



Quantum chemical study on the formation of isopropyl cyanide and its linear isomer in the interstellar medium

Keshav Kumar Singh¹, Poonam Tandon¹ , Alka Misra² , Shivani²,
Manisha Yadav^{1,2} and Aftab Ahmad^{1,2}

¹Department of Physics, University of Lucknow, Lucknow, India and ²Department of Mathematics & Astronomy, University of Lucknow, Lucknow, India

Research Article

Cite this article: Singh KK, Tandon P, Misra A, Shivani , Yadav M, Ahmad A (2021). Quantum chemical study on the formation of isopropyl cyanide and its linear isomer in the interstellar medium. *International Journal of Astrobiology* **20**, 62–72. <https://doi.org/10.1017/S147355042000035X>

Received: 12 December 2019
Revised: 27 October 2020
Accepted: 28 October 2020
First published online: 24 November 2020

Key words:

Astrobiology; astrochemistry; interstellar medium; prebiotic chemistry

Author for correspondence:

Poonam Tandon,
E-mail: tdandon_poonam@lkouniv.ac.in

Abstract

The formation mechanism of linear and isopropyl cyanide (hereafter *n*-PrCN and *i*-PrCN, respectively) in the interstellar medium (ISM) has been proposed from the reaction between some previously detected small cyanides/cyanide radicals and hydrocarbons/hydrocarbon radicals. *n*-PrCN and *i*-PrCN are nitriles therefore, they can be precursors of amino acids via Strecker synthesis. The chemistry of *i*-PrCN is especially important since it is the first and only branched molecule in ISM, hence, it could be a precursor of branched amino acids such as leucine, isoleucine, etc. Therefore, both *n*-PrCN and *i*-PrCN have significant astrobiological importance. To study the formation of *n*-PrCN and *i*-PrCN in ISM, quantum chemical calculations have been performed using density functional theory at the MP2/6-311++G(2d,p)//M062X/6-311+G(2d,p) level. All the proposed reactions have been studied in the gas phase and the interstellar water ice. It is found that reactions of small cyanide with hydrocarbon radicals result in the formation of either large cyanide radicals or ethyl and vinyl cyanide, both of which are very important prebiotic interstellar species. They subsequently react with the radicals CH₂ and CH₃ to yield *n*-PrCN and *i*-PrCN. The proposed reactions are efficient in the hot cores of SgrB2 (N) (where both *n*-PrCN and *i*-PrCN were detected) due to either being barrierless or due to the presence of a permeable entrance barrier. However, the formation of *n*-PrCN and *i*-PrCN from the ethyl and vinyl cyanide always has an entrance barrier impermeable in the dark cloud; therefore, our proposed pathways are inefficient in the deep regions of molecular clouds. It is also observed that ethyl and vinyl cyanide serve as direct precursors to *n*-PrCN and *i*-PrCN and their abundance in ISM is directly related to the abundance of both isomers of propyl cyanide in ISM. In all the cases, reactions in the ice have smaller barriers compared to their gas-phase counterparts.

Introduction

One of the critical questions of biology is how life originated on earth. Besides the Miller–Urey experiment (Miller, 1953), another hypothesis which provides an answer to this question assumes that at-least precursors of biological molecules, particularly precursors of amino acids must have originated in the interstellar medium (ISM) and they have come to earth during the late bombardment period via comets and meteoroids (Abramov and Mojzsis, 2009; Wickramasinghe, 2011). Although none of the amino acids has been found in the ISM to date, their presence is expected because most of the molecules involved in the amino acid synthesis (particularly Strecker synthesis) have been already observed in the ISM in the past few decades. Several research groups around the world are looking for the various other possible roots for the amino acid synthesis (Woon, 2002; Cecchi-Pestellini *et al.*, 2004; Andersen and Haack, 2005; Chiaromello *et al.*, 2005; Mita *et al.*, 2005; Lattelais, Ellinger and Zanda, 2007).

The carbonaceous chondrite such as Murchison meteorite (Lawless, 1973), Allan Hills meteorite and others (Sephton 2000; Pizzarello and Shock 2010) are found to be rich in amino acids and their precursors. These meteoroids are also rich in branched amino acids such as valine, 2-aminoisobutyric acid, etc. Branched amino acids are one of the important constituents of terrestrial biology. Their presence in the meteorites indicates that at least their precursor must have been originated in the ISM. The discovery of several amino acid precursors in ISM provides evidence for this hypothesis (Koch *et al.*, 2000; Basiuk, 2001; Woon 2001; Singh *et al.*, 2018).

Propyl cyanide and its branched isomer (hereafter *n*-PrCN and *i*-PrCN respectively) belong to the family of interstellar cyanides and are currently the largest and most complex members of this family. Interstellar cyanides are one such family of prebiotic molecules. Cyanides play an important role in the Strecker synthesis since they can easily reduce to their corresponding amine (RCHNH₂) (owing to the presence of HCNH₂ moiety, amines serve as directed

precursors of amino acids) (Chakrabarti *et al.*, 2015). Interstellar cyanides are found in a copious amount in interstellar clouds (Jefferts *et al.*, 1970; Guélin and Cernicharo, 1991; Agúndez *et al.*, 2008; Margulès *et al.*, 2009; Daly *et al.*, 2013; Belloche *et al.*, 2014; Cernicharo *et al.*, 2004). Two simplest cyanides viz. HCN and CH₃CN were detected in 1971 (Snyder and Buhl, 1971; Solomon and Jefferts, 1971) and after their initial discovery, several more were detected in ISM ranging from saturated to unsaturated molecules and radicals (Guélin and Cernicharo, 1991; Highberger *et al.*, 2001; Cernicharo *et al.*, 2004; Bera *et al.*, 2009). Due to their importance in the chemistry of life, formation mechanisms of cyanides and related reduced species were investigated by both experimental and theoretical means (Schwartz *et al.*, 1982; Ordu *et al.*, 2012; Shivani and Tandon, 2017; Singh *et al.*, 2018). Currently, the largest member of the family of interstellar cyanides is propyl cyanide (C₃H₇CN), which is not only the largest but also the only interstellar molecule that can have branched isomer. Propyl cyanide (hereafter *n*-PrCN; *n* refers to 'normal') was detected in SgrB2 (N) (Belloche *et al.*, 2009). Since this was the first and only detected molecule which can have a branched structure, the discovery of its branched isomer, isopropyl cyanide (iso-C₃H₇CN, hereafter *i*-PrCN), was much awaited. Later, *i*-PrCN was detected in the hot core of Sagittarius molecular cloud (SgrB2 (N)) along with its linear isomer, *n*-PrCN with column densities of nearly 7.2×10^{16} and 1.8×10^{17} cm⁻², respectively (Belloche *et al.*, 2014). The detection of *i*-PrCN is quite significant for both astrochemistry and astrobiology and since owing to the branched structure, *i*-PrCN can be considered as a precursor for branched amino acids such as leucine (the smallest branched amino acid), isoleucine and valine (the proteinogenic amino acids) and 2-aminoisobutyric acid (non-proteinogenic one).

Both the isomers of propyl cyanide are well studied in the interstellar context. The formation mechanism of *n*-PrCN was investigated by Belloche *et al.* (2009) using a coupled gas-phase and grain surface model suggested by Garrod (2008). They proposed that sequential addition of CH₂ and CH₃ radicals to CN, CH₂CN and C₂H₄CN on the grain surface or direct addition of large hydrocarbon radicals such as C₂H₅ or C₃H₇ to CN is the fastest route to *n*-PrCN. They derived the column density of *n*-PrCN to be nearly 1.5×10^{16} cm⁻² with a local cloud temperature of nearly 150 K. After the detection of *i*-PrCN, the same group also proposed the formation mechanism of *i*-PrCN and *n*-PrCN using chemical kinetics model MAGICKAL (Model for Astrophysical Gas and Ice Chemical Kinetics and Layering) which simulates the time-dependent chemistry of SgrB2 (N) (Belloche *et al.*, 2009; Garrod, 2013). Their study was focused on the accretion and addition of small radicals at the grain surface resulting in the isopropyl radical. These radicals subsequently add to CN and form *i*-PrCN. In their study, *n*-PrCN was formed from the addition of carbon radicals to the pre-existing cyanides. Contrary to the detected results, their model strongly favours the formation of *i*-PrCN (their proposed abundance ratio for *i*-PrCN:*n*-PrCN was 2.2:1 against the detected ratio 0.4:1). Recently Garrod *et al.* (2017) have studied the chemistry of SgrB2 (N) (with a special focus on the branching of complex molecules) by considering the case of propyl and butyl cyanide in the above-mentioned region using the same chemical model as Belloche *et al.* (2014) but with the updated chemical network. They concluded that the addition of CN to the unsaturated carbon plays an important role in smaller cyanide formations, which then grow towards more complex ones. With these

considerations, they successfully obtained the detected abundance ratio between the linear and branched isomers of propyl cyanide.

Both of the previous studies suggest that the growth of less complex small cyanides towards the large one plays an important role in interstellar chemistry. Therefore, we present accurate electronic structure calculations to understand the formation mechanism of both *i*-PrCN and *n*-PrCN in the ISM by the reactions of preexisting, less complex cyanides/cyanide radicals such as CH₂CN, HCCN, etc. with small organic radicals and unsaturated molecules. These molecules are present in a copious amount in ISM (Feuchtgruber, 2000; Polehampton *et al.*, 2005; Agúndez *et al.*, 2008). The proposed reaction schemes for *i*-PrCN and *n*-PrCN formation are listed in Table 1. All of these reaction schemes have also been studied for the catalytic effect of interstellar water ice.

Methodology

In the current study, all the quantum chemical calculations were performed using Gaussian 09 software (Frisch *et al.*, 2009). The structures of molecules/radicals/transition states were optimized at the UM062X/6-311+(2d,p) level of theory with tight convergence criteria. The chosen hybrid meta-exchange correlation density functional M062X includes midrange non-covalent dispersion corrections in its definition which are necessary for the current study since we are studying the reactions at the surface of water ice and non-covalent interactions have a large contribution towards the stability of water ice and reactants adsorbed at its surface. In order to improve the accuracy of the energies reported in this study, single-point calculations have been performed at the UMP2/6-311++(2d,p) level of theory on the structures optimized at the UM062X/6-311+(2d,p) level (Frisch *et al.*, 1990; Zhao and Truhlar, 2011). Our approach (optimization at UM062X/6-311+(2d,p) followed by single-point calculations at the UMP2/6-311++(2d,p) level) is referred as UMP2/6-311+(2d,p)//UM062X/6-311+(2d,p) throughout this paper. To infer the nature of the optimized geometry and to calculate the zero-point vibrational energy (ZPVE) corrections, analytical frequency calculations have been performed at the same level of theory as in the optimization. The minima were found to have only positive frequencies and transition structures were found to have only one negative frequency with the vibrations in the proposed reaction coordinates. The intrinsic reaction coordinate calculations were also performed to ensure that the transition structure connects reactants and products (Gonzalez and Schlegel, 1989). Only relative energies (including ZPVE) are reported in this study. The sum of the energies of reactants in each step has been taken as the reference for calculating relative energies. Our chosen chemical model viz. UMP2/6-311+(2d,p)//UM062X/6-311+(2d,p) has been benchmarked against the UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ level of theory by studying a reaction CH₃CH₂CH₂ (propyl radical) → [TS] → CH₃CHCH₃ (*isopropyl* radical) in the gas phase at both levels of theories (see Fig. 1). This reaction occurs on the doublet reaction surface and produces a radical centre on the secondary carbon which is important for the formation of *i*-PrCN. Thus, it can represent the reaction systems discussed in the subsequent sections. The benchmarking calculations show that the enthalpy of formation and barrier height of this reaction at UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ is differed by nearly 2 and 1.1 kcal mol⁻¹ only from the corresponding UMP2/6-311++(2d,p)//UM062X/

Table 1. List of all the reaction schemes under study for the formation of linear and branched isomers of propyl cyanide (*n*-PrCN and *i*-PrCN, respectively)

Proposed reaction schemes	Barrier height (ΔE , kcal mol ⁻¹)		Enthalpy of formation (ΔH , kcal mol ⁻¹)		
	Gas phase	Ice phase	Gas phase	Ice phase	
<i>Reaction 1</i>					
Step 1	CH ₃ + CH ₂ CN → CH ₃ CH ₂ CN (ethyl cyanide)	-	-	-92.31	-120.86
Step 2a	CH ₃ CH ₂ CN + CH ₂ → [TS] → CH ₃ CH ₂ CH ₂ CN (<i>n</i> -PrCN)	17.01	12.05	-93.37	-96.45
Step 2b	CH ₃ CH ₂ CN + CH ₂ → [TS] → CH ₃ CH(CN)CH ₃ (<i>i</i> -PrCN)	15.50	13.81	-96.45	-108.68
<i>Reaction 2</i>					
Step 1	C ₂ H ₄ + CN → CH ₂ CH ₂ CN → [TS1] → CH ₂ (CH)CN (vinyl cyanide) + H	-21.15	-22.59	-38.91	-39.72
Step 1a	C ₂ H ₄ + CN → CH ₂ CH ₂ CN → [TS2] → CH ₃ (CH)CN → CH ₂ (CH)CN (vinyl cyanide) + H	-33.95	-32.57	-38.91	-39.72
Step 2a ^a	CH ₂ CH ₂ CN + H → CH ₃ CH ₂ CN (ethyl cyanide)	-	-	-	-96.45
Step 2b ^a	CH ₃ (CH)CN + H → CH ₃ CH ₂ CN (ethyl cyanide)	-	-	-	-108.68
<i>Formation of vinyl cyanide (acrylonitrile)</i>					
<i>Reaction 3</i>					
Step 1 ^b	CH ₂ + HCCN → CH ₂ (CH)CN (vinyl cyanide)	-	-	-176.96	-
<i>Reaction 4</i>					
Step 1	C ₂ H ₂ + CN → C ₂ H ₂ CN → [TS1] → HCCCN + H	-10.54	-16.82	-43.53	-49.13
Step 1a	C ₂ H ₂ + CN → C ₂ H ₂ CN → CH ₂ C-CN → HCCCN + H	-17.32	-	-43.53	-49.13
Step 2a ^a	C ₂ H ₂ CN + H → CH ₃ CH ₂ CN (ethyl cyanide)	-	-	-	-165.85
Step 2b ^a	CH ₂ C-CN + H → CH ₃ CH ₂ CN (ethyl cyanide)	-	-	-	-88.60
<i>Formation of i-PrCN from vinyl cyanide</i>					
Step 1	CH ₂ (CH)CN + H → CH ₃ (CH)CN	15.63	16.19	-28.68	-28.43
Step 2	CH ₃ (CH)CN + CH ₃ → CH ₃ CH(CN)CH ₃ (<i>i</i> -PrCN)	-	-	-90.61	-172.88

^aOn surface of ice only.^bIn gas phase only.All the reported energies are calculated at the UMP2/6-311++(2d,p)//UM062X/6-311+(2d,p) level of theory and reported in kcal mol⁻¹ relative to the sum of their respective reactants.

6-311+(2d,p) energy values. This small energy difference is still important in the deep cloud regions of space such a small error in energy is less relevant when the reaction is being studied in the hot cores of molecular clouds such as SgrB2 (N) where temperature can easily go up to 300 K (Schmiedeke *et al.*, 2016). Therefore, we urge that the UMP2/6-311++(2d,p)//UM062X/6-311+(2d,p) level of theory is accurate enough to simulate the chemistry in the SgrB2 (N). Hence, all the calculations in the current study are reported at the UMP2/6-311++(2d,p)//UM062X/6-311+(2d,p) level of theory.

All the reported reactions were studied in the gas phase as well as in the interstellar ice. The ice model in the current study is built by arranging water molecules near one of the reactants under consideration such that water molecules can form hydrogen bonds among themselves and with the reactant. This initial structure is then optimized at the UMP2/6-311++(2d,p)//UM062X/6-311+(2d,p) level of theory. The second reactant is introduced after the optimization of the first reactant-ice structure. This reactant-ice complex represents the icy grain in which radicals are generated due to the interaction of grain and high energy cosmic rays. The ice complex contains up to 11 water molecules. This ice model is large enough to represent the nearest neighbour interactions between reactants and ice. Only exothermic reactions are reported in the current study since under the energy-starved conditions of ISM no external energy is available for endothermic reaction to be feasible.

Results and discussion

The current study is focused on those reactions in which some previously detected, less complex cyanides react with the small hydrocarbons to form large and more complex cyanides (linear and isopropyl cyanides in the present context). In order to understand the formation of *n*-PrCN and *i*-PrCN via the above-mentioned molecules/radicals, the radical-radical and radical-molecule reactions have been studied using CH₂, CH₃, CN, CH₂CN, C₂H₄, atomic hydrogen, etc. as reactants. All of these molecules are plentiful in the ISM and produced frequently in the interstellar ice when it is exposed to the cosmic rays (see Section 'Abundance of reactants in the SgrB2 (N)'). Therefore, they are important ice grain species. In the current study, the reactions were first studied in the gas phase and then in the ice in order to understand the catalytic effect of ice. All the proposed reaction schemes are listed in Table 1 and related energy level diagrams are shown in Figs 2–6. The results for the proposed pathways are discussed in separate sub-sections followed by the comparison of their feasibility.

Abundance of reactants in the SgrB2 (N)

The reactants used in the current study are abundant in the ISM. Methyl radical (CH₃) is an important species found as an impurity in interstellar water ice. Nearly 190 formation pathways for CH₃ radical are listed in the UMIST astrochemistry database,

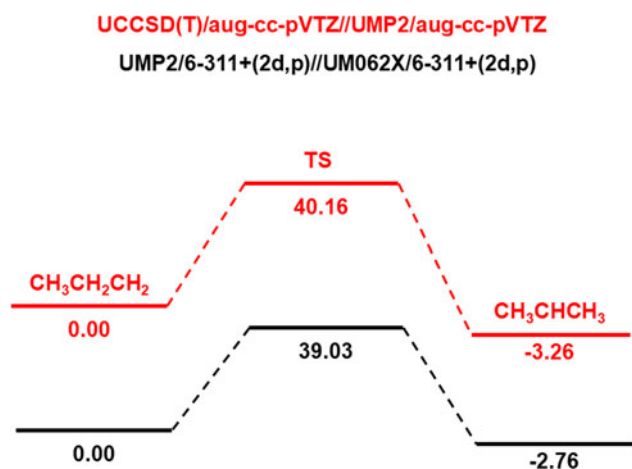


Fig. 1. Formation of isopropyl radical from propyl radical via proton transfer from the central CH_2 to terminal CH_2 studied at UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ (black) and UMP2/6-311+(2d,p)//UM062X/6-311+(2d,p) (red).

the majority of which include either charge transfer from methyl cation (CH_3^+) by another grain surface species or photodissociation of methane followed by the dissociative recombination (DR) ($\text{CH}_4 + h\nu \rightarrow \text{CH}_3^+ + \text{H}$ and $\text{CH}_3^+ + e^- \rightarrow \text{CH}_3$). Methyl radical (CH_3) was first detected by Feuchtgruber (2000) towards the galactic centre in Sgr A with a column density of $8 \times 10^{14} \text{ cm}^{-2}$. The methyl cation is not only responsible for the formation of methyl radical, but also for methylene radical (CH_2) as it is formed by the DR of CH_3^+ (Hollis *et al.*, 1995). Thus, methylene (CH_2) has been detected in a similar abundance of CH_3^+ (Polehampton *et al.*, 2005). C_2H_4 and C_2H_2 are also formed from the radical recombination of CH_2 and H , both of which are present in copious amounts in the ISM (Betz, 1981). Thus, all the hydrocarbon radicals and hydrocarbons involved in the current study can be formed from photodissociation of methane or from the sequential addition of atomic hydrogen to a carbon atom present in the cosmic rays. This procedure of hydrocarbon formation is experimentally confirmed by Bennett *et al.* (2006). Another important radical viz. cyanomethyl radical (CH_2CN) is abundant in the circumstellar envelopes of IRC + 10216, TMC-1 and SgrB2 molecular cloud with column density ranging from 2×10^{13} to $1 \times 10^{14} \text{ cm}^{-2}$ in various sources (Agúndez *et al.*, 2008). It is formed by the reaction $\text{CH}_3^+ + \text{HCN} \rightarrow \text{CH}_3\text{CNH}^+$, followed by the DR of the ion CH_3CNH^+ (Agúndez *et al.*, 2008). Cyanocarbene (HCCN) is a radical of allenic structure which was first detected in IRC + 10216, Orion A and in SgrB2 by Guélin and Cernicharo (1991) with a column density nearly $5 \times 10^{12} \text{ cm}^{-2}$. It is an important precursor for the formation of interstellar prebiotic molecules and appears in several other studies in the context of interstellar chemistry (Gupta *et al.*, 2011; Majumdar *et al.*, 2013). This radical is mostly formed when small hydrocarbons react with the $\text{N}(^2\text{D})$ present in the cosmic rays (Hebrard *et al.*, 2009). Therefore, all the considered reactants are well abundant in the SgrB2 and can be used to study chemistry in SgrB2.

Reaction systems 1 and 2

Reaction system 1 is a radical addition reaction between cyanomethyl radical (CH_2CN) and the methyl radical (CH_3) while

reaction 2 is a radical–molecule reaction between C_2H_4 and CN radicals. The only product of reaction 1 is ethyl cyanide ($\text{CH}_3\text{CH}_2\text{CN}$) while the primary product of reaction 2 is vinyl cyanide ($\text{C}_2\text{H}_3\text{CN}$). Ethyl cyanide produces in a single step in reaction 1. The addition of the two radicals is barrierless and exothermic with reaction energy -92.31 and $-120.86 \text{ kcal mol}^{-1}$ in the gas phase and the ice, respectively (see Fig. 2). This addition step is spontaneous since both the radicals have single unpaired electrons and are therefore very reactive. The sharing of these unpaired electrons results in the formation of a bond between the carbon of CH_3 and CH_2CN , thus forming $\text{CH}_3\text{CH}_2\text{CN}$.

The first step of reaction 2 (addition of C_2H_4 and CN radicals) is also barrierless and exothermic in the gas and ice phases. The addition of CN radical to the unsaturated hydrocarbon in the gas phase is studied experimentally by Balucani *et al.* (2000) and Gannon *et al.* (2007). They also deduce that the addition of multiple bonds to CN is barrierless. Reaction 2 occurs by sharing of an unpaired electron of CN radical with the π electron cloud of C_2H_4 and yields a (doublet) radical ($\text{CH}_2\text{CH}_2\text{CN}$). The reaction energy for this step is $-66.39 \text{ kcal mol}^{-1}$ with respect to the separate reactants in the gas phase (see Fig. 3). The gas-phase reaction energy for this addition is calculated by Balucani *et al.* (2000) and is about $-55.502 \text{ kcal mol}^{-1}$. The difference between the reaction energy calculated by us and Balucani *et al.* (2000) is due to the difference in the theory level and basis set employed for calculations. Radical $\text{CH}_2\text{CH}_2\text{CN}$ can further dissociate via hydrogen abstraction (from one of the carbons of CH_2CH_2 moiety) and yield vinyl cyanide ($\text{C}_2\text{H}_3\text{CN}$) as a stable product (step 1 gas phase, Fig. 3). This dissociation has an entrance barrier of about $45.240 \text{ kcal mol}^{-1}$ with respect to $\text{CH}_2\text{CH}_2\text{CN}$ but this barrier is submerged (about -21.15) when compared to the total energy of the reactants. In study by Balucani *et al.* (2000), the gas-phase entrance barrier is about -18.90 for the formation of vinyl cyanide ($\text{C}_2\text{H}_3\text{CN}$) and hydrogen atom which is close to our computed value. Due to the submerged barrier, they propose that reaction will take place spontaneously as sufficient energy is available to the radical $\text{CH}_2\text{CH}_2\text{CN}$ from the internal energy of the reactants to overcome the entrance barrier. According to Balucani *et al.* (2000), a part of radical $\text{CH}_2\text{CH}_2\text{CN}$ undergo a [1, 2] H atom shift and form CH_3CHCN radical with barrier $-32.54 \text{ kcal mol}^{-1}$ and reaction energy $-68.42 \text{ kcal mol}^{-1}$ with respect to the total reactant energy. CH_3CHCN radical quickly reduces to vinyl cyanide ($\text{C}_2\text{H}_3\text{CN}$) and a hydrogen atom. When we studied this reaction channel in the gas phase, we observe a submerged barrier of about $-33.95 \text{ kcal mol}^{-1}$ and reaction energy of about $-74.17 \text{ kcal mol}^{-1}$ with respect to the reactant energy for the formation of CH_3CHCN radical. The CH_3CHCN radical eventually decays to the cyanide ($\text{C}_2\text{H}_3\text{CN}$) and a hydrogen atom.

Now when this reaction (i.e. $\text{C}_2\text{H}_4 + \text{CN}$) is studied on the surface of the water ice, the calculated entrance barrier for the formation of vinyl cyanide ($\text{C}_2\text{H}_3\text{CN}$) and a hydrogen atom is submerged by $-22.59 \text{ kcal mol}^{-1}$ and has reaction energy $-39.72 \text{ kcal mol}^{-1}$ relative to the reactant energy. As such, this dissociation is efficient in both the gas and ice phase. We also studied the [1, 2] H atom shift in the radical $\text{CH}_2\text{CH}_2\text{CN}$ in the ice phase which has a submerged entrance barrier of about $-32.57 \text{ kcal mol}^{-1}$, very close to the corresponding gas-phase value. When any of these radical ($\text{CH}_2\text{CH}_2\text{CN}/\text{CH}_3\text{CHCN}$) form ice where hydrogen atoms are easily accessible, they can have a chance to be hydrogenated and form ethyl cyanide (see Fig. 3: ice reaction, step 2a/b). Hydrogenation of both these radicals is barrierless and exothermic with reaction energies

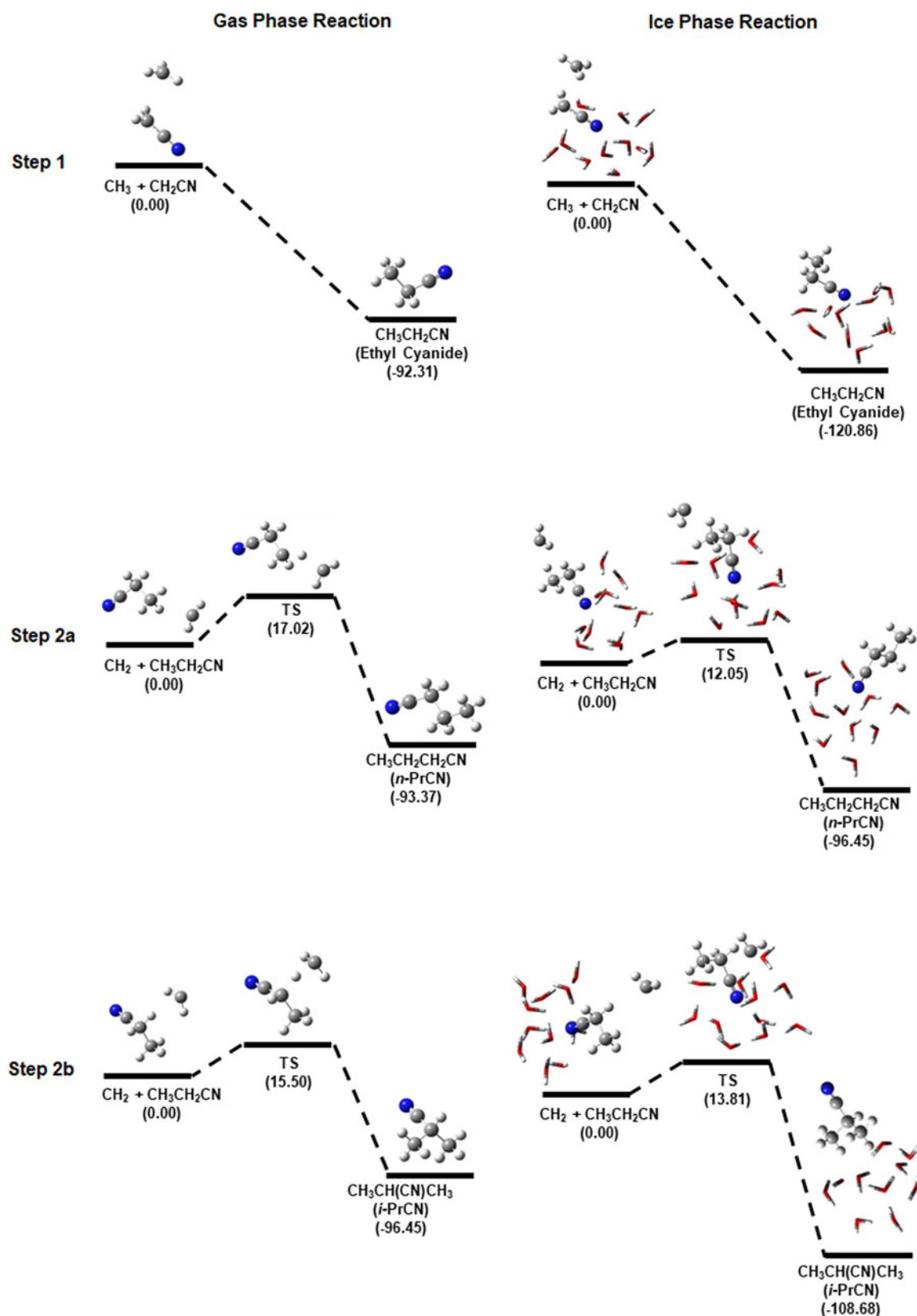


Fig. 2. Schematic potential energy surfaces for reaction scheme 1 in the gas phase and in the ice (all relative energies are given in kcal mol^{-1}).

-96.45 and $-108.68 \text{ kcal mol}^{-1}$, respectively. Therefore, the two likely outcomes of reaction 2 in ice are vinyl and ethyl cyanide.

The ethyl cyanide produced via the two above-mentioned reactions can subsequently react with the CH_2 radical present either in the gas phase or in ice to produce linear and branched isomers

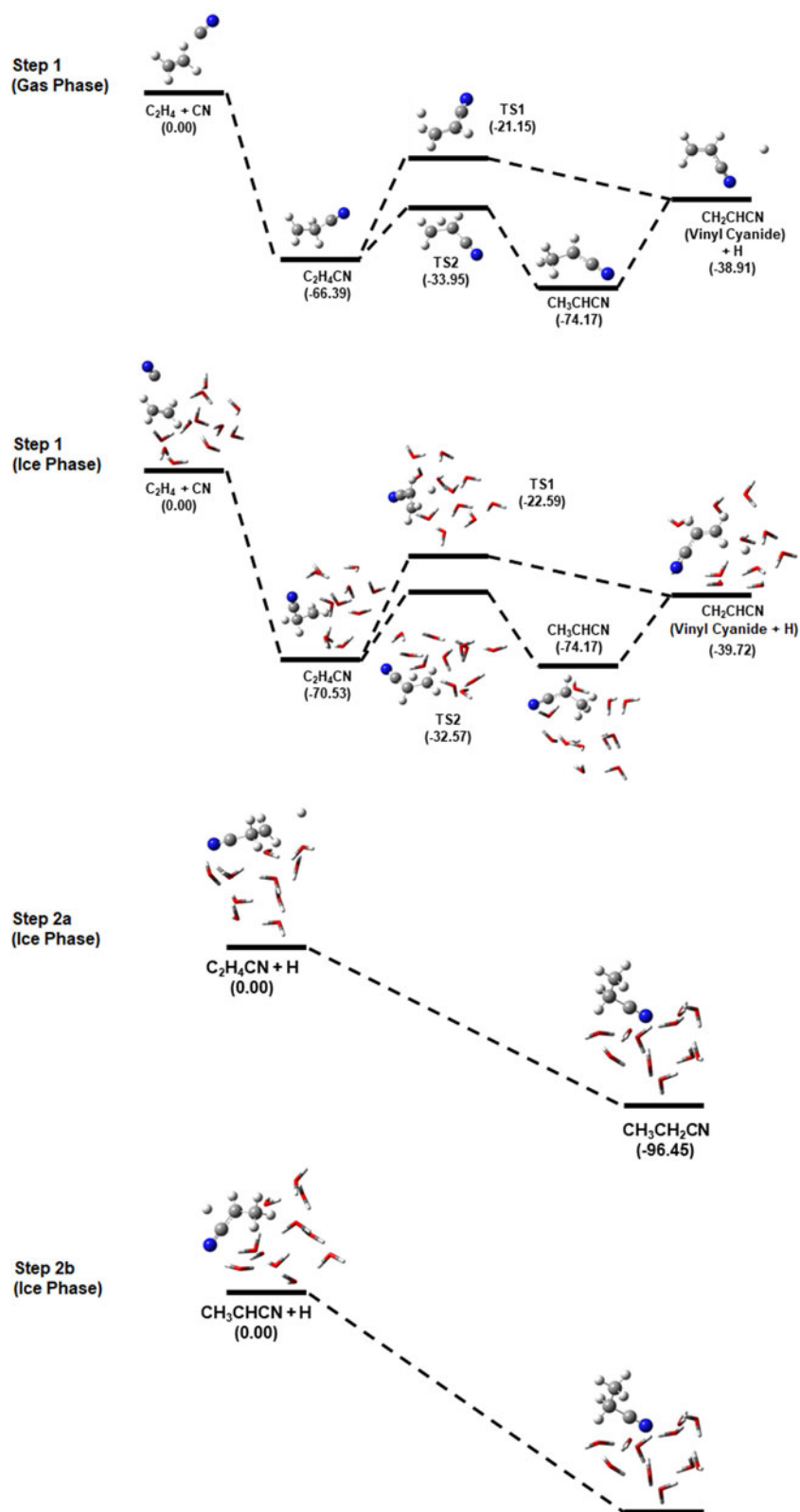


Fig. 3. Schematic potential energy surfaces for indicating all the reactants, products and transition states (TS) for reaction scheme 2 in the gas phase and in the ice (relative energies are given in kcal mol⁻¹).

of propyl cyanide. This reaction is initiated by the nucleophilic attack of CH₂ on one of the hydrogens of either terminal CH₃ group or CH₂ group (next to CN) of ethyl cyanide (see Fig. 2, steps 2a and 2b, respectively). The nucleophilic attack will break the CH bond of the CH₃ (or CH₂) group of ethyl cyanide. Free

hydrogen generated from this bond dissociation will add to CH₂ and form CH₃ radical. This radical will further add to the vacant radical centre created by CH bond dissociation and yield *n*-PrCN (or *i*-PrCN). The gas-phase entrance barriers for these radical–molecule reactions are 17.02 and 15.50 kcal mol⁻¹,

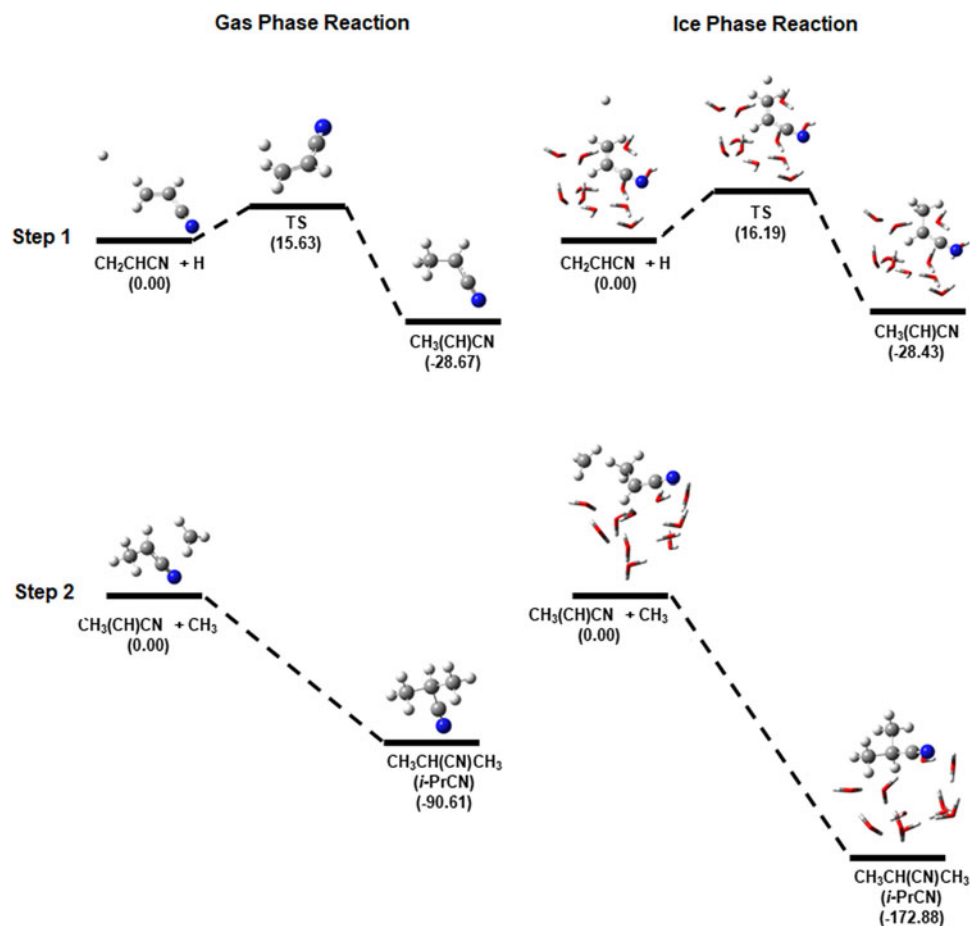


Fig. 4. Schematic potential energy surfaces for reaction scheme proposed for the formation of *i*-PrCN from vinyl cyanide in the gas phase and in the ice (all relative energies are given in kcal mol⁻¹).

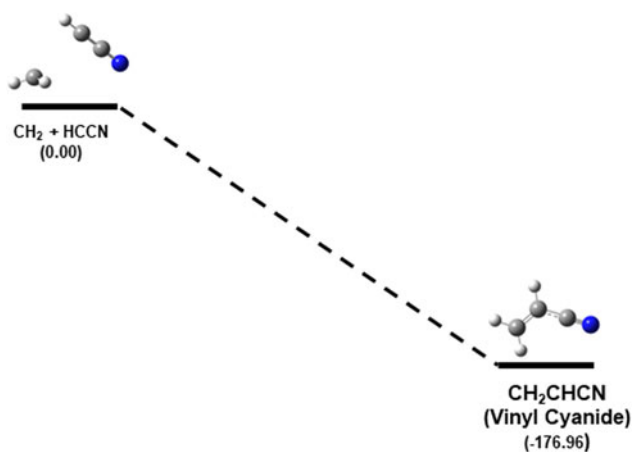


Fig. 5. Schematic potential energy surfaces for reaction scheme 3 in the gas phase. Relative energies are given in kcal mol⁻¹. Reaction 3 is not possible in the ice phase due to the reason stated in the sub-section 'Reaction systems 3 and 4'.

respectively, while the barriers reduce to 12.05 and 13.81 kcal mol⁻¹ in the ice. Here, reaction energies are $\Delta H = -93.37$ and -96.45 kcal mol⁻¹, respectively, in the gas phase and -96.45 and -108.68 kcal mol⁻¹ in the ice. Therefore, these reactions are more efficient in the ice than in the gas phase. The reason for the greater efficiency in ice can be understood by looking at the

partial charge distribution on each atom of the reactants in the gas phase and in ice. Mulliken charges on each hydrogen atom connected to the CH₃ and CH₂ groups of ethyl cyanide are 0.16 and 0.18 esu in the gas phase, which increase to 0.19 and 0.20 esu, respectively, when ethyl cyanide forms and embeds itself in ice. Thus, the nucleophilic nature of hydrogen atoms of ethyl cyanide increases when it is formed in the ice. At the same time, a large negative charge of -0.32 esu is present on the carbon of CH₂ radical. This induces a strong electrostatic interaction of both moieties and hence nucleophilic attack occurs by this CH₂ on the hydrogen atoms of CH₃ and CH₂ groups of ethyl cyanides. This explains the lower entrance barrier of reaction 2: step 2a/b in the ice compared to their gas-phase counterparts. Reaction 2 is efficient in the hot cores of molecular clouds only where temperature can reach up to ~ 200 K (Schmiedeke *et al.*, 2016). At this temperature, there is sufficient energy available to overcome the entrance barrier of about 12–15 kcal mol⁻¹ (Woon, 2002; Singh *et al.*, 2018). However, that much energy is seldom present in the deep and cooler regions of any molecular cloud. Therefore, barriers in reaction 2: step 2a/b forbids the reactions in the deep regions of the cloud SgrB2, which could be the reason why no large nitrile has been detected there to date.

On the other hand, vinyl cyanide produced in reaction 2 can form *i*-PrCN via hydrogenation followed by the barrierless and exothermic CH₃ addition as shown in Fig. 4. This route forms the most viable route for *i*-PrCN formation in ISM from small

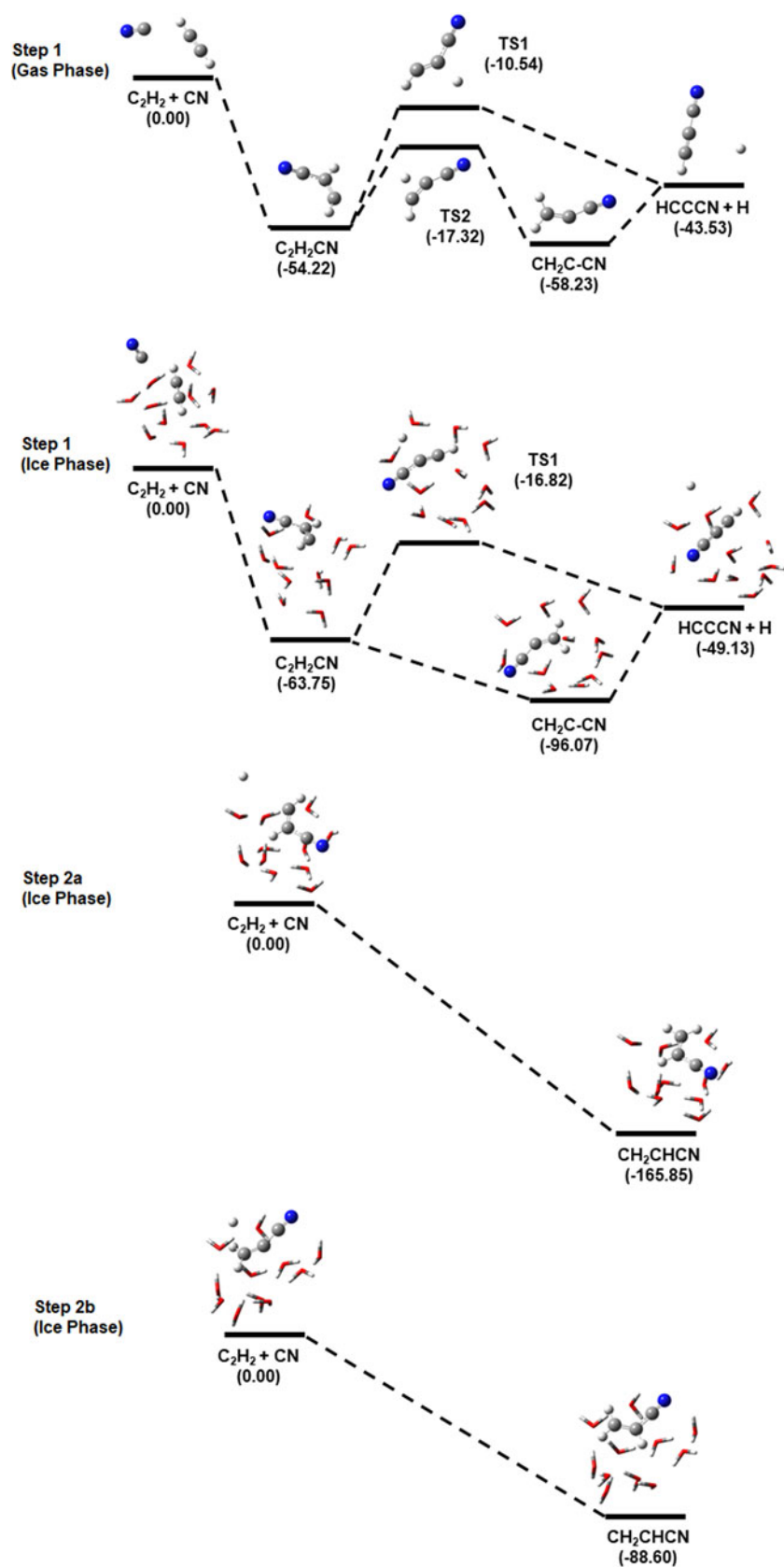


Fig. 6. Schematic potential energy surfaces for reaction scheme 4 in the gas phase and in the ice (relative energies are given in kcal mol^{-1}).

cyanide. Vinyl cyanide is present in a large quantity of nearly $3.8 \times 10^{16} \text{ cm}^{-2}$ in ISM (Müller *et al.*, 2008). It plays an important role in the formation of many other complex interstellar

molecules. The hydrogen addition has a barrier of about $15.63 \text{ kcal mol}^{-1}$ in the gas phase and $16.19 \text{ kcal mol}^{-1}$ in the ice phase. This is again a penetrable entrance barrier in hot cores

of SgrB2. Due to the importance of vinyl cyanide for the formation of the branched isomer viz. *i*-PrCN, in the following subsection; we propose two pathways for its formation in ISM.

Reaction systems 3 and 4

Reaction 3 is a barrierless radical addition between HCCN and CH₂. This addition forms vinyl cyanide (C₂H₃CN) in a single step (Fig. 5). Reaction 3 has been previously studied by Shivani *et al.* (2014) and Shivani and Tandon (2014) where they also observed the reaction to be barrierless with an enthalpy of formation of about $-52.89 \text{ kcal mol}^{-1}$ at B3LYP/6-311++G(d,p) and $-51.78 \text{ kcal mol}^{-1}$ at MP2/6-311++G(d,p) levels of theory. At the UMP2/6-311+(2d,p)//UM062X/6-311+(2d,p) level of theory, the enthalpy of formation for reaction 3 is calculated to be $-176.958 \text{ kcal mol}^{-1}$. When HCCN adsorbs onto the ice, it quickly gets hydrogenated, and therefore, it is destroyed before reacting further with CH₂. Due to this reason, reaction 3 can occur only in the gas phase.

Reaction 4 is a barrierless radical–molecule addition of CN radical to C₂H₂. The first (addition) step of this reaction produces a radical C₂H₂CN which, then reduces to the HCCCN after leaving a hydrogen atom. The entrance barrier of hydrogen abstraction is submerged with energy $-10.54 \text{ kcal mol}^{-1}$ relative to the total energy of reactants and it is exothermic with reaction energy $-43.53 \text{ kcal mol}^{-1}$ (see Fig. 6, step 1, gas phase). Thus primary products of the gas phase reaction are HC₃N and H atom. This reaction is previously studied in the gas phase by Balucani *et al.* (2000) and by Woon and Herbst (1997). Balucani *et al.* (2000) studied this reaction in the gas phase employing crossed molecular beam experiments and perform some limited quantum chemical calculations at the B3LYP/6-311+G(d,p) level of theory. They also propose a barrierless addition of CN and C₂H₂ and but the calculate reaction energy for the formation of the HCCCN and H was about $-22.49 \text{ kcal mol}^{-1}$ and the height of the activation barrier about $-15.55 \text{ kcal mol}^{-1}$. The difference between the values calculated by us and by Balucani *et al.* (2000) is due to the difference in the theory level employed for calculating the electronic structure. We have employed a comparatively recent and more accurate functional M062X along with the single-point calculations at the MP2 level of theory which provides more accurate energies. According to Balucani *et al.* (2000), a part of initial radical intermediate C₂H₂CN undergo a hydrogen transfer from central carbon to the terminal carbon and thus forms CH₂CCN which also decay to the HCCCN and H. We studied this hydrogen transfer in the gas phase which has an entrance barrier of about $40.945 \text{ kcal mol}^{-1}$ relative to the C₂H₂CN which is close to the value calculated by Balucani *et al.* (2000) viz. $42.35 \text{ kcal mol}^{-1}$. However, our calculated barrier ($40.95 \text{ kcal mol}^{-1}$ relative to the C₂H₂CN) is submerged with energy $-17.32 \text{ kcal mol}^{-1}$ with respect to the reactant energy.

According to the study by Bennett *et al.* (2006), C₂H₂ can be produced in the ice containing CH₄ and thus CN can easily add to C₂H₂ adsorbed in the ice. Therefore, reaction 4 can occur in the gas phase as well as in the ice phase. The reaction proceeds in the same way as in the gas phase, however, we observe a slight change in the energetics of the ice-phase reaction. The formation of HC₃N by hydrogen abstraction of C₂H₂CN has a submerged entrance barrier of $-16.82 \text{ kcal mol}^{-1}$ and reaction energy of about $-49.13 \text{ kcal mol}^{-1}$ in the ice phase (step 1, Fig. 6, ice phase). However, in contrast to the gas phase reaction, we could not locate any entrance barrier for the formation of CH₂CCN

in ice. The reason for the absence of the barrier in our calculations could either the absence of a transition state or the presence of a transition state with a very small entrance barrier. In both cases, the formation of CH₂CCN in ice is more favourable than in the gas phase. CH₂CCN also eventually decay to the HCCCN and H. Similar to step 2a/b of reaction 2, there is a possibility of hydrogenation of radical C₂H₂CN as well as radical CH₂CCN both of which yields vinyl cyanide (see Fig. 6, step 2a/b). Hydrogenation of both radicals in ice (C₂H₂CN and CH₂CCN) is barrierless and exothermic with the enthalpies of the formation being $-165.85 \text{ kcal mol}^{-1}$ for C₂H₂CN and $-88.60 \text{ kcal mol}^{-1}$ for CH₂CCN. As such, although the most likely outcome of reaction 4 is HC₃N; however, there is still a possibility for the formation of CH₂CHCN if the reaction occurs in the ice phase.

Astrobiological significance and conclusions

i-PrCN and its linear counterpart *n*-PrCN are very complex molecules by astrochemistry standards. The formation of molecules of such complexity is thought to be next to impossible in the ISM to date. But the detection of *i*-PrCN and *n*-PrCN tells that our understanding of the chemistry of ISM is severely limited. As such, it is important to understand the chemistry prevails in the ISM which leads to the formation of such complex molecules. In the earlier paper, Belloche *et al.*, (2009) proposed the idea of systematic growth of small cyanide towards the more complex one in both gas phase and interstellar ice for the formation of *n*-PrCN and later for the formation of both *i*-PrCN and *n*-PrCN (Belloche *et al.*, 2009). This, together with his cloud model produces the incorrect *i*-PrCN : *n*-PrCN ratio. He suggests less accurate rate constant for gas phase and ice phase reactions as well as fewer reactions in their starting reaction set were to be the primary reason for this inconsistency between calculated versus observed abundance of *i*-PrCN and *n*-PrCN. Although Garrod *et al.* (2017) were able to reproduce the observation with the same cloud model, they used an updated reaction network and rate coefficients. This proves the importance of a large and accurate set of reactions in cloud modelling. The quantum chemical approach facilitates us to accurately study the reactions in the interstellar context.

The importance of cyanide chemistry, as well as their astrobiology significance as an amino acid precursor, has already been emphasized in the Introduction. Therefore, it is important to understand their chemistry in the context of the ISM. Our study is dedicated to understanding the formation pathways of the largest cyanides in the ISM. Based on the study of previous research group, our current study utilizes the same approach used by Belloche *et al.* (2014) and Garrod *et al.* (2017) in their research to study the formation of *i*-PrCN and *n*-PrCN, i.e. evolution of small cyanides towards the more complex one. However, we have used a different set of formation pathways leading to *i*-PrCN and *n*-PrCN and used accurate quantum chemical calculations to study these pathways. As such, our study of new reaction pathways for the formation of *i*-PrCN and *n*-PrCN with quantum chemical approach provides information about some additional unexplored roots for the formation of the large and complex molecules in ISM in general and *i*-PrCN and *n*-PrCN in particular. The current study also proposed new formation roots for ethyl cyanide, vinyl cyanide as well as the formation of *i*-PrCN form it. Both ethyl and vinyl cyanide are considered precursors of many other prebiotic molecules. Our research studied four reaction schemes (Table 1) in the gas phase as well as at

the surface of interstellar water ice. The following conclusions may be drawn from this study.

1. It is observed that in the hot cores of SgrB2 (N), both *n*-PrCN and *i*-PrCN can be formed via nearly all the proposed reactions (from ethyl and vinyl cyanide). However, the formation of *n*-PrCN and *i*-PrCN from ethyl and vinyl cyanide has a sufficiently large activation barrier which is penetrable in the hot cores of molecular clouds only, thus forbids the reaction under deep cold cloud conditions.
2. Ethyl and vinyl cyanides are the most important precursors for the *n*-PrCN and *i*-PrCN, respectively. Therefore, their abundance is directly related to the abundance of *n*-PrCN and *i*-PrCN.
3. Reaction 2 can produce both precursors (ethyl and vinyl cyanides) if a reaction occurs in the ice but will only produce vinyl cyanide in the gas phase; however, reaction 4 can produce vinyl cyanide in the ice only while in the gas phase, it will not contribute towards formation of ethyl and vinyl cyanide.
4. In general, the reactions on the surface of ice are more efficient than their gas-phase counterparts. Also, since most of the ethyl and vinyl cyanide will produce in the ice phase, thus, ice reactions will contribute more significantly towards the formation of both isomers.

Acknowledgement. Financial support to K. K. Singh and P. Tandon from the Indian Space Research Organization (ISRO) under RESPOND project (grant no. ISRO/RES/2/386/15-16) and to A. Misra and Shivani from the Council of Science and Technology, Uttar Pradesh (CST, U.P.) major research project CST/8324, is gratefully acknowledged. We thank Dr Debraj Gangopadhyay, University of Lucknow and D. E. Woon, the University of Illinois Urbana-Champaign for their valuable suggestions. All the *ab initio* calculations in the current study have been performed with the help of the Central Facility for Computational Research (CFCR) at the Department of Chemistry, University of Lucknow.

References

- Abramov O and Mojzsis SJ** (2009) Microbial habitability of the Hadean earth during the late heavy bombardment. *Nature* **459**, 419–422. DOI: 10.1038/nature08015.
- Agúndez M, Fonfría JP, Cernicharo J, Pardo JR and Guélin M** (2008) Detection of circumstellar CH₂CHCN, CH₂CN, CH₃CCH, and H₂CS. *Astronomy and Astrophysics* **479**, 493–501. DOI: 10.1051/0004-6361/20078956.
- Andersen AC and Haack H** (2005) Carbonaceous chondrites: tracers of the prebiotic chemical evolution of the Solar System. *International Journal of Astrobiology* **4**, 13–17. DOI: 10.1017/S1473550405002491.
- Balucani N, Asvany O, Huang LC, Lee YT, Kaiser RI, Osamura Y and Bettinger HF** (2000) Formation of nitriles in the interstellar medium via reactions of cyano radicals, CN(X²Σ⁺), with unsaturated hydrocarbons. *Astrophysical Journal* **545**, 892–906. DOI: 10.1086/317848.
- Basiuk V** (2001) Formation of amino acid precursors in the interstellar medium. A DFT study of some gas-phase reactions starting with methylenimine. *The Journal of Physical Chemistry A* **105**, 4252–4258. DOI: 10.1021/jp004116t.
- Belloche A, Garrod RT, Müller HSP, Menten KM, Comito C and Schilke P** (2009) Increased complexity in interstellar chemistry: detection and chemical modeling of ethyl formate and *n*-propyl cyanide in Sagittarius B2 (N). *Astronomy and Astrophysics* **499**, 215–232.
- Belloche A, Garrod RT, Müller HSP and Menten KM** (2014) Detection of a branched alkyl molecule in the interstellar medium: iso-propyl cyanide. *Science* **345**, 1584–1587.
- Bennett CJ, Jamieson CS, Osamura Y and Kaiser RI** (2006) Laboratory studies on the irradiation of methane in interstellar, cometary, and Solar System ices. *Astrophysical Journal* **653**, 792–811. DOI: 10.1086/508561.
- Bera PP, Lee TJ and Schaefer HF** (2009) Are isomers of the vinyl cyanide ion missing links for interstellar pyrimidine formation? *Journal of Chemical Physics* **131**, 074303. DOI: 10.1063/1.3206298.
- Betz AL** (1981) Ethylene in IRC+10216. *Astrophysical Journal* **244**, L103–L105.
- Cecchi-Pestellini C, Scappini F, Saija R, Iati MA, Giusto A, Aiello S, Borghese F and Denti P** (2004) On the formation and survival of complex prebiotic molecules in interstellar grain aggregates. *International Journal of Astrobiology* **3**, 287–293. DOI: 10.1017/S1473550404001971.
- Cernicharo J, Guélin M and Pardo JR** (2004) Detection of the linear radical HC₄N in IRC+10216. *The Astrophysical Journal Letters* **615**, L145.
- Chakrabarti SK, Majumdar L, Das A and Chakrabarti S** (2015) Search for interstellar adenine. *Astrophysics and Space Science* **357**, 90. DOI: 10.1007/s10509-015-2239-1.
- Chiaromello JM, Talbi D, Berthier G and Ellinger Y** (2005) Theoretical study of prebiotic precursors: the peptide bond and its silicon, sulphur and phosphorous analogues. *International Journal of Astrobiology*, **4**, 125–133. doi: 10.1017/S1473550405002636.
- Daly AM, Bermúdez C, López A, Tercero B, Pearson JC, Marcelino N, Alonso JL and Cernicharo J** (2013) Laboratory characterization and astrophysical detection of vibrationally excited states of ethyl cyanide. *Astrophysical Journal* **768**, 1–39. DOI: 10.1088/0004-637X/768/1/81.
- Feuchtgruber H** (2000) Detection of interstellar CH₃. *Astrophysical Journal* **535**, L111–L114. DOI: 10.1086/312711.
- Frisch MJ, Head-Gordon M and Pople JA** (1990) A direct MP2 gradient method. *Chemical Physics Letters* **166**, 275–280.
- Frisch M, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson A and Nakatsuji H, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson A and Nakatsuji H** (2009) *Gaussian 09, revision a. 02, Gaussian*.
- Gannon KL, Glowacki DR, Blitz MA, Hughes KJ, Pilling MJ and Seakins PW** (2007) H atom yields from the reactions of CN radical with C₂H₂, C₂H₄, C₃H₆, *trans*-2-C₄H₈, and iso-C₄H₈. *Journal of Physical Chemistry A* **111**, 6679–6692.
- Garrod RT** (2008) A new modified-rate approach for gas-grain chemical simulations. *Astronomy and Astrophysics* **491**, 239–251. DOI: 10.1051/0004-6361:200810518.
- Garrod RT** (2013) A three-phase chemical model of hot cores: the formation of glycine. *Astrophysical Journal* **765**, 60.
- Garrod RT, Belloche A, Müller HSP and Menten KM** (2017) Exploring molecular complexity with ALMA (EMoCA): simulations of branched carbon-chain chemistry in Sgr B2(N). *Astronomy and Astrophysics* **601**, A48. DOI: 10.1051/0004-6361/201630254.
- Gonzalez C and Schlegel HB** (1989) An improved algorithm for reaction path following. *Journal of Chemical Physics* **90**, 2154–2161.
- Guélin M and Cernicharo J** (1991) Astronomical detection of the HCCN radical – toward a new family of carbon-chain molecules? *Astronomy and Astrophysics* **244**, L21–L24.
- Gupta VP, Tandon P, Rawat P, Singh RN and Singh A** (2011) Quantum chemical study of a new reaction pathway for the adenine formation in the interstellar space. *Astronomy and Astrophysics* **528**, A129.
- Hebrard E, Dobrijevic M, Pernot P, Carrasco N, Bergeat A, Hickson KM, Canosa A, Le Picard SD and Sims IR** (2009) How measurements of rate coefficients at low temperature increase the predictivity of photochemical models of Titan's atmosphere. *Journal of Physical Chemistry A* **113**, 11227–11237. DOI: 10.1021/jp905524e.
- Highberger JL, Savage C, Biegging JH and Ziurys LM** (2001) Heavy-metal chemistry in proto-planetary nebulae: detection of MgNC, NaCN, and AlF toward CRL 2688. *Astrophysical Journal* **562**, 790.
- Hollis JM, Jewell PR and Lovas FJ** (1995) Confirmation of interstellar methylene. *Astrophysical Journal* **438**, 259–264.
- Jefferts KB, Penzias AA and Wilson RW** (1970) Observation of the CN radical. *Astrophysical Journal* **161**, L87–L89.
- Koch DM, Toubin C, Peslherbe GH and Hynes JT** (2000) A theoretical study of the formation of the aminoacetonitrile precursor of glycine on icy grain mantles in the interstellar medium. *Journal of Physical Chemistry C* **112**, 2972–2980. DOI: 10.1021/jp076221+.

- Lattalais M, Ellinger Y and Zanda B** (2007) Theoretical study of prebiotic precursors-2: about glycine, its N-carboxyanhydride and their protonated ions. *International Journal of Astrobiology* **6**, 37–49. DOI: 10.1017/S1473550406003521.
- Lawless JG** (1973) Amino acids in the Murchison meteorite. *Geochimica et Cosmochimica Acta* **37**, 2207–2212. DOI: 10.1016/0016-7037(73)90017-3.
- Majumdar L, Das A, Chakrabarti SK and Chakrabarti S** (2013) Study of the chemical evolution and spectral signatures of some interstellar precursor molecules of adenine, glycine & alanine. *New Astronomy* **20**, 15–23.
- Margulès L, Motiyenko R, Demyk K, Tercero B, Cernicharo J, Sheng M, Weidmann M, Gripp J, Mäder H and Demaison J** (2009) Rotational spectrum of deuterated and 15 N ethyl cyanides: CH₃CHDCN and CH₂DCH₂CN and of CH₃CH₂C₁₅N. *Astronomy and Astrophysics* **493**, 565–569. DOI: 10.1051/0004-6361:200810889.
- Miller SL** (1953) A production of amino acids under possible primitive earth conditions. *Science* **117**, 528–529.
- Mita H, Nomoto S, Terasaki M, Shimoyama A and Yamamoto Y** (2005) Prebiotic formation of polyamino acids in molten urea. *International Journal of Astrobiology* **4**, 145–154. DOI: 10.1017/S1473550405002545.
- Müller HS, Belloche A, Menten KM, Comito C and Schilke P** (2008) Rotational spectroscopy of isotopic vinyl cyanide, H₂CCHCN, in the laboratory and in space. *Journal of Molecular Spectroscopy* **251**, 319–325.
- Ordu MH, Müller HSP, Walters A, Nuñez M, Lewen F, Belloche A, Menten KM and Schlemmer S** (2012) The quest for complex molecules in space: laboratory spectroscopy of *n*-butyl cyanide, *n*-C₄H₉CN, in the millimeter wave region and its astronomical search in Sagittarius B2 (N). *Astronomy and Astrophysics* **541**, A121.
- Pizzarello S and Shock E** (2010) The organic composition of carbonaceous meteorites: the evolutionary story ahead of biochemistry. *Cold Spring Harbor Perspectives in Biology* **2**, 1–20. DOI: 10.1101/cshperspect.a002105.
- Polehampton ET, Menten KM, Brünken S, Winnewisser G and Baluteau JP** (2005) Far-infrared detection of methylene. *Astronomy and Astrophysics* **431**, 203–213.
- Schmiedeke A, Schilke P, Möller T, Sánchez-Monge Á, Bergin E, Comito C, Csengeri T, Lis DC, Molinari S, Qin SL and Roloffs R** (2016) The physical and chemical structure of Sagittarius B2. *Astronomy and Astrophysics* **588**, A143. DOI: 10.1051/0004-6361/201527311.
- Schwartz AW, Joosten H and Voet AB** (1982) Prebiotic adenine synthesis via HCN oligomerization in ice. *BioSystems* **15**, 191–193. DOI: 10.1016/0303-2647(82)90003-X.
- Sephton MA** (2000) Organic compounds in carbonaceous meteorites. *Natural Product Reports* **19**, 292–311. DOI: 10.1039/b103775g.
- Shivani, Misra A and Tandon P** (2014) Reaction between CH₂ and HCCN: a theoretical approach to acrylonitrile formation in the interstellar medium. *Origins of Life and Evolution of the Biosphere: The Journal of the International Society for the Study of the Origin of Life* **44**, 143–157. DOI: 10.1007/s11084-014-9373-6.
- Shivani, Misra A and Tandon P** (2017) Formation of E-cyanomethamine in a nitrile rich environment. *Research in Astronomy and Astrophysics* **17**, 1.
- Singh KK, Shivani, Tandon P and Misra A** (2018) A quantum chemical study on the formation of ethanimine (CH₃CHNH) in the interstellar ice. *Astrophysics and Space Science* **363**, 213. DOI: 10.1007/s10509-018-3399-6.
- Snyder LE and Buhl D** (1971) Observations of radio emission from interstellar hydrogen cyanide. *Astrophysical Journal* **163**, L47. DOI: 10.1086/180664.
- Solomon P and Jefferts K** (1971) Detection of millimeter emission lines from interstellar methyl cyanide. *Astrophysical Journal* **168**, 107. DOI: 10.1086/180794.
- Wickramasinghe C** (2011) Bacterial morphologies supporting cometary panspermia: a reappraisal. *International Journal of Astrobiology* **10**, 25–30. DOI: 10.1017/S1473550410000157.
- Woon DE** (2001) *Ab initio* quantum chemical studies of reactions in astrophysical ices 3. Reactions of HOCH₂NH₂ formed in H₂CO/NH₃/H₂O ices. *Journal of Physical Chemistry A* **105**, 9478–9481. DOI: 10.1021/jp011830h.
- Woon DE** (2002) Pathways to glycine and other amino acids in ultraviolet-irradiated astrophysical ices determined via quantum chemical modeling. *Astrophysical Journal* **571**, L177–L180. DOI: 10.1086/341227.
- Woon DE and Herbst E** (1997) The rate of the reaction between CN and C₂H₂ at interstellar temperatures. *The Astrophysical Journal* **477**, 204.
- Zhao Y and Truhlar DG** (2011) Applications and validations of the Minnesota density functionals. *Chemical Physics Letters* **502**, 1–13.