



The Possibility of Forming Propargyl Alcohol in the Interstellar Medium



Prasanta Gorai^a, Ankan Das^{a,*}, Liton Majumdar^{a,b}, Sandip Kumar Chakrabarti^{a,c},
Bhalamurugan Sivaraman^d, Eric Herbst^e

^a Indian Centre for Space Physics, Chalantika 43, Garia Station Rd., Kolkata, 700084, India

^b Laboratoire d'astrophysique de Bordeaux, Univ. Bordeaux, CNRS, B18N, alle Geoffroy Saint-Hilaire, 33615 Pessac, France

^c S. N. Bose National Centre for Basic Sciences, Salt Lake, Kolkata, 700098, India

^d Atomic Molecular and Optical Physics Division, Physical Research Laboratory, Ahmedabad, 380009, India

^e Departments of Chemistry and Astronomy, University of Virginia, Charlottesville, VA 22904, USA

ARTICLE INFO

Article history:

Received 21 August 2016

Revised 18 January 2017

Accepted 23 January 2017

Available online 24 January 2017

Keywords:

Astrochemistry

ISM: molecules

ISM: abundances

ISM: evolution

Method: numerical

ABSTRACT

Propargyl alcohol ($\text{HC}_2\text{CH}_2\text{OH}$, PA) has yet to be observed in the interstellar medium (ISM) although one of its stable isomers, propenal (CH_2CHCHO), has already been detected in Sagittarius B2(N) with the 100-meter Green Bank Telescope in the frequency range 18 – 26 GHz. In this paper, we investigate the formation of propargyl alcohol along with one of its deuterated isotopomers, $\text{HC}_2\text{CH}_2\text{OD}$ (OD-PA), in a dense molecular cloud. Various pathways for the formation of PA in the gas and on ice mantles surrounding dust particles are discussed. We use a large gas-grain chemical network to study the chemical evolution of PA and its deuterated isotopomer. Our results suggest that gaseous $\text{HC}_2\text{CH}_2\text{OH}$ can most likely be detected in hot cores or in collections of hot cores such as the star-forming region Sgr B2(N). A simple LTE (Local thermodynamic equilibrium) radiative transfer model is employed to check the possibility of detecting PA and OD-PA in the millimeter-wave regime. In addition, we have carried out quantum chemical calculations to compute the vibrational transition frequencies and intensities of these species in the infrared for perhaps future use in studies with the James Webb Space Telescope (JWST).

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The discovery of large numbers of interstellar and circumstellar species regularly refreshes our understanding of the physical conditions of the sources of astrochemical interest (Herbst, 2006). Astronomical observations along with laboratory investigations of various meteoritic samples have discovered the presence of numerous organic molecules of biological interest (Cronin and Chang, 1993). It is also believed that the production of such molecules in star- and planet-forming regions of interstellar clouds, which tend to be partially saturated species containing the elements nitrogen and/or oxygen in addition to carbon and hydrogen, should be connected in some manner with the production of terrestrial bio-molecules. Other types of organic molecules are also present in the ISM. There is strong evidence for species astronomers refer to as “carbon chains” in cold and dense interstellar clouds. These carbon chains are unsaturated and linear species, which can be simple hydrocarbons or species with other heavy atoms such

as cyanopolynes, which contain a terminal cyano (CN) group. Various infrared (UIR) emission bands in the 3 – 15 μm range have been observed in different astrophysical sources (Allamandola et al., 1985; Tielens and Allamandola, 1987). Laboratory investigations along with theoretical calculations led to the hypothesis that the carriers of these bands are aromatic in nature, consisting most probably of free molecular polycyclic aromatic hydrocarbons (PAHs), possibly with other heavy atoms such as nitrogen (Noble et al., 2015; Salama and Ehrenfreund, 2014). Other suggestions include surface functional groups on small grains, quenched carbonaceous composites, amorphous carbon, hydrogenated amorphous carbon and condensed phase PAHs (Brenner and Barker, 1992; Jäger et al., 2009). Recently, two fullerenes, C_{60} and C_{70} , have been discovered in infrared emission in post-stellar objects (Cami et al., 2010) while the cation C_{60}^+ has been confirmed in near-infrared absorption in a diffuse cloud (Walker et al., 2015).

In order to understand the synthesis of PAHs, either in interstellar or circumstellar regions, it is essential to understand the formation of the six-member aromatic species, benzene (C_6H_6). So far there are only two experimentally studied pathways that might result in the synthesis of interstellar or circumstellar ben-

* Correspondence author.

E-mail address: ankan.das@gmail.com (A. Das).

zene. The first is the addition of three acetylene (C_2H_2) molecules (Zhou et al., 2010) and the second is the recombination of two propargyl (C_3H_3) radicals (Wilson et al., 2003). The formation of these radicals could occur in a number of ways. (Sharath et al., 2014) carried out an experiment to study the thermal decomposition of PA, and found the products to include OH and C_3H_3 , suggesting that PA could be a precursor to benzene formation. In addition, (Sivaraman et al., 2015) found that benzene is the major product from PA irradiation, and suggested that the dissociation of PA plays a key role in the synthesis of benzene in interstellar icy mantles.

Since PA might play a crucial role in the formation of PAH molecules, it is of interest to explore various aspects of its interstellar chemistry and spectroscopy in detail. Although PA has not been detected unambiguously in the ISM, propenal (CH_2CHCHO), one of its isomers, has been detected (Hollis et al., 2004) towards the star-forming region Sgr B2(N). (Requena-Torres et al., 2008) estimated the abundance of CH_2CHCHO to be around $0.3 - 2.3 \times 10^{-9}$ with respect to the H_2 molecule in the galactic center. Moreover, PA has a well-known rotational spectrum. Depending upon the internal motion of the OH group, PA could possess two stable conformers, named *gauche* and *trans*. However, microwave studies of PA show that the molecule exists only as the *gauche* isomer, in which the hydroxyl H atom lies $\sim 60^\circ$ out of the $H-C \equiv C-C-O$ plane (Hirota, 1968). (Pearson and Drouin, 2005) summarized other rotational studies of PA, extended the experimental work of Hirota (1968) through 600 GHz and obtained rotational and distortional constants for the *gauche* form of PA and its -OD singly deuterated isotopomer. According to their studies, the *gauche* state is split by inversion into two states, separated by 652.4 GHz for normal PA and 213.5 GHz for the -OD isotopomer. Other spectroscopic work on PA and related species has also been undertaken. (Nyquist, 1971) recorded and assigned Infrared and Raman spectra for PA, and its deuterated isotopomers, while (Devendra and Arunan (2013) carried out experiments to determine the structure of the Ar..PA complex and its two deuterated isotopologues. They found PA to have a *gauche* structure, with Ar located in between the -OH and $-C \equiv C-H$ groups. In another study, (Devendra and Arunan, 2014) carried out experiments for the pure rotational spectra of the PA dimer and its three deuterium isotopologues.

In this paper, we report the use of our interstellar chemical model to explore various pathways for the formation and destruction of PA (*gauche* form), and to estimate the possibility of detecting this molecule in a dense molecular cloud. Since there are some existing laboratory results for the spectrum of the -OD deuterated form of PA and since some observational evidence for deuterium fractionation of large complex species exists (see for instance $DCOOCH_3/HCOOCH_3$, (Demyk et al., 2010)), we also consider the -OD isotopomer of PA. Various vibrational transitions of PA are computed and compared with the existing experimental results.

The remainder of this paper is organized as follows. In Section 2, we discuss various reaction pathways and their rate coefficients for the formation and destruction of PA and OD-PA. In Section 3.1, modeling details are presented while in Section 3.2 we discuss modeling results. LTE radiative transfer results are presented in Section 4.1, while computed vibrational spectra for PA and OD-PA are discussed in Section 4.2. Finally, in Section 5, we draw our conclusions.

2. Chemical network

2.1. Formation pathways

In Table 1, all formation and destruction pathways of PA utilized are presented with rate coefficients, if applicable, in both the gas and dust phases. The rate coefficients are shown for two tem-

peratures ($T = 10$ K and 100 K) to represent the temperature dependency (if any). The determination of the rate coefficients actually used is discussed in the next few subsections. Most rate coefficients for the case of deuterated PA are not very different, and are not tabulated. Reaction numbers R1-R6 of Table 1 represent various possible pathways for the formation of PA (HC_2CH_2OH). Reaction numbers R1-R5 are found to be exothermic in both phases and are included in our network. The reaction exothermicities or endothermicities for all these reactions have been calculated by using the Gaussian 09 (Frisch et al., 2013) program with a B3LYP functional (Becke, 1988; Lee et al., 1988) and basis set 6-311g++(d,p). Note that reaction exothermicities or endothermicities do not differ significantly between the gaseous and ice mantle phases. We calculated the endothermicity/exothermicity (ΔH) of a reaction by taking the difference between the total optimized enthalpy including zero point corrections of the products and reactants. If ΔH is positive, we label the reaction endothermic and if ΔH is negative, we label the reaction exothermic. Another formation reaction, R6, is considered only in the gas phase. The individual formation reactions are discussed in the following paragraphs.

Reaction R1 ($O + C_3H_3$) in the gas phase was studied by Kwon et al. (2006), who carried out an experiment as well as ab initio statistical calculations. They found that the reaction is barrierless and can produce propynal (HC_2CHO) and H. The conversion of propynal into PA then can occur via two association reactions (R3, R4) with atomic hydrogen. In the gas phase, the process occurs via radiative association, in which emission of a photon stabilizes the intermediate reaction complex. (Lee et al., 2006) predicted that the barrier-less addition of $O(^3P)$ to propargyl radical (C_3H_3) on the lowest doublet potential energy surface could produce several energy-rich intermediates, which undergo subsequent isomerization and decomposition steps to generate various exothermic reaction products. Their statistical calculation also suggests that the primary reaction channel leads to the formation of propynal. Reaction R2, in which the radical CCH and formaldehyde produce propynal + H, was studied by Dong et al. (2005) and by Petrie (1995). (Dong et al., 2005) calculated a very small barrier of 2.1 kcal/mol at the highest level of theory, while (Petrie, 1995) assumed the channel to be barrier-less based on similar reactions. The propynal product can then also be hydrogenated to PA via R3 and R4.

As an alternative to two successive H-atom association reactions involving atomic hydrogen, we checked the reaction of H_2 with propynal (HC_2CHO) to form PA but found it to be highly endothermic. We tried a few other pathways for the formation of PA via single step reactions, sometimes involving a radical. In this effort, we considered the reaction between C_2H_4 and CO, the reaction between propynal and H_2O , and the reaction between the propargyl radical and OH (reaction number R5). The reactions between C_2H_4 and CO and between propynal and H_2O are found to be highly endothermic in nature whereas reaction R5 is highly exothermic and is likely barrier-less, since the reactants are both radicals. Since both reactants in R5 (C_3H_3 and OH) are reasonably abundant in the ISM, we think that this reaction can contribute towards the formation of interstellar PA, although, in the gas phase, it must proceed via a radiative route, so that it must be looked at closely. On ice mantles, however, radical-radical association reactions are normally quite efficient. As can be seen in Table 1, R4 and R5 are the sole radical-radical reactions leading directly to the formation of PA, both in the gas and on the ice. A gas phase dissociative recombination (DR) reaction (R6), in which protonated PA and an electron recombine to form smaller neutral products, is also included. This reaction may contribute significantly to the gas phase formation of PA unless the two-body product channel shown is unimportant if ion-neutral processes can produce protonated PA efficiently. Similar pathways to all those considered for the syn-

Download English Version:

<https://daneshyari.com/en/article/5431262>

Download Persian Version:

<https://daneshyari.com/article/5431262>

[Daneshyari.com](https://daneshyari.com)