown in Figures 5 and 6.

First, excited CyH^+ , UrH^+ , and ThH^+ ions can dissociate. In previous unimolecular dissociation studies of CyH^+ (Yao et al. 2007) and UrH^+ (Sadr-Arani et al. 2014; Molina et al. 2016) using experimental and theoretical methods, various dissociation channels have been found. For both ions, the loss of NH_3

was the lowest-energy channel in the primary dissociation. Therefore, we calculated PESs for losses of NH_3 from CyH^+ , UrH^+ , and ThH^+ (Figure 5). Although the dissociation of ThH^+ has, to the best of our knowledge, not been reported, it is highly probable that the loss of NH_3 also is the lowest-energy channel considering its structural similarity with UrH^+ . As shown in Figure 5, losses of NH_3 can occur through three steps, a ring opening, H shift, and the C– NH_3 bond cleavage, for all three protonated pyrimidines. Their overall activation energies are 298, 239, and 245 kJ mol^{-1} in the dissociation of CyH^+ , UrH^+ , and ThH^+ , respectively. RRKM dissociation rate constants were calculated by assuming that each loss occurred

one step through its highest TS, TS19, TS21, or TS23, respectively. For cases A and B, the dissociation rate constants are in the range of 10^5 – 10^6 s $^{-1}$ and 10^7 – 10^8 s $^{-1}$, respectively, as listed in Table 1. Considering other parallel dissociation channels, total dissociation rate constants would be somewhat higher than calculated values. This indicates that the protonated pyrimidine bases formed in case A or B would dissociate rapidly before radiative relaxations having typical rate constants of 10^1 – 10^3 s $^{-1}$, if we do not consider other processes.

Second, the protonated pyrimidine bases can undergo further bimolecular reactions. After the formation of $\text{CyH}^+ \dots \text{H}_2\text{O}$ by the association of CyH^+ with H_2O , cytosine or UrH^+ can be formed by the loss of H_3O^+ or NH_3 , respectively (Figure 6). When CyH^+ reacts with NH_3 or CH_3OH , cytosine is formed with NH_4^+ or CH_3OH^+ , respectively. In the interstellar gas phase, however, these bimolecular reactions cannot compete with unimolecular dissociation of PYU^+ due to an extremely low gas density. For example, the rate constant of the formation of $\text{CyH}^+ \dots \text{NH}_3$ by the association of CytH^+ and NH_3 in L483 was estimated. $n(\text{NH}_3)$ in L483 is $\sim 3 \times 10^{-4}$ cm $^{-3}$, estimated from the reported abundance (Agúndez et al. 2019). Because $n(\text{NH}_3) \gg n(\text{CytH}^+)$, the rate equation is approximated as $dn(\text{CyH}^+ \dots \text{NH}_3)/dt \approx k'_b n(\text{CytH}^+)$. Here, $k'_b = k_b n(\text{NH}_3)$ and k_b is the association rate constant, estimated to be 1×10^{-8} cm 3 s $^{-1}$ using the Su–Chesnavich formula. The electric dipole moment (1.47 D; Haynes et al. 2017) and polarizability (2.10×10^{-24} cm 3 ; Maryott & Buckley 1953) of NH_3 were used in the calculation. Then, k'_b is 3×10^{-12} s $^{-1}$, which is much smaller than the calculated dissociation rate constants of CytH^+ of 10^5 – 10^7 s $^{-1}$ (Table 1). This indicates that CytH^+ formed from PYU^+ would dissociate rapidly before its association with NH_3 and hence could not form cytosine in the ISM.

When these reactions occur on icy grain mantles, the starting reactants, HC_3N and H_2NCO^+ , are already solvated with NH_3 , H_2O , and/or CH_3OH . Then, these bimolecular association steps are unnecessary as described above. Activation energies for these reactions are lower than the activation energy for the dissociation of CyH^+ as shown in Figure 6. Therefore, these reactions can compete with the dissociation when occurring on icy grain mantles. UrH^+ can undergo a dissociative recombination with NH_3 , H_2O , or CH_3OH , to form uracil. Their activation energies are lower than the activation energy for the dissociation of UrH^+ . Reactions from UrH^+ to CyH^+ and ThH^+ are highly unfavorable because their activation energies are much higher than those for the formation of uracil + NH_4^+ and uracil + CH_3OH^+ , respectively. Similarly, ThH^+ can undergo a dissociative recombination with NH_3 , H_2O , or CH_3OH , to form thymine more favorably than the reaction to UrH^+ or the dissociation when the reactions occur on icy grain mantles. The energetics for the dissociative recombination of the three protonated pyrimidine bases with electrons are also shown in Figure 6. Cytosine, uracil, and thymine thus formed by dissociation recombination can survive for a long time against dissociation. For example, the available energy for the formation of uracil + NH_4^+ in case B is 437 kJ mol $^{-1}$. This energy is distributed to internal energies of uracil and NH_4^+ and the released kinetic energy. Therefore, a portion of uracil molecules, which have internal energies below the activation energy for the dissociation of uracil (estimated to be higher than 239 kJ $^{-1}$), can be stabilized by radiative relaxation.

Uracil has been discovered in meteorites (Stoks & Schwartz 1979; Martins et al. 2008), whereas cytosine and

thymine have not been yet. This has led to the RNA-world hypothesis, in which the first genetic material for all life on Earth would be based on RNA which includes uracil delivered to the early Earth, not DNA which includes thymine instead (Gilbert 1986; Sandford et al. 2020). Could the present results explain that the formation of uracil is more favorable than the formation of cytosine and thymine in the ISM? Typical abundances of NH_3 and CH_3OH in interstellar icy grain mantles are $\sim 5\%$ with respect to H_2O , which is the most abundant constituent (Boogert et al. 2015). Therefore, PYU^+ formed in the first stage would react with H_2O more favorably than with NH_3 or CH_3OH . The best scenario that can be drawn from mechanisms proposed here is as follows. HC_3N and H_2NCO^+ can form PYU^+ after adsorption onto the H_2O -rich surfaces of interstellar icy grain mantles. Excited PYU^+ ions solvated with H_2O can rapidly form UrH^+ , followed by a rapid dissociative recombination with H_2O , leading to stable uracil. Two H_2O molecules can participate as reactants in this overall reaction. Less probably, cytosine and thymine can be formed through similar pathways on icy grain surfaces containing NH_3 and CH_3OH .

4. Conclusion

Pathways for barrierless reactions to form CyH^+ , UrH^+ , and ThH^+ from molecules detected in the ISM such as HC_3N and H_2NCO^+ , and one of NH_3 , H_2O , and CH_3OH , respectively, were proposed in this study. The kinetic analysis showed that the formation of CyH^+ and UrH^+ was possible through thermal reactions along the proposed pathways in the gas phase of the ISM, but not for ThH^+ because of a barrier in the next stage, $\text{PYU}^+ + \text{CH}_3\text{OH} \rightarrow \text{ThH}^+$. However, the next steps to form cytosine and uracil from CyH^+ and UrH^+ by dissociative recombination reactions were found to barely occur in the gas phase because highly excited ions would dissociate rapidly, considering an extremely low gas density of the ISM. This does not entirely rule out the possibility of the occurrence of reactions along the proposed pathways in the ISM. When reactions occur after adsorption on the surfaces of icy grain mantles containing NH_3 , H_2O , and CH_3OH , dissociative recombination reactions might compete with dissociations and formed pyrimidine bases might survive for a long time in nonenergetic environments of the ISM. This shows that icy grain mantles might play an important role in prebiotic syntheses of building blocks of life in the ISM. Further theoretical studies using more explicit modeling of interstellar icy grain surfaces (Woon 2011; Choe 2019; Zamirri et al. 2019) will be helpful to support the present proposition.

This study was supported by the National Institute of Supercomputing and Network/Korea Institute of Science and Technology Information, with supercomputing resources including technical support (grant No. KSC-2020-CRE-0224).

ORCID iDs

Joong Chul Choe  <https://orcid.org/0000-0001-6722-0655>

References

- Agúndez, M., Marcelino, N., Cernicharo, J., Roueff, E., & Tafalla, M. 2019, *A&A*, **625**, A147
- Baer, T., & Hase, W. L. 1996, *Unimolecular Reaction Dynamics: Theory and Experiments* (New York: Oxford Univ. Press)
- Becke, A. D. 1993, *JChPh*, **98**, 5648

- Bera, P. P., Nuevo, M., Materese, C. K., Sandford, S. A., & Lee, T. J. 2016, *JChPh*, **144**, 144308
- Bera, P. P., Nuevo, M., Milam, S. N., Sandford, S. A., & Lee, T. J. 2010, *JChPh*, **133**, 104303
- Bera, P. P., Stein, T., Head-Gordon, M., & Lee, T. J. 2017, *AsBio*, **17**, 771
- Boogert, A. C. A., Gerakines, P. A., & Whittet, D. C. B. 2015, *ARA&A*, **53**, 541
- Choe, J. C. 2017, *Bull. Korean Chem. Soc.*, **38**, 1531
- Choe, J. C. 2018, *CPL*, **708**, 71
- Choe, J. C. 2019, *Bull. Korean Chem. Soc.*, **40**, 205
- Choe, J. C. 2020a, *Bull. Korean Chem. Soc.*, **41**, 382
- Choe, J. C. 2020b, *ApJ*, **898**, 13
- Choe, J. C., & Kim, M. H. 2019, *CPL*, **730**, 538
- Choe, J. C., Moon, C. J., Choi, M. Y., & Kim, M. H. 2017, *RSCAd*, **7**, 47689
- Dunbar, R. C., Klippenstein, S. J., Hrušák, J., Stöckigt, D., & Schwarz, H. 1996, *JChS*, **118**, 5277
- Ferris, J. P., Sanchez, R. A., & Orgel, L. E. 1968, *J. Mol. Biol.*, **33**, 693
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., et al. 2016, Gaussian, Inc. 16, Revision A (Wallingford CT: Gaussian, Inc.), 03
- Gilbert, W. 1986, *Natur*, **319**, 618
- Gupta, H., Gottlieb, C. A., Lattanzi, V., Pearson, J. C., & McCarthy, M. C. 2013a, *ApJL*, **778**, L1
- Gupta, V. P., Tandon, P., & Mishra, P. 2013b, *AdSpR*, **51**, 797
- Haynes, W. M., Lide, D. R., & Bruno, T. J. 2017, CRC Handbook of Chemistry and Physics (97th ed.; Boca Raton, FL: Taylor and Francis)
- Herbst, E. 1985, *ApJ*, **291**, 226
- Herbst, E. 2001, *Chem. Soc. Rev.*, **30**, 168
- Herbst, E. 2017, *IRPC*, **36**, 287
- Jeilani, Y. A., Fearce, C., & Nguyen, M. T. 2015, *PCCP*, **17**, 24294
- Jeilani, Y. A., Nguyen, H. T., Newallo, D., Dimandja, J.-M. D., & Nguyen, M. T. 2013, *PCCP*, **15**, 21084
- Jeilani, Y. A., Williams, P. N., Walton, S., & Nguyen, M. T. 2016, *PCCP*, **18**, 20177
- Jiang, X.-J., Wang, J.-Z., Gao, Y., & Gu, Q.-S. 2017, *A&A*, **600**, A15
- Jung, S. H., & Choe, J. C. 2013, *AsBio*, **13**, 465
- Kaur, S., & Sharma, P. 2019, *IJC*, **119**, e25886
- Kobayashi, K. 2019, in *Astrobiology*, ed. A. Yamagishi, T. Kakegawa, & T. Usui (Singapore: Springer), 43
- Lee, H. M., & Choe, J. C. 2017, *CPL*, **675**, 6
- Marcelino, N., Agúndez, M., Cernicharo, J., Roueff, E., & Tafalla, M. 2018, *A&A*, **612**, L10
- Marcus, R. A., & Rice, O. K. 1951, *J. Phys. Colloid. Chem.*, **55**, 894
- Martins, Z., Botta, O., Fogel, M. L., et al. 2008, *E&PSL*, **270**, 130
- Maryott, A. A., & Buckley, F. 1953, US National Bureau of Standards Circular No. 537 (Washington, DC: National Bureau of Standards)
- Materese, C. K., Nuevo, M., Bera, P. P., Lee, T. J., & Sandford, S. A. 2013, *AsBio*, **13**, 948
- Materese, C. K., Nuevo, M., McDowell, B. L., Buffo, C. E., & Sandford, S. A. 2018, *ApJ*, **864**, 44
- Materese, C. K., Nuevo, M., & Sandford, S. A. 2017, *AsBio*, **17**, 761
- McGuire, B. A. 2018, *ApJS*, **239**, 17
- Molina, E. R., Salpin, J.-Y., Spezia, R., & Martinez-Nunez, E. 2016, *PCCP*, **18**, 14980
- Montgomery, J. A., Jr., Frisch, M. J., Ochterski, J. W., & Petersson, G. A. 1999, *JChPh*, **110**, 2822
- Morris, M., Turner, B. E., Palmer, P., & Zuckerman, B. 1976, *ApJ*, **205**, 82
- Nguyen, H. T., Jeilani, Y. A., Hung, H. M., & Nguyen, M. T. 2015, *J. Phys. Chem. A*, **119**, 8871
- Nuevo, M., Materese, C. K., & Sandford, S. A. 2014, *ApJ*, **793**, 125
- Nuevo, M., Milam, S. N., & Sandford, S. A. 2012, *AsBio*, **12**, 295
- Nuevo, M., Milam, S. N., Sandford, S. A., Elsil, J. E., & Dworkin, J. P. 2009, *AsBio*, **9**, 683
- Oba, Y., Takano, Y., Naraoka, H., Watanabe, N., & Kouchi, A. 2019, *NatCo*, **10**, 4413
- Pearce, B. K., & Pudritz, R. E. 2015, *ApJ*, **807**, 85
- Ruf, A., Lange, J., Eddhif, B., et al. 2019, *ApJL*, **887**, L31
- Sadr-Arani, L., Mignon, P., Chermette, H., & Douki, T. 2014, *CPL*, **605**, 108
- Sanchez, R. A., Ferris, J. P., & Orgel, L. E. 1966, *Sci*, **154**, 784
- Sandford, S. A., Nuevo, M., Bera, P. P., & Lee, T. J. 2020, *ChRev*, **120**, 4616
- Sephton, M. A. 2002, *Nat. Prod. Rep.*, **19**, 292
- Smith, I. W. M., Talbi, D., & Herbst, E. 2001, *A&A*, **369**, 611
- Stoks, P. G., & Schwartz, A. W. 1979, *Natur*, **282**, 709
- Su, T., & Chesnavich, W. J. 1982, *JChPh*, **76**, 5183
- Suzuki, H., Yamamoto, S., Ohishi, M., et al. 1992, *ApJ*, **392**, 551
- Turner, B. E. 1971, *ApJL*, **163**, L35
- Wakelam, V., Smith, I. W. M., Herbst, E., et al. 2010, *SSRv*, **156**, 13
- Wang, T., & Bowie, J. H. 2012, *Org. Biomol. Chem.*, **10**, 652
- Wolfé, S., Kim, C.-K., Yang, K., Weinberg, N., & Shi, Z. 1995, *JChS*, **117**, 4240
- Woon, D. E. 2011, *ApJ*, **728**, 44
- Yao, C., Tureček, F., Polce, M. J., & Wesdemiotis, C. 2007, *IJMSp*, **265**, 106
- Yim, M. K., & Choe, J. C. 2011, *J. Phys. Chem. A*, **115**, 3087
- Yim, M. K., & Choe, J. C. 2012, *CPL*, **538**, 24
- Zamirri, L., Ugliengo, P., Ceccarelli, C., & Rimola, A. 2019, *ESC*, **3**, 1499