

Solid-state production of complex organic molecules: H-atom addition versus UV irradiation

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Abstract. Complex organic molecules (COMs) have been observed in comets, hot cores and cold dense regions of the interstellar medium. It is generally accepted that these COMs form on icy dust grain through the recombination reaction of radicals triggered by either energetic UV-photon or non-energetic H-atom addition processing. In this work, we present for the first time laboratory studies that allow for quantitative comparison of hydrogenation and UV-induced reactions as well as their cumulative effect in astronomically relevant CO:CH₃OH=4:1 ice analogues. The formation of glycolaldehyde (GA) and ethylene glycol (EG) is confirmed in pure hydrogenation experiments at 14 K, except methyl formate (MF), which is only clearly observed in photolysis. The fractions for MF:GA:EG are 0 : (0.2-0.4) : (0.8-0.6) for pure hydrogenation, and 0.2 : 0.3 : 0.5 for UV involving experiments and can offer a diagnostic tool to derive the chemical origin of these species. The GA/EG ratios in the laboratory (0.3-1.5) compare well with observations toward different objects.

Keywords. astrochemistry, atomic processes, methods: laboratory, ISM: atoms, ISM: molecules, ultraviolet: ISM

1. Introduction

COMs have been identified in low and high-mass proto-stellar envelopes and in dark cloud cores (Herbst & van Dishoeck 2009). Among the observed COMs, glycolaldehyde (GA), the sugar-related molecule, and its related species, i.e. methyl formate (MF) and ethylene glycol (EG), have been detected toward solar mass proto-stars (Jorgensen *et al.* 2012, Jørgensen *et al.* 2016) and in comets (Crovisier *et al.* 2004, Biver *et al.* 2014, Goesmann *et al.* (2005), LeRoy *et al.* 2015). It is widely accepted that the O-bearing COMs form on icy dust grains through the recombination of reactive intermediates, e.g. HCO, CH₂OH and CH₃O that are generated by energetic processing such as UV photolysis (Oberg 2016), electron impact (Maity *et al.* 2015) and ion bombardment (Moore & Hudson 2005), as well as non-energetic processing, e.g. hydrogenation (Fedoseev *et al.* 2015, Chuang *et al.* 2016). The formations of GA, EG and MF are the most common COM products in above processing, indicating that the completely different triggers result in the qualitatively similar results. However, the quantitative comparison of COM abundances is not necessarily the same in different scenarios. Hence, it can be used as a tool to relate the role of specific chemical processes to specific astronomical environments. We present for the first time laboratory studies that aim to quantitatively study COM formation, i.e. GA, EG and MF, through hydrogenations and UV photolysis, as well as their cumulative effect in CO:CH₃OH ice mixtures. The results of MF/EG, MF/GA and GA/EG solid-state abundance ratios for different experiments can also be compared with those found for the gas-phase abundance ratio in different astronomical environments.

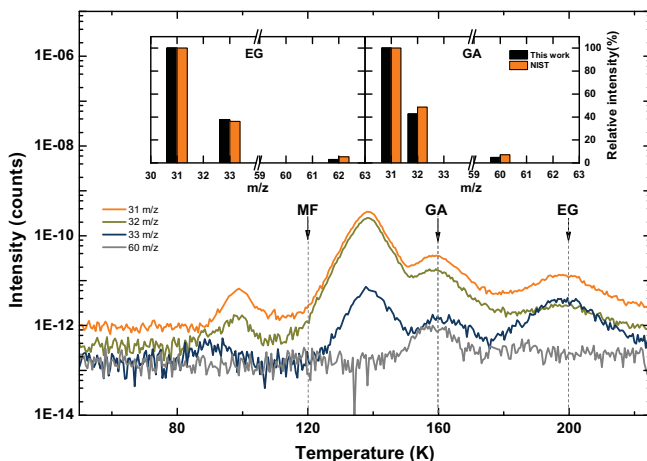


Figure 1. The TPD QMS spectra obtained after co-deposition of CO:CH₃OH = 4:1 ice mixtures with H-atom bombardment at 14 K. Product fragmentation patterns are compared to the NIST database values.

2. EXPERIMENTAL

All experiments are performed under ultra-high vacuum conditions, using SURFRE-SIDE2. The details of the set-up and procedure have been described in literature (Ioppolo *et al.* 2013, Chuang *et al.* 2017). The icy sample of CO and CH₃OH are introduced simultaneously through two molecular dosing lines, and face a Hydrogen Atom Beam Source and a UV-photon source generated by a Microwave Discharge Hydrogen flowing Lamp (MDHL). Ices are monitored in situ by Fourier Transform Reflection-Absorption InfraRed Spectroscopy (FT-RAIRS) in the range from 700 to 4000 cm⁻¹, with a 1 cm⁻¹ resolution. After the co-deposition, the icy sample is studied by a temperature-programmed desorption experiment using a Quadrupole Mass Spectrometer (TPD QMS). Analyzing the unique desorption temperature and ionization fragment pattern for each species allows for identification of the newly formed COM products, i.e. GA, EG and MF.

3. RESULTS AND DISCUSSION

Figure 1 presents a QMS TPD spectra of a typical experiment after the hydrogenation of a CO:CH₃OH ice mixture at 14 K. Two desorption profiles at 100 and 140 K can be assigned to H₂CO and CH₃OH, respectively. Two other peaks at 160 and 200 K are identified as GA and EG, respectively. Furthermore, the comparison of the electron ionization (70 eV) fragment pattern for GA and EG shows that they are largely consistent with the NIST database values. A trace signal of 60 m/z centered around 120 K can be assigned to MF. The similar QMS TPD spectra are observed in pure UV photolysis and cumulative experiments.

In addition to the qualitative identification of the newly formed COMs, the integration of the QMS TPD desorption intensity can also give further quantitative information. The absolute formation abundances of three COMs are presented on the upper panel of Figure 2 revealing that (1) the hydrogenation experiment (+H) produces the lowest yield of COMs when using the relative high H-atom flux, which is intentionally chosen to reach H-atom/UV-photon=1. However, performing an experiment with the same total H-atom fluence as other experiments in a longer timescale (+H(slow)), the COMs yields are comparable with those of the pure UV-photolysis experiment (+hν) except for MF;

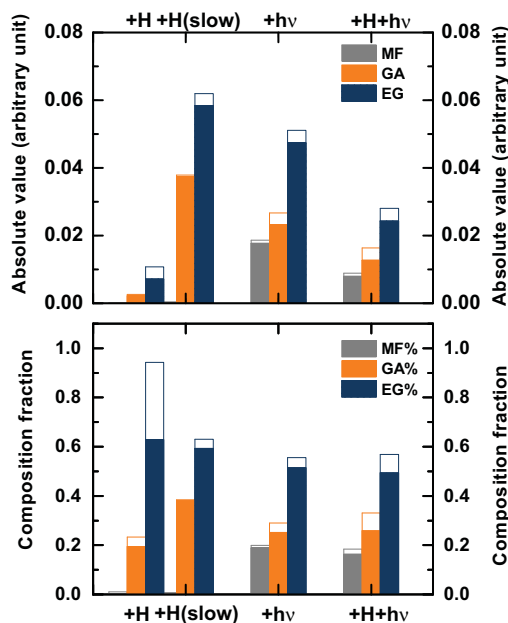


Figure 2. Absolute abundances (upper panel) and composition fractions (lower panel) for MF, GA and EG as obtained in QMS TPD experiments for pure hydrogenation (+H,+H(slow)), pure UV photolysis (+h ν) and their cumulative effect (+H+h ν), all for 14 K CO:CH₃OH = 4:1 ice mixtures.

(2) the three COMs have the most abundant yields in UV-photolysis experiment; (3) the combination of H-atoms and UV-photons experiment (+H+h ν) only reach half the amount of those of the pure UV-photolysis experiment.

In the bottom panel of Figure 2, the total composition fraction of total COMs is given as 0.0 for MF, 0.2-0.4 for GA and 0.8-0.6 for EG, respectively, in the hydrogenation experiments. The longer exposition experiment has a higher GA fraction (lower EG fraction) than those of the higher H-atom flux experiment. The unambiguous detection of MF is only found in the experiments when UV-photons are involved. Although the absolute abundances of COMs in the cumulative experiment only reach 50 per cent of the pure UV photolysis experiment, the composition fractions in both experiment are 0.2 for MF, 0.3 for GA and 0.5 for EG. It shows that the COM yields are rather uniformly reduced in the combination experiment.

In the Figure 3, the extended formation scheme for MF, GA, EG and other complex species from the CO hydrogenation is presented (Chuang *et al.* 2016). The three COM formations at low temperature can be explained by the barrier-less recombination of radicals, i.e. HCO, CH₂OH, CH₃O, that are either generated by H-atom addition/abstraction reactions on the CO-H₂CO-CH₃OH network or by UV photo-dissociation of CH₃OH (H₂CO) (Oberg 2016). For the hydrogenation scenario, ices go through successive H-addition forming fully hydrogen saturated molecule and H-abstraction reactions resulting in partially hydrogen saturated radicals or simple molecule. In these forward/backward reactions, the C-O bond is always preserved. In contrast, the UV-photons applied here (≤ 10.2 eV) cannot directly dissociate the CO ice, but the photon energy is above the dissociation energy of C-O single bond of CH₃OH (3.91 eV) resulting in CH₃ and OH radicals. This gives the UV-photolysis scenario an extra mechanism to form new products, i.e. CH₄ and H₃CC-bearing COMs (Oberg *et al.* 2009). In the combination experiment

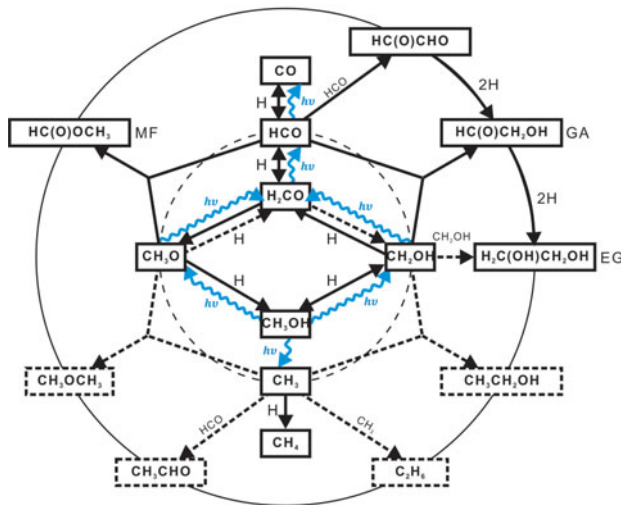


Figure 3. Extended COM formation scheme as obtained from hydrogenation and UV-photolysis experiments in CO-H₂CO-CH₃OH reaction network.

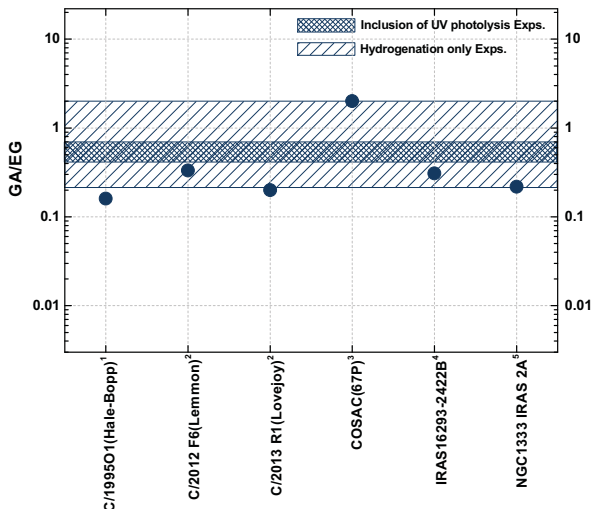


Figure 4. The GA/EG ratio derived from astronomical observations. The data are taken from (1) Crovisier *et al.* (2004) (upper limits), (2) Biver *et al.* (2014) (upper limits), (3) Goesmann *et al.* (2005), (4) Jørgensen *et al.* (2016), (5) Coutens *et al.* (2015).

of H-atoms and UV-photons, the H-atom not only has an effect on enhancing CH₄ formation, but also reduces the three COMs formation by converting the C-bearing radicals into simple H₂CO and CH₃OH.

4. ASTROCHEMICAL IMPLICATIONS AND CONCLUSIONS

Figure 4 compares the laboratory results with the data derived from observations in different astronomical environments. The GA/EG relative ratio in observations is found to be in good agreement with the experimental values of hydrogenation and UV-photolysis processing (0.3-1.5), supporting a solid-state formation pathway for GA and EG. The other ratios, MF/EG and MF/GA, are about 1–3 orders of magnitude greater than

those found in hydrogenation and UV-photolysis experiments. This is likely due to the lack of H₂CO in the initial ice (Chuang *et al.* 2016), or suggests that MF is produced via other reactions in the gas phase (Taquet *et al.* 2015). For more details on this work see (Chuang *et al.* 2017).

The take home message of these findings is that:

- In pure hydrogenation experiments, COMs can be formed without UV photons at a low *T*. Their yields and fractions depend on H-atom/CO:CH₃OH ratios and accretion rates of the involved species.

- The fractions for MF:GA:EG are 0: (0.2-0.4) : (0.8-0.6) for pure hydrogenation, and 0.2 : 0.3 : 0.5 for UV photolysis experiments.

- The GA/EG ratio observed in comets and in solar-mass proto-stars is consistent with the laboratory values (0.3-1.5), suggesting a solid-state formation pathway.

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References

- Biver, N., Bockelée-Morvan, D., Debout, V., Crovisier, J., Boissier, J., Lis, D. C., Dello Russo, N., Moreno, R., Colom, P., Paubert, G., Vervack, R., & Weaver, H. A. 2003, *ARAA*, 566, L5
- Chuang, K.-J., Fedoseev, G., Ioppolo, S., van Dishoeck, E. F., & Linnartz, H. 2016, *MNRAS*, 467, 2552
- Chuang, K.-J., Fedoseev, G., Qasim, D., Ioppolo, S., van Dishoeck, E. F., & Linnartz, H. 2017, *MNRAS*, 540, L49
- Coutens, A., Persson, M. V., Jørgensen, J. K., Wampfler, S. F., & Lykke, J. M. 2015, *ARAA*, 576, 5
- Crovisier, J., Bockelée-Morvan, D., Biver, N., Colom, P., Despois, D., & Lis, D. C. 2004, *ARAA*, 418, L35
- Fedoseev, G., Cuppen, H. M., Ioppolo, S., Lamberts, T., & Linnartz, H. 2015, *MNRAS*, 448, 1288
- Goesmann, F., Rosenbauer, H., Bredehöft, J. H., Cabane, M., Ehrenfreund, P., Gautier, T., Giri, C., Krüger, H., Le Roy, L., MacDermott, A. J., McKenna-Lawlor, S., Meierhenrich, U. J., Caro, G. M.M., Raulin, F., Roll, R., Steele, A., Steininger, H., Sternberg, R., Szopa, C., Thiemann, W., & Ulamec, S. 2005, *Science*, 349, 2
- Herbst, H. & van Dishoeck, E. F. 2009, *Annu. Rev. Astron. Astrophys.*, 47, 427
- Ioppolo, S., Fedoseev, G., Lamberts, T., Romanzin, C., & Linnartz, H. 2013, *Rev. Sci. Instrum.*, 84, 073112
- Jørgensen, J. K., Favre, C., Bisschop, S. E., Bourke, T. L., van Dishoeck, E. F., & Schmalzl, M. 2012, *ApJ(Letter)*, 757, L4
- Jørgensen, J. K., van der Wiel, M. H.D., Coutens, A., Lykke, J. M., Müller, H. S.P., van Dishoeck, E. F., Calcutt, H., Bjerkeli, P., Bourke, T. L., Drozdovskaya, M. N., Favre, C., Fayolle, E. C., Garrod, R. T., Jacobsen, S. K., Öberg, K. I., Persson, M. V., & Wampfler, S. F. 2016, *ARAA*, 595, 117
- Maity, S., Kaiser, R. I., & Jones, B. M. 2015, *Phys. Chem. Chem. Phys.*, 17, 3081
- Moore, M. H., & Hudson, R. L. 2005, *Proceedings of the International Astronomical Union*, 1, 247
- Öberg, K. I., Garrod, R. T., van Dishoeck, E. F., & Linnartz, H. 2009, *ARAA*, 504, 891
- Öberg, K. I. 2016, *Chemical Reviews*, 116, 9631

- Le Roy, L., Altwegg, K., Balsiger, H., Berthelier, J.-J., Bieler, A., Briois, C., Calmonte, U., Combi, M. R., De Keyser, J., Dhooghe, F., Fiethe, B., Fuselier, S. A., Gasc, S., Gombosi, T. I., Hässig, M., Jäckel, A., Rubin, M., & Tzou, C.-Y. 2015, *ARAA*, 583, 1
- Taquet, V., López-Sepulcre, A., Ceccarelli, C., Neri, R., Kahane, C., & Charnley, S. B. 2015, *ApJ*, 804, 81