

# The Possibility of Forming Propargyl Alcohol in the Interstellar Medium

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## A B S T R A C T

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 ( $\text{CH}_2\text{CHCHO}$ ), 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).

### Keywords:

Astrochemistry

ISM: molecules

ISM: abundances

ISM: evolution

Method: numerical

## 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  $\mu\text{m}$  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,  $\text{C}_{60}$  and  $\text{C}_{70}$ , have been discovered in infrared emission in post-stellar objects (Cami et al., 2010) while the cation  $\text{C}_{60}^+$  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 ( $\text{C}_6\text{H}_6$ ). So far there are only two experimentally studied pathways that might result in the synthesis of interstellar or circumstellar ben-

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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  $D_2COCH_3/H_2COCH_3$ , (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 ( $\Delta H$ ) of a reaction by taking the difference between the total optimized enthalpy including zero point corrections of the products and reactants. If  $\Delta H$  is positive, we label the reaction endothermic and if  $\Delta H$  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-

**Table 1**  
Formation and destruction pathways of PA and its related species.

Reaction number (type)	Reaction	$\alpha$	$\beta$	$\gamma$	Gas phase rate coefficient at $T = 10$ K (100 K)	Ice phase rate coefficient at $T = 10$ K (100K)
<b>Formation pathways</b>						
R1 (NR)	$O(^3P) + C_3H_3 \rightarrow HC_2CHO + H(-252.30^a, -231.11^b)$	$2.3 \times 10^{-10}$	0.0	0.0	$2.3 \times 10^{-10}(2.3 \times 10^{-10})^c$	$2.83 \times 10^{-7}(2.51 \times 10^4)^d$
R2 (NR)	$C_2H + H_2CO \rightarrow HC_2CHO + H(-109.17^a, -106.307^b)$	$1.00 \times 10^{-10}$	0.0	0.0	$1.00 \times 10^{-10}(1.00 \times 10^{-10})^c$	$2.84 \times 10^{-17}(3.03 \times 10^3)^d$
R3 (NR)	$HC_2CHO + H \rightarrow HC_2CH_2O(-86.69^a, -86.23^b)$	–	–	–	$0(1.96 \times 10^{-15})^c$	$6.24 \times 10^{-9}(8.94 \times 10^{-3})^d$
R4 (RR)	$HC_2CH_2O + H \rightarrow HC_2CH_2OH(-420.35^a, -421.67^b)$	$1.00 \times 10^{-10}$	0.0	0.0	$1.00 \times 10^{-10}(1.00 \times 10^{-10})^c$	$1.77 \times 10^{-1}(2.54 \times 10^5)^d$
R5 (RR)	$C_3H_3 + OH \rightarrow HC_2CH_2OH(-301.35^a, -298.97^b)$	$1.00 \times 10^{-10}$	0.0	0.0	$1.00 \times 10^{-10}(1.00 \times 10^{-10})^c$	$7.86 \times 10^{-29}(2.19 \times 10^2)^d$
R6 (DR)	$HC_2CH_2OH_2^+ + e^- \rightarrow HC_2CH_2OH + H$	$2.67 \times 10^{-8}$	-0.59	0.0	$2.00 \times 10^{-7}(5.16 \times 10^{-8})^c$	–
<b>Destruction pathways</b>						
R7 (NR)	$HC_2CH_2OH + OH \rightarrow HOC_2HHCHOH$	$9.20 \times 10^{-12}$	0.0	0.0	$9.20 \times 10^{-12}(9.20 \times 10^{-12})^c$	$3.58 \times 10^{-38}(3.64 \times 10^1)^d$
R8 (NR)	$HC_2CH_2OH + OD \rightarrow HOC_2HHCHOD$	$9.20 \times 10^{-12}$	0.0	0.0	$9.20 \times 10^{-12}(9.20 \times 10^{-12})^c$	$3.48 \times 10^{-38}(3.54 \times 10^1)^d$
R9 (IN)	$HC_2CH_2OH + C^+ \rightarrow HC_2CH_2O^+ + CH$	$2.03 \times 10^{-09}$	-0.5	0.0	$1.22 \times 10^{-08}(4.63 \times 10^{-09})^c$	–
R10 (IN)	$HC_2CH_2OH + C^+ \rightarrow C_3H_3^+ + HCO$	$2.03 \times 10^{-09}$	-0.5	0.0	$1.22 \times 10^{-08}(4.61 \times 10^{-09})^c$	–
R11 (IN)	$HC_2CH_2OH + H_3O^+ \rightarrow HC_2CH_2OH_2^+ + H_2O$	$1.70 \times 10^{-09}$	-0.5	0.0	$1.02 \times 10^{-08}(3.85 \times 10^{-09})^c$	–
R12 (IN)	$HC_2CH_2OH + HCO^+ \rightarrow HC_2CH_2OH_2^+ + CO$	$1.46 \times 10^{-09}$	-0.5	0.0	$8.79 \times 10^{-09}(3.32 \times 10^{-09})^c$	–
R13 (IN)	$HC_2CH_2OH + H_3^+ \rightarrow C_3H_3^+ + H_2O + H_2$	$3.78 \times 10^{-09}$	-0.5	0.0	$2.27 \times 10^{-08}(8.56 \times 10^{-09})^c$	–
R14 (IN)	$HC_2CH_2OH + H_3^+ \rightarrow HC_2CH_2OH_2^+ + H_2$	$3.78 \times 10^{-09}$	-0.5	0.0	$2.27 \times 10^{-08}(8.56 \times 10^{-09})^c$	–
R15 (IN)	$HC_2CH_2OH + He^+ \rightarrow C_3H_3^+ + He + OH$	$3.31 \times 10^{-09}$	-0.5	0.0	$1.99 \times 10^{-08}(7.51 \times 10^{-09})^c$	–
R16 (IN)	$HC_2CH_2OH + He^+ \rightarrow C_3H_3 + He + OH^+$	$3.31 \times 10^{-09}$	-0.5	0.0	$1.99 \times 10^{-08}(7.51 \times 10^{-09})^c$	–
R17 (IN)	$HC_2CH_2OH + CH_3^+ \rightarrow HC_2CH_2O^+ + CH_4$	$1.86 \times 10^{-09}$	-0.5	0.0	$1.12 \times 10^{-08}(4.21 \times 10^{-09})^c$	–
R18 (IN)	$HC_2CH_2OH + H^+ \rightarrow C_3H_3^+ + H_2O$	$6.43 \times 10^{-09}$	-0.5	0.0	$3.86 \times 10^{-08}(1.46 \times 10^{-08})^c$	–
R19 (IN)	$HC_2CH_2OH + H^+ \rightarrow HC_2CH_2O^+ + H_2$	$6.43 \times 10^{-09}$	-0.5	0.0	$3.86 \times 10^{-08}(1.46 \times 10^{-08})^c$	–
R20 (IN)	$HC_2CH_2OH + H^+ \rightarrow HC_3O^+ + H_2 + H_2$	$6.43 \times 10^{-09}$	-0.5	0.0	$3.86 \times 10^{-08}(1.46 \times 10^{-08})^c$	–
R21 (IN)	$HC_2CH_2OH + H^+ \rightarrow HC_2CH_2OH^+ + H$	$6.43 \times 10^{-09}$	-0.5	0.0	$3.86 \times 10^{-08}(1.46 \times 10^{-08})^c$	–
R22 (IN)	$HC_2CH_2OH + H_2D^+ \rightarrow HC_2CH_2OHD^+ + H_2$	$3.21 \times 10^{-09}$	-0.5	0.0	$1.93 \times 10^{-08}(7.29 \times 10^{-09})^c$	–
R23 (IN)	$HC_2CHO + C^+ \rightarrow HC_3O^+ + CH$	$3.80 \times 10^{-09}$	-0.5	0.0	$2.19 \times 10^{-08}(7.64 \times 10^{-09})^c$	–
R24 (IN)	$HC_2CHO + C^+ \rightarrow C_3H^+ + HCO$	$3.80 \times 10^{-09}$	-0.5	0.0	$2.19 \times 10^{-08}(7.64 \times 10^{-09})^c$	–
R25 (IN)	$HC_2CHO + H_3O^+ \rightarrow HC_2CH_2O^+ + H_2O$	$3.17 \times 10^{-09}$	-0.5	0.0	$1.83 \times 10^{-08}(6.38 \times 10^{-09})^c$	–
R26 (IN)	$HC_2CHO + HCO^+ \rightarrow HC_2CH_2O^+ + CO$	$2.74 \times 10^{-09}$	-0.5	0.0	$1.58 \times 10^{-08}(5.51 \times 10^{-09})^c$	–
R27 (IN)	$HC_2CHO + H_3^+ \rightarrow C_3H^+ + H_2O + H_2$	$7.03 \times 10^{-09}$	-0.5	0.0	$4.04 \times 10^{-08}(1.41 \times 10^{-08})^c$	–
R28 (IN)	$HC_2CHO + H_3^+ \rightarrow HC_2CH_2O^+ + H_2$	$7.03 \times 10^{-09}$	-0.5	0.0	$4.04 \times 10^{-08}(1.41 \times 10^{-08})^c$	–
R29 (IN)	$HC_2CHO + He^+ \rightarrow C_3H^+ + He + OH$	$6.17 \times 10^{-09}$	-0.5	0.0	$3.55 \times 10^{-08}(1.24 \times 10^{-08})^c$	–
R30 (IN)	$HC_2CHO + He^+ \rightarrow C_3H + He + OH^+$	$6.17 \times 10^{-09}$	-0.5	0.0	$3.55 \times 10^{-08}(1.24 \times 10^{-08})^c$	–
R31 (IN)	$HC_2CHO + CH_3^+ \rightarrow HC_2CH_2O^+ + CH_2$	$3.47 \times 10^{-09}$	-0.5	0.0	$2.00 \times 10^{-08}(6.98 \times 10^{-09})^c$	–
R32 (IN)	$HC_2CHO + H^+ \rightarrow C_3H_2 + H_2O$	$1.20 \times 10^{-08}$	-0.5	0.0	$6.89 \times 10^{-08}(2.41 \times 10^{-08})^c$	–
R33 (IN)	$HC_2CHO + H^+ \rightarrow C_3H_2 + OH^+$	$1.20 \times 10^{-08}$	-0.5	0.0	$6.89 \times 10^{-08}(2.41 \times 10^{-08})^c$	–
R34 (IN)	$HC_2CHO + H^+ \rightarrow HC_3O^+ + H_2$	$1.20 \times 10^{-08}$	-0.5	0.0	$6.89 \times 10^{-08}(2.41 \times 10^{-08})^c$	–
R35 (IN)	$HC_2CHO + H^+ \rightarrow C_3O^+ + H_2$	$1.20 \times 10^{-08}$	-0.5	0.0	$6.89 \times 10^{-08}(2.41 \times 10^{-08})^c$	–
R36 (IN)	$HC_2CHO + H_2D^+ \rightarrow HC_2CH_2O^+ + HD$	$5.98 \times 10^{-09}$	-0.5	0.0	$3.44 \times 10^{-08}(1.20 \times 10^{-08})^c$	–
R37 (IN)	$HC_2CH_2O + C^+ \rightarrow HC_3O^+ + CH_2$	$1.41 \times 10^{-09}$	-0.5	0.0	$8.86 \times 10^{-09}(3.57 \times 10^{-09})^c$	–
R38 (IN)	$HC_2CH_2O + C^+ \rightarrow C_3H_3^+ + HCO$	$1.41 \times 10^{-09}$	-0.5	0.0	$8.86 \times 10^{-09}(3.57 \times 10^{-09})^c$	–
R39 (IN)	$HC_2CH_2O + H_3O^+ \rightarrow HC_2CH_2O^+ + H_2O$	$1.18 \times 10^{-09}$	-0.5	0.0	$7.40 \times 10^{-09}(2.92 \times 10^{-09})^c$	–
R40 (IN)	$HC_2CH_2O + HCO^+ \rightarrow HC_2CH_2O^+ + HCO$	$1.02 \times 10^{-09}$	-0.5	0.0	$6.38 \times 10^{-09}(2.58 \times 10^{-09})^c$	–
R41 (IN)	$HC_2CH_2O + H_3^+ \rightarrow C_3H_3^+ + H_2O + H_2$	$2.62 \times 10^{-09}$	-0.5	0.0	$1.64 \times 10^{-08}(6.62 \times 10^{-09})^c$	–
R42 (IN)	$HC_2CH_2O + H_3^+ \rightarrow HC_2CH_2O^+ + H_2 + H$	$2.62 \times 10^{-09}$	-0.5	0.0	$1.64 \times 10^{-08}(6.62 \times 10^{-09})^c$	–
R43 (IN)	$HC_2CH_2O + He^+ \rightarrow C_3H^+ + He + H_2O$	$2.30 \times 10^{-09}$	-0.5	0.0	$1.44 \times 10^{-08}(5.80 \times 10^{-09})^c$	–
R44 (IN)	$HC_2CH_2O + He^+ \rightarrow C_4H + He + OH^+$	$2.30 \times 10^{-09}$	-0.5	0.0	$1.44 \times 10^{-08}(5.80 \times 10^{-09})^c$	–
R45 (IN)	$HC_2CH_2O + CH_3^+ \rightarrow HC_2CH_2O^+ + CH_3$	$1.29 \times 10^{-09}$	-0.5	0.0	$8.09 \times 10^{-09}(3.26 \times 10^{-09})^c$	–
R46 (IN)	$HC_2CH_2O + H^+ \rightarrow C_3H_2^+ + H_2O$	$4.46 \times 10^{-09}$	-0.5	0.0	$2.80 \times 10^{-08}(1.13 \times 10^{-08})^c$	–
R47 (IN)	$HC_2CH_2O + H^+ \rightarrow C_3H_2 + OH^+ + H$	$4.46 \times 10^{-09}$	-0.5	0.0	$2.80 \times 10^{-08}(1.13 \times 10^{-08})^c$	–
R48 (IN)	$HC_2CH_2O + H^+ \rightarrow HC_3O^+ + H_2 + H$	$4.46 \times 10^{-09}$	-0.5	0.0	$2.80 \times 10^{-08}(1.13 \times 10^{-08})^c$	–
R49 (IN)	$HC_2CH_2O + H^+ \rightarrow HC_3O^+ + H_2$	$4.46 \times 10^{-09}$	-0.5	0.0	$2.80 \times 10^{-08}(1.13 \times 10^{-08})^c$	–
R50 (IN)	$HC_2CH_2O + H_2D^+ \rightarrow HC_2CH_2O^+ + HD + H$	$2.23 \times 10^{-09}$	-0.5	0.0	$1.40 \times 10^{-08}(5.63 \times 10^{-09})^c$	–
R51 (PH)	$HC_2CH_2OH + PHOTON \rightarrow C_3H_3 + OH$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R52 (PH)	$HC_2CH_2OH + PHOTON \rightarrow HC_2CH_2O + H$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R53 (PH)	$HC_2CH_2O + PHOTON \rightarrow C_3H_2 + OH$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R54 (PH)	$HC_2CH_2O + PHOTON \rightarrow H_2CO + C_2H$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R55 (PH)	$HC_2CH_2O + PHOTON \rightarrow HC_2CHO + H$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R56 (PH)	$HC_2CHO + PHOTON \rightarrow C_2H + HCO$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R57 (PH)	$HOC_2HHCHOH + PHOTON \rightarrow HC_2CH_2OH + OH$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R58 (PH)	$HOC_2HHCHOD + PHOTON \rightarrow HC_2CH_2OH + OD$	$6.0 \times 10^{-10}$	0.0	1.8	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$	$9.14 \times 10^{-18}(9.14 \times 10^{-18})^d$
R59 (CR)	$HC_2CH_2OH + CRPHOT \rightarrow C_3H_3 + OH$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R60 (CR)	$HC_2CH_2OH + CRPHOT \rightarrow HC_2CH_2O + H$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R61 (CR)	$HC_2CH_2O + CRPHOT \rightarrow C_3H_2 + OH$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R62 (CR)	$HC_2CH_2O + CRPHOT \rightarrow H_2CO + C_2H$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R63 (CR)	$HC_2CH_2O + CRPHOT \rightarrow HC_2CHO + H$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R64 (CR)	$HC_2CHO + CRPHOT \rightarrow C_2H + HCO$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R65 (CR)	$HOC_2HHCHOH + CRPHOT \rightarrow HC_2CH_2OH + OH$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R66 (CR)	$HOC_2HHCHOD + CRPHOT \rightarrow HC_2CH_2OH + OD$	$1.3 \times 10^{-17}$	0.0	752	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$	$2.44 \times 10^{-14}(2.44 \times 10^{-14})^d$
R67 (DR)	$HC_2CH_2O^+ + e^- \rightarrow CO + C_2H_2 + H$	$2.0 \times 10^{-7}$	-0.5	0.0	$1.10 \times 10^{-6}(3.46 \times 10^{-7})^c$	–
R68(DR)	$HC_2CH_2O^+ + e^- \rightarrow HCO + C_2H + H$	$2.0 \times 10^{-7}$	-0.5	0.0	$1.10 \times 10^{-6}(3.46 \times 10^{-7})^c$	–
R69(DR)	$HC_2CH_2O^+ + e^- \rightarrow H_2CO + C_2H$	$2.0 \times 10^{-7}$	-0.5	0.0	$1.10 \times 10^{-6}(3.46 \times 10^{-7})^c$	–
R70(DR)	$HC_2CH_2OH_2^+ + e^- \rightarrow C_3H_3 + H_2O$	$8.01 \times 10^{-8}$	-0.59	0.0	$5.95 \times 10^{-7}(1.52 \times 10^{-7})^c$	–

(continued on next page)

**Table 1** (continued)

Reaction number (type)	Reaction	$\alpha$	$\beta$	$\gamma$	Gas phase rate coefficient at $T = 10$ K (100 K)	Ice phase rate coefficient at $T = 10$ K (100K)
R71(DR)	$\text{HC}_2\text{CH}_2\text{OH}_2^+ + \text{e}^- \rightarrow \text{C}_3\text{H}_3 + \text{OH} + \text{H}$	$4.54 \times 10^{-7}$	-0.59	0.0	$3.34 \times 10^{-6}(8.6 \times 10^{-7})^c$	–
R72(DR)	$\text{HC}_2\text{CH}_2\text{OH}_2^+ + \text{e}^- \rightarrow \text{C}_3\text{H}_2 + \text{H}_2\text{O} + \text{H}$	$1.87 \times 10^{-7}$	-0.59	0.0	$1.41 \times 10^{-6}(3.63 \times 10^{-7})^c$	–
R73(DR)	$\text{HC}_2\text{CH}_2\text{OH}_2^+ + \text{e}^- \rightarrow \text{H}_2\text{CO} + \text{C}_2\text{H}_2 + \text{H}$	$8.9 \times 10^{-8}$	-0.59	0.0	$6.6 \times 10^{-7}(1.7 \times 10^{-7})^c$	–
R74(DR)	$\text{HC}_2\text{CH}_2\text{OH}^+ + \text{e}^- \rightarrow \text{C}_3\text{H}_3 + \text{OH}$	$3.00 \times 10^{-7}$	-0.5	0.0	$1.64 \times 10^{-6}(5.20 \times 10^{-7})^c$	–
R75(DR)	$\text{HC}_2\text{CH}_2\text{OH}^+ + \text{e}^- \rightarrow \text{HC}_2\text{CH}_2\text{O} + \text{H}$	$3.00 \times 10^{-7}$	-0.5	0.0	$1.64 \times 10^{-6}(5.20 \times 10^{-7})^c$	–

Notes: For the two-body reactions (R1-R2, R4-R8, R67-R75), rate coefficients are tabulated as  $\alpha \left(\frac{T}{300}\right)^\beta \exp(-\frac{\gamma}{T})$ . For the photo-dissociation reactions with external interstellar photons (R51-R58), rate coefficients are tabulated as  $\alpha \exp(-\gamma A_\nu)$ . For photo-dissociation by cosmic ray induced photons (R59-R66), rate coefficients are tabulated as  $\alpha \frac{J_{\nu}}{A_\nu}$ . For the rate coefficients of ion-polar neutral reactions (R9-R50), we use the relation discussed in [Su and Chesnavich \(1982\)](#). Tabulated rate coefficients for these ion-neutral reactions in terms of  $\alpha \left(\frac{T}{300}\right)^\beta \exp(-\frac{\gamma}{T})$  are valid for the low temperature regime only.

<sup>a</sup> gas phase enthalpy in kJ/mol

<sup>b</sup> ice phase enthalpy in kJ/mol

<sup>c</sup> rate coefficient in  $\text{cm}^3\text{s}^{-1}$

<sup>d</sup> rate coefficient in  $\text{s}^{-1}$

thesis of PA are assumed to be responsible for the production of OD-PA.

## 2.2. Destruction pathways

As shown in [Table 1](#), the destruction of gaseous PA occurs via ion-neutral (IN) and photo-dissociative (PH & CR) pathways, as well as via two radical-neutral (NR) reactions. The destruction of gas phase PA also occurs via adsorption onto ice, but the reverse process of desorption also occurs. These processes are in our network, but not listed in [Table 1](#). The rate coefficient for the gas phase NR reaction between the hydroxyl radical (OH) and PA was measured by [Upadhyaya et al. \(2001\)](#), who used laser photolysis combined with the laser induced fluorescence technique at room temperature. According to their study, this reaction (R7) produces an adduct,  $\text{HOC}_2\text{HHCHOH}$ . Since the abundances of OH and OD are comparable in a dense cloud ([Millar et al., 1989](#)), a similar destruction mechanism with OD (R8) is also considered here. In addition to the gas-phase, reactions R7 and R8 are included in the ice phase as well. For the ion-neutral (IN) destruction of gas phase PA, we include reactions R9-R22 by following the similar gas phase ion-neutral (IN) destruction pathways available for methanol in [Woodall et al. \(2007\)](#). Similar IN destruction reactions (R23-R50) for  $\text{HC}_2\text{CHO}$  and  $\text{HC}_2\text{CH}_2\text{O}$  are also considered. Photo-dissociation reactions (direct or cosmic ray induced) (R51-R66) are also responsible for the destruction of PA and its associated species in both phases. In [Table 1](#), DR reactions R6 and R67-R75 involve the ions ( $\text{HC}_2\text{CH}_2\text{O}^+$ ,  $\text{HC}_2\text{CH}_2\text{OH}_2^+$  and  $\text{HC}_2\text{CH}_2\text{OH}^+$ ); these ions are produced by various formation/destruction pathways of PA and its related species. For the destruction of OD-PA and other associated species similar destruction pathways to all those considered for PA are included.

## 2.3. Rate coefficients

### 2.3.1. Gas phase rate coefficients

([Slagle et al., 1991](#)) experimentally obtained a temperature independent rate coefficient of  $\sim 2.31 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for reaction R1. According to their study, this reaction proceeds through a fast and irreversible association-fragmentation process. We utilize the rate coefficient obtained by [Slagle et al. \(1991\)](#). ([Petrie, 1995](#)) estimated a rate coefficient of  $1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for reaction R2 with the assumption that it occurs without a barrier in the gas phase. Although this assumption contradicts the calculation of a small barrier by [Dong et al. \(2005\)](#), we assume the reaction to be barrier-less, and use the estimated rate coefficient of [Petrie \(1995\)](#).

As can be seen in [Table 1](#), reactions R3, R4, and R5 are highly exothermic in nature. Based on the high exothermicity of these re-

actions, one might assume that these reactions can process without barriers.

The Hydrogen addition reaction of  $\text{HC}_2\text{CHO}$  (reaction R3) may occur in two ways. First, H addition may occur with the O atom of the CHO group and produce  $\text{HC}_2\text{CHOH}$  and secondly H addition may occur with the C atom of the CHO group and produce  $\text{HC}_2\text{CH}_2\text{O}$ . Our quantum chemical calculation found that the hydrogen addition to carbon is more favourable than the hydrogen addition to oxygen in the CHO group. Using the DFT/6-31+G(d,p) method, we found that the gas-phase activation barrier ( $\Delta E^\ddagger$ ) and Gibbs energy of activation ( $\Delta G^\ddagger$ ) for the second possibility of reaction R3 ( $\text{H} + \text{HC}_2\text{CHO} \rightarrow \text{HC}_2\text{CH}_2\text{O}$ ) is 3.74 kcal/mol and 9.63 kcal/mol respectively.

For the computation of the gas phase rate coefficient for reaction R3, we use transition state theory, which leads to the Eyring equation ([Eyring, 1935](#)):

$$k = (k_B T / hc) \exp(-\Delta G^\ddagger / RT). \quad (1)$$

The rate coefficient calculated by the above equation thus has a strong temperature dependence. In [Table 1](#), we have included the rate coefficient for two temperatures; 10 K and 100 K. At 10 K, rate coefficient is  $\sim 0$  and at 100 K it becomes  $1.96 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ . Thus in the low temperature regime, R3 does not contribute at all to the gas phase formation of PA, while it could play a role for the formation of PA in the high temperature regime.

In the case of reactions R4 and R5, we were unable to locate any suitable transition state and assume that these two reactions are barrier-less, as is customary for radical-radical reactions. The rate coefficients of these two reactions are assumed to be  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . The formation of OD-PA is treated with similar pathways and rate coefficients.

For the formation of PA by the DR mechanism, which involves the destruction of  $\text{HC}_2\text{CH}_2\text{OH}_2^+$  (R6, R67-R75), we follow the destruction of  $\text{CH}_3\text{OH}_2^+$  from [Woodall et al. \(2007\)](#) for the rate coefficients and product channels. Rate coefficients between two species are standardly parameterized as a function of temperature by the equation

$$k = \alpha (T/300)^\beta \exp^{-\gamma/T}. \quad (2)$$

In this particular case, the values of the parameters for the formation of PA are  $\alpha = 2.67 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ,  $\beta = -0.59$  and  $\gamma = 0$ . Similar product channels and rate coefficients are used for the formation of OD-PA by a DR reaction.

Now let us consider the destruction of gaseous PA. ([Upadhyaya et al., 2001](#)) studied the rate coefficient of the NR reaction between PA and the OH radical (R7). According to their study, it produces an adduct with a rate coefficient of  $(9.2 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , which we use with no temperature dependence. Here also, we assume a similar rate coefficient for reaction R8, which involves OD. Similar

destruction reactions and rate coefficients are adopted for OD-PA as well.

Ion Neutral (IN) reactions are the dominant means for the destruction of neutral interstellar species. If the neutral species is non-polar, we use the Langevin collision rate coefficient (Herbst, 2006; Wakelam et al., 2010). If the neutral species is polar, we employ the trajectory scaling relation found in Su and Chesnavich (1982) and Woon and Herbst (2009). From our quantum chemical calculations, we find that the polarizability  $\alpha_d = 5.62 \times 10^{-24}$  cm<sup>3</sup> and dipole moment  $\mu_D = 1.6548$  Debye for PA. For the destruction reactions of the other two associated species (HC<sub>2</sub>CHO, HC<sub>2</sub>CH<sub>2</sub>O), in reaction numbers R23-R36, we use  $\alpha_d = 5.26 \times 10^{-24}$  cm<sup>3</sup> and  $\mu_D = 3.08$  Debye, and for R37-R50 we use  $\alpha_d = 5.93 \times 10^{-24}$  cm<sup>3</sup> and  $\mu_D = 1.1480$  Debye. For deuterated PA, the ion-neutral destruction reactions have similar rate coefficients to those of normal PA, the only differences being due to the reduced mass, which are rather small. Deuterated reactions and their rate coefficients are not tabulated here.

For the photo-dissociation reactions of PA and its associated species by external interstellar photons and cosmic ray-induced photons, we use analogous products and the same first-order rate coefficients (s<sup>-1</sup>) as the case of CH<sub>3</sub>OH (Woodall et al., 2007). For the case of external photons, we use the following relation for the rate coefficients:

$$k = \alpha \exp(-\gamma A_V) \quad (3)$$

where  $\alpha$  represents the rate coefficient (s<sup>-1</sup>) in the unshielded interstellar ultraviolet radiation field,  $A_V$  is the visual extinction, for which we use a value of 10, and  $\gamma$  is used to take into account the increased extinction of dust in the UV. Here, following Woodall et al. (2007), we use  $\alpha = 6.0 \times 10^{-10}$  s<sup>-1</sup>, and  $\gamma = 1.8$  in our model. Incorporating all the parameters into the above equation, we obtain a photo-dissociation rate coefficient of about  $9.14 \times 10^{-18}$  s<sup>-1</sup>.

For cosmic-ray-induced photo-reactions, we use the following relation, which was originally developed by (Gredel et al., 1989):

$$k = \alpha \gamma' / (1 - \omega) \quad (4)$$

where  $\alpha$  is the cosmic-ray ionization rate (s<sup>-1</sup>),  $\gamma'$  is the number of photo-dissociative events that take place per cosmic-ray ionization and  $\omega$  is the dust grain albedo in the far ultraviolet. Here, we use  $\omega = 0.6$ ,  $\alpha = 1.3 \times 10^{-17}$  s<sup>-1</sup>, and  $\gamma' = 752.0$  by following the cosmic-ray-induced photo-reactions of CH<sub>3</sub>OH in Woodall et al. (2007). By including these parameters into the above equation, we obtain a rate coefficient of  $2.44 \times 10^{-14}$  s<sup>-1</sup>, which is roughly 4 orders higher than the rate of external photo-dissociative reactions. Cosmic ray induced photo-reactions can play an important role in interstellar chemistry. The choices of these parameters are highly reaction specific and a wrong estimation might lead to misleading results. In the UMIST 2006 database,  $\gamma'$  ranges as high as 5290 and as low as 25.0. Though the higher values of  $\gamma'$  are more reliable for the larger molecules because of the increasing overlap between the cross sections for photo-dissociation and the cosmic-ray-induced emission spectrum (Gredel et al., 1989), we use  $\gamma' = 752.0$  (in Table 1, we presented it under the column head marked  $\gamma$ ) for our calculations of the cosmic-ray-induced photo-dissociative reactions. The same photo-dissociation rate coefficients are adopted for the destruction of OD-PA and its associated species.

Dissociative recombination (DR) reactions and rate coefficients for some of the associated ions of PA are shown in reactions R67-R75. Pathways and rate coefficients of these reactions are adopted by following the similar DR pathways available for CH<sub>3</sub>O<sup>+</sup>, CH<sub>3</sub>OH<sub>2</sub><sup>+</sup>, and CH<sub>3</sub>OH<sup>+</sup> in Woodall et al. (2007). Since for all these reactions,  $\beta \neq 0$ , the reactions are temperature dependent. The same DR rate coefficients are used for the associated ions of OD-PA.

For two or three-body gas-phase reactions in Table 1, the rate coefficients are represented in terms of the three rate coefficients,  $\alpha$ ,  $\beta$  and  $\gamma$ . Most of the gas phase rate coefficients adopted here are either estimated or taken from similar kind of reactions. For reactions R1-R2, R4-R5 and R7-R8, we assign  $\beta$  and  $\gamma$  to be zero. For the dissociative recombination reactions (R6 and R68-R75), these three coefficients are estimated based on similar reactions listed in Woodall et al. (2007). For reaction R3, we calculate the gas phase rate coefficient by using transition state theory, which leads to the Eyring equation (Eyring, 1935). Thus for reaction R3, these three parameters are not shown. For destruction by photo-reactions, we supply these three coefficients following the similar type of reactions available in Woodall et al. (2007). For the destruction of polar neutral species by ions, we use the two relations discussed in Su and Chesnavich (1982). These relations cannot be represented over the whole temperature range in terms of one set of three coefficients. However, we can tabulate  $\alpha$ ,  $\beta$  and  $\gamma$  for reactions R9-R50 in the low temperature regime.

### 2.3.2. Ice phase rate coefficients

Chemical enrichment of interstellar grain mantles depends on the binding energies ( $E_d$ ) and barriers against diffusion ( $E_b$ ) of the adsorbed species. The binding energies of these species are often available from past studies (Allen and Robinson, 1977; Hasegawa and Herbst, 1993; Hasegawa et al., 1992; Tielens and Allamandola, 1987). But these binding energies mostly pertain to silicates. Binding energies of the most important surface species on ice, which mostly control the chemical composition of interstellar grain mantles, are available from some recent studies (Cuppen and Herbst, 2007; Garrod, 2013). We use these latter energies in our model. For the rest of the species for which binding energies are still unavailable, we use the same values as in past studies or estimate new values. For barriers against diffusion, which are poorly known, we use values equal to  $0.35E_d$  (Garrod, 2013).

For the formation of PA in the ice phase, we include surface reactions R1-R5. The rate coefficients ( $R_{diff}$ ) of these reactions were calculated by the method described in Hasegawa et al. (1992), which is based on thermal diffusion. They defined a probability factor  $\kappa$  to differentiate between exothermic reactions without activation energy barriers and reactions with activation energy barriers ( $E_a$ ) in such a way that the effective rate coefficient becomes  $R_{ij} = \kappa \times R_{diff}$ . The factor  $\kappa$  is unity in the absence of a barrier. For reactions with activation energy barriers,  $\kappa$  is defined as the quantum mechanical probability for tunneling through a rectangular barrier of thickness  $a (= 1 \text{ \AA})$ , which is calculated from the equation

$$\kappa = \exp[-2(a/\hbar)(2\mu E_a)^{1/2}]. \quad (5)$$

Binding energies to the surface for some complex organics with a hydroxyl group are normally considered to be higher due to the phenomenon of hydrogen bonding (Collings et al., 2004; Garrod, 2013; Lattelais et al., 2011). Since PA has an -OH group, creating hydrogen bonds with a water substrate, this molecule is therefore expected to have a higher binding energy, close to that of water. Here, we assume the binding energy of both PA and OD-PA to be the same as methanol (5530 K). Since HC<sub>2</sub>CHO forms by the reaction between C<sub>3</sub>H<sub>3</sub> and O, we add the binding energies of C<sub>3</sub>H<sub>3</sub> (2220 K) and O (800 K) to determine a binding energy value 3020 K. In the case of the binding energy of HC<sub>2</sub>CH<sub>2</sub>O, we add the binding energies of HC<sub>2</sub>CHO (3020 K) and H (450 K) to obtain 3470 K. For other binding energies for species in reaction R1, R2, R3, R4 and R5, we use  $E_d(\text{C}_2\text{H}) = 1460$  K,  $E_d(\text{H}_2\text{CO}) = 2050$  K and  $E_d(\text{OH}) = 2850$  K. Our transition state theory calculation found that reaction R3 (hydrogen addition to the carbon atom of the CHO group) contains an activation barrier of about 3.59 kcal/mol (1807 K) in the ice phase.













