Modeling atomic hydrogenation on icy grain surfaces

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A simple way to increase molecular complexity in the interstellar medium (ISM) is the hydrogenation of small molecules. Gas-phase reactions cannot efficiently produce all detected species. Therefore, a consensus has gradually emerged that hydrogenation process can be fostered by the icy grain mantles. However the question whether activation energy is required in order to promote hydrogenation sequences is still open.

We here present a computational model suitable for depicting atomic hydrogenation processes on water ices in the ISM, that should be simple enough to bypass systematic expensive solid state simulations and avoid the question of the ice structure. We use H_3O complexes to represent atomic hydrogen adsorbed at the surface of ice. This model allows the use of high level quantum calculations such as coupled cluster CCSD and CCSD(T) treatments associated to large basis sets aug-cc-pVTZ and diffuse functions in order to obtain reliable estimates.

Methanol, which constitutes up to 25% of icy grain mantles, plays an active role in the formation of complex organic molecules and molecules of prebiotic relevance [1-4]. A natural mechanism for CH_3OH formation is the successive hydrogenation of CO [5-6]:

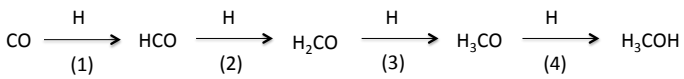

Figure 1: The 4 stages of the H+CO hydrogenation sequence

On a theoretical side, the first and the third stages are known to have activation barriers on the reaction paths for gaz phase process [7-11]. Ineffective attempts were made to take into account the ice support [12]. However, on the experimental side, methanol is formed when bombing a CO surface by hydrogen atoms at 10K [13]. The study by Pirim and Krim [14-15] highlighting the catalytic role of water led us to look at hydrogenation processes from a different viewpoint, considering water ice not only as a support but mainly as an essential partner for essential to the reaction. Therefore, the synthesis of methanol is used as a case study.

Our calculations show that, using H_3O complexes to represent atomic hydrogen adsorbed at the surface of ice, the first and the third stages are now barrierless. This is due to the fact that the hydrogen departure is counterbalanced by the creation of the bond between H and the incoming species to which might be added the stabilization due to the readjustment of the ice support to reach the Bernal-Fowler arrangement [16].

The present approach proved to be able to account for the formation methanol by successive hydrogenation of CO on icy grain surfaces. It appears as a simple way to get a fair insight into

the important class of atomic hydrogenations on icy surfaces when H is first adsorbed on the ice.

References

[1] Whittet, D. C. B., Bode, M. F., Longmore, A. J., et al. 1988, Monthly Notices of the Royal Astronomical Society, 233, 321
[2] Dartois, E., Cox, P., Roelfsema, P. R., et al. 1998, Astronomy and Astrophysics, 338, L21
[3] Boogert, A. C. A., Pontoppidan, K. M., Knez, C., et al. 2008, The Astrophysical Journal, 678, 985
[4] Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2011, The Astrophysical Journal, 740, 109
[5] Tielens, A. G. G. M. & Hagen, W. 1982, Astronomy and Astrophysics, 114, 245
[6] Tielens, A. G. G. M. & Whittet, D. C. B. 1997, Symposium - International Astronomical Union, 178, 45
[7] Woon, D. E. 1996, The Journal of Chemical Physics, 105, 9921
[8] Woon, D. E. 2002, The Astrophysical Journal, 569, 541
[9] Marenich, A. V. & Boggs, J. E. 2003, The Journal of Physical Chemistry A, 107, 2343
[10] Fuchs, G. W., Cuppen, H. M., Ioppolo, S., et al. 2009, Astronomy and Astrophysics, 505, 62
[11] Stoecklin, T., Halvick, P., Yu, H.-G., Nyman, G., & Ellinger, Y. 2018, Monthly Notices of the Royal Astronomical Society, 475, 2545
[12] Tomasi, J. & Persico, M. 1994, Chemical Reviews, 94, 2027
[13] Watanabe, N. & Kouchi, A. 2002, The Astrophysical Journal Letters, 571, L173
[14] Pirim, C. & Krim, L. 2011a, Chemical Physics, 380, 67
[15] Pirim, C. & Krim, L. 2014, RSC Advances, 4, 15419
[16] Bernal, J.D. & Fowler, R.H. 1933, The Journal of Chemical Physics, 1, 515