Theoretical study of the reactivity between HCO and CH₂ in interstellar medium

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Research Article

Keywords: Astrochemistry, interstellar molecules, molecular processes

Posted Date: February 25th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1368759/v1>

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Abstract

Barrierless radical-radical reactions may be considered as a favorable process for the formation of interstellar organic molecules. Vinyloxy radical can be separated into two fragments namely CH_2 and HCO . Both of these have been detected in the interstellar medium. However, vinyloxy radical is not yet detected in the interstellar medium. Two reaction channels have been studied for the reaction between CH_2 and HCO in the gas phase and in the presence of one water molecule. Product of channel 1 is vinyloxy radical while in channel 2, CO and CH_3 are formed. Density functional theory (DFT) and complete active self-consistent field (CASSCF) calculations predict both the reactions to be barrierless. Therefore, non-detection of vinyloxy radical cannot be explained on the basis of potential energy surface scans obtained by DFT and CASSCF calculations. However, study of frontier orbitals provides a reasonable explanation for the validity of channel 2 and prohibition of channel 1. Further, the Mulliken charge and electrostatic surface potential map also supports that the H atom of HCO will have higher probability of interacting with C atom of CH_2 (formation of $\text{CH}_3 + \text{CO}$ via hydrogen abstraction) compared to the coupling of carbon-carbon atom (formation of vinyloxy radical via C-C bonding).

1. Introduction

Our galaxy's ten percent of the mass is an interstellar medium (ISM) and almost 99% of ISM is gaseous content (Hollenbach & Thronson, 1987; Wilson et al., 1992). The neutral hydrogen (93.38%) is the most abundant species of ISM followed by helium (6.49%) while oxygen, carbon, and nitrogen account for 0.11%. All other elements only contribute 0.02%. The radicals, molecules, and ions present in the ISM also cogitate this classification. In the interstellar medium, more than 200 molecules have been detected. The interstellar clouds comprise various gaseous Complex molecules. It has been nearly five decades that radio astronomy has been majorly used for analyzing these gaseous contents. The spectrum observed through this method is associated with the atom's fine structure spectra and polar molecule's rotational spectra. These are uniquely matched with known species.

The interstellar complex organic molecules (iCOMs) consist of at least one carbon atom (Herbst 2017; Ceccarelli et al., 2017). The organic chemical evolution of terrestrial life lies somewhere deep in the roots of astrochemistry and the iCOMs play a key role in establishing the link. The ubiquity of iCOMs in the Universe is supported by detections reported by many researchers. iCOMs are found in external galaxies (Muller et al., 2013), circumstellar envelopes of AGB stars (Cernicharo, Guelin & Kahane 2000) and most importantly in hot star-forming regions (eg. Rubin et al. 1971; Belloche et al., 2017; M Guire et al., 2018). The history of detection of iCOMs is a few decades old. However, the formation/synthesis still stands open and debatable (Herbst & van Dishoeck 2009; Caselli & Ceccarelli 2012; Woods et al. 2013; Balucani, Ceccarelli & Taquet 2015; Fedoseev et al. 2015; Enrique Romero et al. 2016; Butscher et al. 2017; Gal et al. 2017; Rivilla et al. 2017; Vasyunin et al. 2017; Rimola et al. 2018; Butscher et al. 2019; Enrique-Romero et al. 2019; Lamberts et al. 2019).

The formation of iCOMs can take up two pathways; namely formation (i) on the grain surfaces (e.g. Garrod & Herbst 2006; Woods et al. 2013; Fedoseev et al. 2015; Oberg 2016, Zamiri et al., 2019) and (ii) via reactions in the gas phase (e.g. Charnley, Tielens & Millar 1992; Balucani et al. 2015; Skouteris et al. 2018). The formation of iCOMs on the grain surface further follows three steps: (i) The saturated species – say for example CH_3OH from CO molecule (Watanabe & Kouchi 2002; Rimola et al., 2014) is formed by hydrogenation of frozen molecules/atoms in the pre-stellar phase. (ii) As the cosmic/UV rays interact with the ice mantles, the formation of free radical from frozen hydrogenated species takes place (Charnley, Tielens & Millar 1992; Garrod & Herbst 2006; Oberg et al., 2009; Ruaud et al, 2015). (iii) During the protostellar phase, the radical-radical reactions couples which further lead to the formation of iCOMs that diffuse on the ice grains (Charnley, Tielens & Millar 1992; Garrod & Herbst 2006; Oberg et al., 2009; Ruaud et al, 2015) due to a rise in temperature.

The formation of iCOMs via reactions in the gas phase (e.g. Charnley, Tielens & Millar 1992; Balucani et al. 2015; Skouteris et al. 2018) proceeds by following two steps. The first step involves the formation of iCOMs through hydrogenation. This step is the same as that of the grain model. In the second step as the grain temperature becomes higher than $\sim 100\text{K}$ (hot corinos), the hydrogenated species via thermal evaporation or photo-desorption due to UV photons present in the interstellar gets released in the gas phase (Enrique-Romero 2016). These further react with other species leading to a series of reactions and finally resulting in the formation of iCOMs (Enrique-Romero 2016). This process is barrierless. The iCOM formation processes via these two methods involve hydrogenation by adding the H atom as a first precursory stage. Depending upon the molecules and the condition, these two processes may be suggested responsible for the iCOM formations.

Vinoxy radical (CH_2CHO), an important intermediate in hydrocarbon combustion has not been detected in an interstellar medium so far. It is considered to be composed of two fragments; namely CH_2 and HCO . Barrierless radical-radical reaction may be considered as a favorable process for the formation of interstellar complex organic molecules on the icy grain surfaces. Based on this coupling process between CH_2 and HCO would lead to the formation of vinoxy radical, which is absent in the interstellar medium. However, both the species (CH_2 and HCO) have been detected in the interstellar medium. Therefore, the reaction between them has got our attention. Recently, Enrique et al. (2020) have reported their results of the reaction between CH_3 and HCO using density functional theory and CASPT2 calculations. This report was an extension of their previous work on the same system (Enrique-Romero et al. 2016). Thus, the study of the system $\text{CH}_2 + \text{HCO}$ is of equal importance. In this manuscript, we present the results of the calculations of the $\text{CH}_2 + \text{HCO}$ system. These results are obtained within the framework of DFT and CASSCF calculations.

The manuscript is organized under the following sections: Section 2: In this section we describe the computational details and discuss the spin multiplicity selection used in the reaction. Section 3: In this we present the results and discussion. Section 4: In this we provide the conclusion.

2. Requirement Of The High-level Quantum Chemical Method

In bond formation/breaking processes, the Hartree-Fock, and DFT are not very useful. The complete active space self-consistent field (CASSCF) method is one of the electronic structure theories that is employed most frequently for the study of chemical reactions. CASSCF is a specific multiconfigurational self-consistent field (MCSCF) method in which the number of determinants or CSFs used in the expansion of the CI vectors are defined by dividing the orbitals into three subspaces. In the first subspace, all orbitals are doubly occupied. The second subspace is known as the active space and within this orbital space, a full-CI expansion is considered. The electrons and orbitals of the active space contribute to the multireference character of the system. Finally, the third subspace, known as the virtual space, consists of orbitals that are unoccupied.

3. Computational Details

Ground state electronic structure of the radicals depend upon the number of unpaired electrons. Therefore, the ground state of CH_2 and HCO , considered in the present study, are in triplet and doublet state respectively. When electronic calculations are performed for a system consisting of two or more radicals, multiplicity is evaluated as the total number of unpaired electrons for the whole system, regardless of their behavior with respect to the distance between them. Using density functional theory (DFT) with two functionals namely M06-2X and revTPSS along with three basis sets 6-31G(d, P), cc-PVDZ, and TZ2P. We place both these radicals at a distance of 10 Å apart and calculate the single point energy with multiplicities 2, 4, and 6. This distance between them is decreased in steps and the procedure is repeated again and again. At the larger distances – 10 Å to 7 Å, all the states are found to be degenerate. When the reactants come closer, a redistribution of electrons occurs. And hence, when we further decrease the distance, a significant change in the total energy is observed and the states with multiplicity 2 become more and more stable. Finally, when optimized under unconstrained geometry optimization, a reaction occurs between them, leading to the formation of $\text{CO} + \text{CH}_2$ or CH_2CHO depending upon the relative orientation of the radicals. However, no reaction is observed when the same procedure is repeated with multiplicity 4 and 6.

All the CASSCF results are obtained by using a (5,5) active space which includes the three orbitals having unpaired electrons of the radicals in their respective orbitals, one π orbital of $\text{C}=\text{O}$ and one virtual orbital. CASSCF calculations were performed using different basis sets namely 6-31G(d, P), cc-PVDZ, TZ2P and TZV with spin multiplicity 2. All the results of the above said calculations are obtained by using the GAMESS package (Barca et al. 2020). The graphical package Gchemical is used to draw the molecules and Macmolplt is used to visualize the results.

Input files for all calculations are provided in SI.

4. Result And Discussion

4.1 Reactions in gas phase

We propose and explore two possible reactions for the system $\text{HCO} + \text{CH}_2$.

It is well known that the temperature in the dark cloud is about 10K in ISM. Therefore, the reactions experiencing even a small energy barrier should not be considered as a possible reaction between HCO and CH_2 in ISM. By employing the DFT, we perform a potential energy surface scan (PES) in a gaseous state using the M06-2X functional with a TZ2P basis set. These results are presented in Fig. 1. Both the reactions are found to be barrierless. Therefore, based on these results we cannot conclude that first is prohibited and second is probable. The probability of occurrence of the second reaction will support that the vinoxy radical is absent in ISM. We have also calculated the PES for other probable reactions but these reactions show a barrier.

We simulate the effect of the relative orientation of the reactants by geometry optimization, without application of any constraints. We have used density functional theory (M06-2X and revTPSS functional) with different basis sets (6-31G(d,p), cc-PVDZ, and TZ2P). The formation of the final product is found to be sensitive towards the relative orientation of the reactants. When the H atom of HCO is slightly oriented towards the C atom of CH_2 then a reaction between them leads to the formation of $\text{CO} + \text{CH}_3$. When both the reactants are parallelly oriented, they eventually form CH_2CHO (vinoxy radical).

In order to explore the formation of $\text{CO} + \text{CH}_3$ via $\text{HCO} + \text{CH}_2$ reaction with doublet spin multiplicity, in an interstellar environment, we have calculated the potential energy surface for the reaction in gaseous form. Figure 2. represents the potential energy surface scan curves (PESs) at CASSCF level with different basis sets for the reaction between HCO and CH_2 to form $\text{CO} + \text{CH}_3$. We start our calculations by generating the starting orbitals for CASSCF calculations. For this, we performed ROHF calculations with the same basis sets as we have to use in CASSCF calculations. We have used multiplicity equal to 4 in ROHF calculations. Therefore, this generates the orbitals with unpaired electrons in the corresponding orbitals of HCO and CH_2 . These orbitals are then used in the CASSCF calculations as starting orbitals. Thus, the starting orbitals in CASSCF calculations consist of two HOMO of CH_2 , having two unpaired electrons, one SOMO of HCO having one unpaired electron, one π orbital of $\text{C}=\text{O}$ and one virtual unoccupied orbital of the composite system. This makes our active space consisting of 5 electrons in 5 orbitals. Although the choice of π orbital of $\text{C}=\text{O}$ in active space is not necessary, we have taken this orbital to check its effects. This orbital would have played a vital role in the formation of vinoxy radical from HCO and CH_2 . We have also performed the scan by replacing the π orbital of $\text{C}=\text{O}$ with the sigma orbital of C-H of HCO radical and found no significant difference in the results. To obtain the potential energy surface scan, we fix the x coordinate of the carbon atom of CH_2 and allow the hydrogen atom of the HCO radical to move towards the carbon atom of the CH_2 . We scan a path of a distance of approximately 5Å. The coordinates of the

estimated transition state (TS) are obtained with the help of these curves and further optimized to get an optimized TS.

We also performed unconstrained geometry optimization at the CASSCF level. When the H atom of HCO is slightly oriented towards the C atom of CH₂ then a reaction between them leads to the formation of CO + CH₃. Based on these descriptions and results, we can conclude that the reaction between HCO and CH₂ to form CO + CH₃ is barrierless. Figure 4. shows the PESs for the reaction between HCO and CH₂ to form CO + CH₃ at CASSCF level with basis sets 6-31G(d,P) and cc-pVDZ. Reactants and products have fully optimized geometry. The energy reference 0.0 is set for the reactants HCO + CH₂. Product is lower in energy than the reactants by 438.94 kJ mol⁻¹ and 439.83 kJ mol⁻¹ with 6-31G(d,p) and cc-pVDZ basis sets respectively.

The PESs for HCO + CH₂ to form a vinoxy radical is shown in Fig. 5. Results are obtained with CASSCF/6-31G(d,p) and CASSCF/cc-pVDZ level of theory respectively. We have used the same active space as it was used for HCO + CH₂ to form CO + CH₃. The only difference is in the starting configuration, where we place both the reactants along the x-axis and carbon atoms face each other. The HCO radical is allowed to move towards the CH₂. The path of ~ 4.4 Å was divided into 53 segments and energy is calculated on each step. We don't observe any TS for this reaction. Therefore, we conclude that the reaction between the HCO radical and CH₂ to form a vinoxy radical is barrierless.

4.2 Reactions in the presence of one water molecule

To ensure the feasibility of the reactions occurring on the interstellar icy grain surfaces we have simulated unrestricted geometry optimization in presence of one water molecule. It is worth mentioning that the final product entirely depends upon the orientation of the radicals. We observe that the water molecule forms a complex with the radical via hydrogen bonding if the distance of the water molecule from that particular radical is slightly less than the distance from the other radicals. When the distance between the radicals is less than their distance from the water molecule and the H atom of HCO is slightly oriented towards the C atom of the CH₂ then they form CO + CH₃ by the transfer of the H atom. These results also predict a barrierless reaction between HCO and CH₂.

In the presence of one water molecule, the PESs for the formation of CO + CH₃ and vinoxy radical, from the reaction between CH₂ and HCO are shown in Fig. 6 (a) and 6 (b) respectively. All the results were obtained from CASSCF calculations using four basis sets (TZ2P, TZV, 6-31G(d,p), cc-pVDZ). In both the reaction channels, the product is stable in comparison to the reactants with an energy difference ranging from ~ 420 to 520 KJmol⁻¹. In these reactions, huge energy is released. Therefore, the presence of a third body (like water ice surface) dissipating the nascent energy is utmost required for the feasibility of these reactions. Formation of CO + CH₄ from the reaction between HCO and CH₃ via direct hydrogen abstraction had a negligibly small barrier (Enrique et al. 2020). Present study indicates that the formation of CO + CH₃

and vinoxy radical from the reaction between HCO and CH₂ in the presence of water molecule seems to be spontaneous in nature.

Non-existence of vinoxy radical in interstellar medium can only be considered if reaction (2) will occur and reaction (1) is prohibited but there seems to be no reason for the same. Both the reactions are predicted to be barrierless. Therefore, the reaction rate will be proportional to the collision frequency. The orbital analysis may help us to understand the difference in reactivities of these two reactions. Figure 7 shows the frontier orbitals plots for reactants obtained by DFT with revTPSS functional and TZ2P basis set. Since the HOMO (highest occupied molecular orbital) – LUMO (lowest unoccupied molecular orbital) separation of HCO is smaller than that of CH₂, HCO is a reactive species to be attacked by other radical species. The contribution of the orbital coefficients of the H atom to the HOMO of CH₂ is negligible. While in the case of HCO, the H atom has a significant contribution of orbital coefficients to its SOMO (singly occupied molecular orbital). Therefore, SOMO of HCO has significant electron density over hydrogen atom. Consequently, SOMO-HOMO interaction between the HCO and CH₂ radicals is favorable to form a C-H bond. Therefore, considering the fact that the C-H bond is stronger than C-C bond, reaction (2) should be considered more probable than reaction (1).

Further, it is worth mentioning that according to Mulliken charge population analysis (DFT with different basis sets) the carbon atom in CH₂ is always negatively charged. In the case of HCO the hydrogen atom is more positively charged in comparison to carbon atom. Figure 8 represents the electrostatic surface potential (ESP) map of the reactants which illustrates the trend of the interaction between them. It is observed that (i) in case of CH₂: the carbon atom has negative potential which shows that it is capable of interacting with positive potential regions of other reactants, (ii) in case of HCO: there is more positive potential around the H atom compared to carbon atom. Therefore, the H atom of HCO will have a higher probability of interacting with the C atom of CH₂ resulting in the formation of CH₃ + CO as products.

5. Astrophysical Implications

Formyl radical is an important intermediate in many chemical and biochemical reactions. It is a main building block of many iCOMs such as methanol, glycolaldehyde and the sugar-alcohol ethylene glycol. In interstellar medium its abundance on the dust grain is quite enough to form iCOMs. Origin of life is directly linked with the formation of different iCOMs. Therefore, to study the reactivity of HCO with other molecules/radicals/ions is of utmost importance. This study highlights that in the formation of different iCOMs involving HCO, hydrogen abstraction is a dominant process in comparison to forming a C-C or C-O bond.

5. Conclusion

More than 200 molecules have been detected in the ISM. However, the formation process of many iCOMs is unknown. Radical-radical reactions may be considered as a possible process. We present here a study

of $\text{HCO} + \text{CH}_2$ reaction. Two reaction pathways have been proposed: channel 1 which leads to the formation of vinoxy radical and channel 2 which leads to the formation of $\text{CO} + \text{CH}_3$. We can summarize the main finding of our study as.

1. Both the channels are found to be barrierless in the gas phase and in the presence of one water molecule. However, coupling will never happen in the gas phase without the presence of a third body dissipating the energy released by reaction.
2. Type of product formed is entirely dependent on the relative orientation of the reactants.
3. With water molecule both the species are found to be forming a complex via hydrogen bonding which depends upon their relative distance from the water molecule.
4. In comparison to PESs, the orbital analysis is rather more helpful to draw conclusions about the probability of one channel over the other. Based on these findings direct hydrogen transfer may be considered more feasible rather than coupling between the chemical species HCO and CH_2 .
5. The Mulliken charge and ESP map analysis indicates that the H atom of HCO will have higher probability of interacting with C atom of CH_2 (formation of $\text{CH}_3 + \text{CO}$ via hydrogen abstraction) compared to the coupling of carbon-carbon atom (formation of vinoxy radical via C-C bonding).

Declarations

ACKNOWLEDGEMENTS

Authors are highly thankful to Dr. Eric V. Patterson, Department of Chemistry, Stony Brook University for detailed discussions on calculations (input and output files). Authors are also thankful to all GAMESS users who had replied to many queries related to present problem, posted on the GAMESS Google group.

Funding

No funding were received from anywhere.

Conflicts of interest/Competing interests

There are no conflicts of interest to declare.

Availability of data and material

Input files for all calculations are provided in SI. All the results presented in the manuscript can be reproduced using these files.

Code availability

The data underlying this article can be reproduced using the input files provided in the online supplementary material. All the used softwares are “open source code” which are freely available on their respective sites.

Authors' contributions

All the authors have contributed equally.

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Figures

Figure 1

Potential energy surface scan curves (PESs) at DFT level with TZ2P basis sets for the reactions between HCO and CH₂. Energetics are plotted against distances (Red curve between C₁-H₁; Black curve between C₁-C₂). Total energy units are in hartree and distances are in angstrom.

Figure 2

Potential energy surface scan curves (PESs) at CASSCF level with different basis sets for the reaction between HCO and CH₂ to form CO + CH₃. Energetics are plotted against distance between C₁-H₁. Total energy units are in hartree and distances are in angstrom.

Figure 3

Geometry of the transition state of the $\text{HCO} + \text{CH}_2$ reaction. Distances are in angstrom and angles are in degrees.

Figure 4

PESs at CASSCF level with different basis sets for the reaction between HCO and CH₂ to form CO + CH₃. The energy reference 0.0 is set for the reactants HCO + CH₂. The presented molecular structure corresponds to the optimized geometry at CASSCF/cc-pVDZ level of theory. Total energy units are in KJ/mol and distances are in angstrom

Figure 5

Potential energy surface scan curves (PESs) at CASSCF level with different basis sets for the reaction between HCO and CH₂ to form vinyloxy radical. Energetics are plotted against distance between C₁-C₂. Total energy units are in hartree and distances are in angstrom.

Figure 6

(a). PESs at CASSCF level with different basis set for the reaction between HCO and CH₂ to form CO + CH₃ in the presence of one water molecule. The energy reference 0.0 is set for the reactants HCO + CH₂. The total energy units are in KJ/mol.

(b). PESs at CASSCF level with different basis set for the reaction between HCO and CH₂ to form vinoxy radical in the presence of one water molecule. The energy reference 0.0 is set for the reactants HCO + CH₂. The total energy units are in KJ/mol.

Figure 7

Frontier orbitals diagram

Figure 8

ESP map of the optimized geometry of the reactants (a) CH₂ and (b) HCO obtained from revTPSS/TZ2P [ESP colour scheme: Red (negative) – Green (Positive)]

Supplementary Files

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