iCOM Formation From Radical-Radical Chemistry: a Mechanistic Study Using Cryogenic Matrix, EPR Coupled to IR, and QMS-TPD

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Interstellar complex organic molecules (iCOMs) have been identified in different interstellar environments including star forming regions as well as cold dense molecular clouds¹. Laboratory studies show that iCOMs can be formed either in gas-phase or in the solid state, on icy grains, from "non-energetic" (atom-addition/abstraction) or energetic (UV-photons, particle bombardments) processes²⁻⁴.

In this contribution, using a new experimental approach mixing matrix isolation technique, mass spectrometry, and infrared and EPR spectroscopies, we want to investigate the COM formation at 35 K from a complex mixture of ground state radicals trying to draw a general reaction scheme. We photolyze (121 nm) CH₃OH diluted in argon at low temperature (below 15 K) to generate H[•]CO, HO[•]CO, [•]CH₂OH, [•]CH₃O, [•]OH and [•]CH₃ radicals and "free" H-atoms within the matrix. Radicals have been identified using infrared and EPR spectroscopies.

With the disappearance of the argon matrix (35 K), these unstable species are then free to react, forming new species in a residual solid film. Some recombination products have been detected using infrared spectroscopy and mass spectrometry in the solid film after argon removal, namely methyl formate (CH₃OCHO), glycolaldehyde (HOCH₂CHO), ethylene glycol (HOCH₂CH₂OH), glyoxal (CHOCHO), ethanol (CH₃CH₂OH), formic acid (HCOOH), dimethyl ether (CH₃OCH₃), methoxymethanol (CH₃OCH₂OH) and CH₄O₂ isomers (methanediol and/or methyl hydroperoxide).

The detected molecules are fully consistent with the radicals detected and strongly support the solid-state scenario of iCOM formation in interstellar ices based on radical-radical recombination. Most of our results are in great concordance with a recent theoretical work simulating radical-radical coupling in water clusters⁵.

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