A THEORETICAL STUDY OF VINYL ALCOHOL FORMATION IN THE INTERSTELLAR MEDIUM.

V.A. Basiuk[1] and K. Kobayashi[2], [1] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior C.U., 04510 México D.F., MEXICO, [2] Dept. of Chemistry and Biotechnology, Faculty of Engineering, Yokohama Natl. Univ., Hodogaya-ku, Yokohama 240-8501, JAPAN; e-mail: basiuk@nuclecu.unam.mx

Introduction: Vinyl alcohol (VA) is one of the most recently detected interstellar species. It was identified in emission toward Sagittarius B2N [1]. Although chemical pathways leading to its formation are not completely clear yet, the authors suggested that VA could possibly form through the following reaction [1]: $CH_3^+ + H_2CO \rightarrow H_2C=CH\text{-}OH$. It requires high abundances of the reactants, whereas none of the two belongs to very abundant interstellar species. We suggest that the formation of VA can be alternatively explained based on the reactions of simple, commonly found and most abundant species. In particular, there is no need to look for a process capable of forming the C-C bond of VA, since it can be found in other interstellar species, such as acetylene and acetylene-related radicals $HC\equiv C\cdot$ and C_2. The missing atoms are available as ubiquitous H atoms and OH radicals. Radical reactions normally proceed without activation barriers, and are highly exothermic. In the present work, we estimated an energetic feasibility of some pathways to vinyl alcohol, starting from common and abundant interstellar species acetylene, radicals C_2, $HC\equiv C\cdot$, $\cdot OH$ and $H\cdot$.

Computational Method: The Gaussian 98W suite of programs [2] was used. All the computations were performed with Becke's three-parameter hybrid method [3] and the exchange functional of Lee, Yang and Parr (B3LYP) [4] included in the program package, using the 6-31++G(d,p) basis set [5-7]. Unrestricted B3LYP was used to treat all mono and biradical species. The search for transition states was carried out using the QST2 and QST3 procedures. The stationary point geometries were fully optimized and characterized as minima (0 imaginary frequencies) or first-order saddle points (1 imaginary frequency) by calculations of vibration frequencies. Zero-point energies (ZPEs, not discussed here) were retrieved from the vibration frequency calculations.

Results and Discussion: A simplified potential energy surface (PES) for the reactions leading to vinyl alcohol, involving common and abundant radical species C_2, $HC\equiv C\cdot$, $H\cdot$ and $\cdot OH$, as well as acetylene, is presented in Fig. 1. As expected, the reactions are highly exothermic and most of them need no activation. An overall exothermicity of the conversion of (C_2 + $\cdot OH$ + $3H\cdot$) into *anti* (P2) and *syn*-VA (P1) isomers is –434.8 and –436.3 kcal mol^{-1}, respectively.

Starting with the above reactants, we consider different reaction sequences, which can be subdivided into two general pathways depending on what is the first step: either $\cdot OH$ or $H\cdot$ attachment to C_2. The upper part of the potential energy surface corresponds to the former option. It is interesting to note that, while the $C_2 + \cdot OH$ combination might be expected to produce a hydroxy ethynyl radical IM1 and the corresponding minimum was indeed obtained, a direct geometry optimization for the reactants gave [C=C=OH]$\cdot$ (IM2).

For further chemical transformations through hydrogenation with H-atoms, several choices exist. The most favorable energetically is the formation of a closed-shell species, hydroxyacetylene $HC\equiv C\text{-}OH$, which is 127.5 kcal mol^{-1} exothermic relative to the level of ([C=C=OH]$\cdot$ + $3H\cdot$). On the other hand, such closed-shell species are not very reactive with hydrogen atoms and other non-polar radicals; for example, it was experimentally shown by Hiraoka et al. [8] for the case of solid films of acetylene and CO at interstellar temperatures. According to the results of our calculations, van der Waals interactions between $HC\equiv C\text{-}OH$ and a H-atom are extremely weak. After that, there are two possibilities to add $H\cdot$: either to the terminal or to central carbon atom. In the latter case, there is a possibility of isomerism depending on the mutual spatial orientation of the carbon-bound H-atoms (*cis* or *trans*), as well as *syn* or *anti*-orientation of the hydroxy group with respect to the double bond: four isomers IM5-IM8 are possible, IM5 (*cis-syn*) being the most stable one. As regards the other product of hydrogen atom addition, $H_2C=C(\cdot)\text{-}OH$ (IM9), the only conformation for which an energy minimum was found is *anti*. The height of activation barrier TS3 for its formation is of only 0.2 kcal mol^{-1} relative to ($HC\equiv C\text{-}OH$ + $2H\cdot$); for TS4 to IM5 it is 2.4 kcal mol^{-1} relative to the same level. This makes the latter transformation hardly feasible under the cold interstellar conditions, whereas the formation of *anti*-$H_2C=C(\cdot)\text{-}OH$ may occur in warmer molecular clouds (hot cores and circumstellar envelopes). After that, IM9 can combine with the last missing H atom, and its *anti*-conformation predetermines *anti*-VA to form. The reaction is 111.8 kcal mol^{-1} exothermic.

Less energetically favorable than the formation of hydroxyacetylene is the addition of $H\cdot$ to the central carbon atom, producing :C=CH-OH biradical (IM4). Its further combination with $H\cdot$ can give both *cis* and *trans* forms of *syn*-$HC(\cdot)=CH\text{-}OH$ (IM5 and IM6). The reactions are 99.8 and 98.5 kcal mol^{-1} exothermic, respectively. Once formed, the isomers can easily inter-

Fig. 1. Simplified potential energy surface for the reactions leading to vinyl alcohol. Relative energies are in kcal mol⁻¹. HC≡C˙ and HC≡CH are included as intermediates, and the reference point to calculate energies of all species is the sum of energies of separated C_2 (singlet state), ˙OH and three hydrogen atoms.
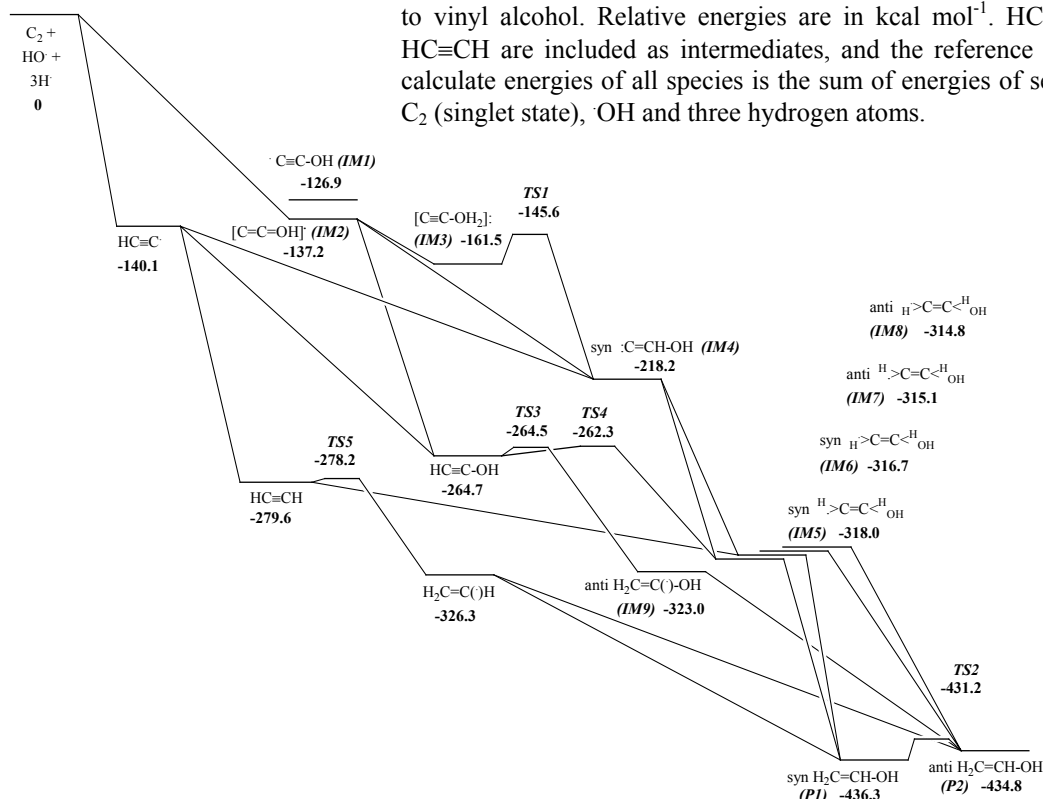
convert: for example, the *trans* → *cis* conversion needs 2.2 kcal mol⁻¹. Two similar *anti*-isomers of HC(˙)=CH-OH (IM7 and IM8) can be produced by rotating the OH-group. All four isomers can finally produce *syn* and *anti*-VA by adding the last H atom.

One should note that the addition of a hydrogen atom to IM1 can also occur at the O atom, forming [C≡C-OH₂]: biradical (IM3). Among the three possible intermediates considered, this one is the most energetically unfavorable due to a comparatively low exothermicity of 24.3 kcal mol⁻¹. Nevertheless, IM3 can undergo immediate isomerization into IM4, since the corresponding transition state TS1 lays below the level of (˙C≡C-OH + 3H˙) by 8.4 kcal mol⁻¹.

An alternative (to C₂+˙OH reaction) first step is the formation of HC≡C˙. It can combine with either ˙OH or H˙. The first process again can give HC≡C-OH. The ˙OH attack is also possible on the second carbon atom, producing :C=CH-OH biradical (IM4).

Another possible pathway to VA is the one through acetylene. Since it is a closed-shell species, further adding radicals on the triple bond might require some activation energy. Van der Waals interaction between acetylene and a hydrogen atom is negligible: H˙ does not approach HC≡CH closer than at 3.94 Å, and the energy remains at the level of iso-

lated reactants (HC≡CH + H˙ + ˙OH). The transition of this weak complex to H₂C=C(˙)H radical requires 1.4 kcal mol⁻¹ (TS5) which makes the reaction hardly feasible under the cold interstellar conditions. On the other hand, it might be possible in warmer molecular clouds or in the solid phase [14] due to proton-tunneling effects. Further adding of ˙OH on H₂C=C(˙)H is a radical combination, which can produce any of the two VA isomers.

References: [1] Turner B.E. and Apponi A.J. (2001) *Astrophys. J.*, *561*, L207. [2] Frisch M.J. et al. (1998) *Gaussian 98W*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA. [3] Becke A.D. [1993] *J. Phys. Chem.*, *98*, 5648. [4] Lee C. et al. (1988) *Phys. Rev. B*, *37*, 785. [5] Hariharan P.C. and Pople J.A. (1972) *Chem. Phys. Lett.*, *66*, 217. [6] Binkley J.S. and Pople J.A. (1975) *Int. J. Quantum. Chem.*, *9*, 229. [7] Krishnan R. et al. (1980) *J. Chem. Phys.*, *72*, 4244. [8] Hiraoka K. et al. (1999) *Astrophys. J.*, *514*, 524.