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ASTROCHEMISTRY – QUO VADIS?

Recent space probes such as the Hayabusa 2 spacecraft to the carbonaceous asteroid Ryugu [1] and the New Horizons mission to the Kuiper Belt [2] – a doughnut-shaped region of a few 10,000 icy objects beyond the orbit of Neptune, including Pluto – have fundamentally enhanced our knowledge of the chemical makeup of the Solar System. Along with the identification of complex organics within the framework of the GOTHAM [3] and QUIJOTE [4] searches toward cold molecular clouds and star forming regions, planetary scientists and astronomers have identified some 300 molecular species in deep space predominantly in the gas phase but also in the condensed phase (ices). With the identification of complex organics – among them astrobiologically relevant molecules such as sugar derivatives, alcohols, ketones, aldehydes, carboxylic acids, and amines – expected to increase over the next decades, critical questions must be addressed how these molecules are formed in cold and often hostile environments of deep space. After all, space missions and astronomical observations probe the chemical composition of deep space (**What is there?**), but they cannot answer the key question on the formation mechanisms of molecules (**How are they formed?**). An understanding of the formation pathways of these organics requires an intimate knowledge of the underlying chemical dynamics of elementary reactions and hence their mechanisms on the molecular level. This knowledge can be obtained by conducting laboratory simulation experiments, which mimic the conditions in the gas phase (interstellar medium as well as atmospheres of planets and their moons) or condensed phase (icy surfaces of planets and their moons or ice coated interstellar nanoparticles, i.e., icy grains) in deep space following the principle “Physical Chemistry First”. Two case studies, one for gas phase reactions and another for ice chemistry, exemplify recent accomplishments and future challenges in the rapidly evolving field of astrochemistry.

Let us focus first on the gas phase formation and detection of aromatic hydrocarbons in the Taurus Molecular Cloud-1 (TMC-1). TMC-1 is characterized by number densities of 10^4 cm^{-3} and temperatures as low as 10 K. Hence, neutral–neutral reactions must be bimolecular, should not have any entrance barrier, must be exoergic, and all transition states

involved should be below the total energy of the separated reactants. Molecular beams experiments merged with computational investigations of the pertinent potential energy surface (PES) provide compelling evidence that the reaction of 1,3-butadiene (C_4H_6) with the ethynyl radical (C_2H) leads to benzene (C_6H_6) under single collision conditions. As documented in molecular beams studies, consecutive bimolecular reactions of benzene (C_6H_6) with a cyano radical forms cyanobenzene ($\text{C}_6\text{H}_5\text{CN}$), which was detected later in TMC-1. These findings clearly highlight the power of molecular beams studies to predict the formation of aromatics in deep space. The concept of aromatization can be expanded further, and molecular beams studies revealed eight fundamental mechanisms driving molecular mass growth processes in aromatics. These are

1. Hydrogen Abstraction aCetylene Addition (HACA) [5],
2. Hydrogen Abstraction Vinylacetylene Addition (HAVA) [6],
3. Phenyl Addition dehydroCyclization (PAC) [7],
4. Methylidyne Addition Cyclization Aromatization (MACA) [8],
5. Radical-Radical Reaction (RRR) [9],
6. Propargyl Addition BenzAnnulation (PABA) [10],
7. Fulvenallenyl Addition Cyclization Aromatization (FACA) [11], and
8. Phenylethynyl Addition Cyclization Aromatization (PACA) [12] (Figure 1).

Here, three mechanisms (HAVA, MACA, PACA) are bimolecular, have no entrance barrier, and are exoergic - thus fulfilling the conditions of a rapid, efficient synthesis of aromatics in cold molecular clouds. The remaining pathways have entrance barriers and/or are not of a bimolecular nature and thus they are irrelevant in TMC-1 at 10 K. However, these mechanisms could be important in high-temperature circumstellar envelopes of carbon-rich Asymptotic Giant Branch (AGB) stars and planetary nebulae as their descendants holding temperatures of a few 10^3 K. Nevertheless, despite sophisticated laboratory studies and astronomical observations, astrochemical models could not replicate the observation of abundant cyanonaphthalene molecules ($\text{C}_{10}\text{H}_7\text{CN}$) toward TMC-1 with modeled abundances falling short by three orders of magnitude. This shortcoming highlights the necessity for the incorporation of a comprehensive, chemically consistent reaction network following fundamental principles of physical chemistry (kinetics, reaction dynamics).

These aromatics represent fundamental molecular building blocks and hence the raw material of carbonaceous nanoparticles (grains), on which ice mantles of a few 100 nm can accrete at 10 K in interstellar clouds. These ices are typically water (H_2O) rich and may contain ammonia (NH_3), methane (CH_4), oxides (such as carbon monoxide (CO) or carbon dioxide (CO_2)), methanol (CH_3OH), formaldehyde (H_2CO), and even carbonyl sulfide

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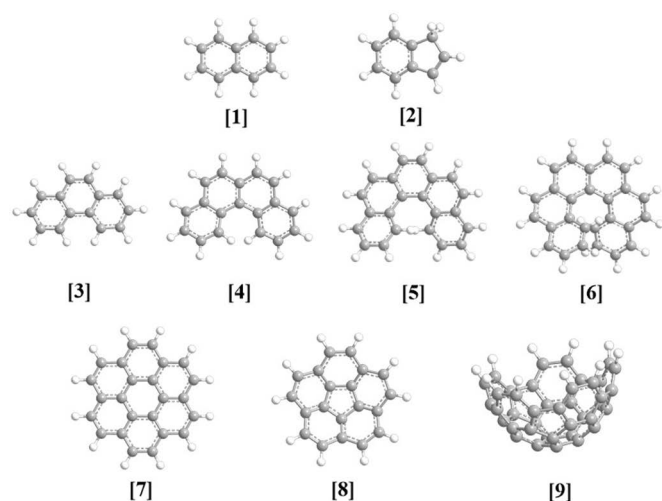


Fig. 1: Molecular structures of naphthalene ($C_{10}H_8$, 1), indene (C_9H_8 , 2), [3]-[6] helicenes (3-6), coronene ($C_{24}H_{12}$, 7), corannulene ($C_{20}H_{10}$, 8), and the C40 nanobowl ($C_{40}H_{10}$, 9) formed in the molecular beams studies.

(COS) along with sulfur dioxide (SO_2) as probed recently with the James Webb Space Telescope (JWST) in the infrared region of the electromagnetic spectrum [13]. The controversial assignment of the complex organics [13, 14] ethanol (C_2H_5OH), acetaldehyde (CH_3CHO), formic acid ($HCOOH$), and acetic acid (CH_3COOH) suffers from non-unique and hence overlapping functional groups of alcohols and organic acid. This highlights the limits of infrared spectroscopy in the detection of organics not only in laboratory simulation experiments, but also in space hence limiting the detection of individual, isomer-specific molecules in the condensed phase. However, an exposure of these ices on interstellar grains to (non) ionizing radiation in the form of high energy Galactic Cosmic Rays (GCRs) and to Lyman- α photons (VUV) drives an often existing non-equilibrium chemistry involving suprathreshold atoms such as atomic hydrogen, carbon, nitrogen, and sulfur and also radical-radical reactions. Exploiting an isomer selective photoionization (PI) reflectron time-of-flight mass spectrometry (Re-TOF-MS) (condensed phase) analysis of those molecules subliming in the temperature programmed desorption (TPD) phase, multiple key classes of organic molecules have been identified in our laboratory such as alcohols, aldehydes, ketones, and carboxylic acids. Here, it is critical to highlight that GCRs penetrate

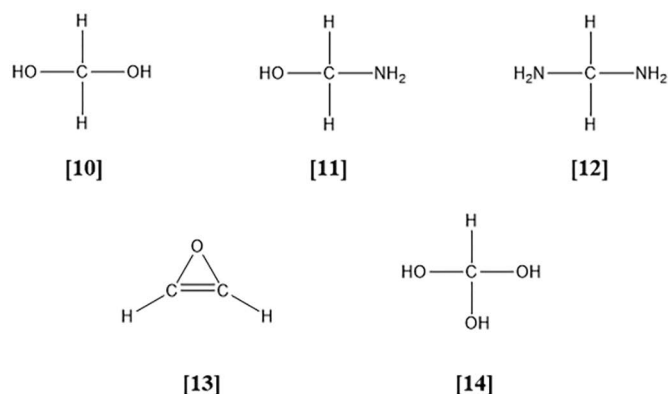


Fig. 2: Molecular structures of methanediol (10), aminomethanol (11), methanediamine (12), oxirene (13), and methanetriol (14) detected in the PI-ReTOF-MS studies.

throughout the ice-coated nanoparticles [15, 16], and evidence suggests that these processes form complex organics in the ‘bulk’ of the ices at 10 K, but not on the surface of those ices, although these processes have been favored in the astronomy community. Most importantly, PI-Re-TOF-MS has led to the detection of exotic molecules [17-21], many of which should not exist on Earth (Figure 2).

These showcases highlight the unusual chemistry in deep space which cannot be predicted by ‘paper chemistry’, but which requires novel laboratory simulation vessels incorporating PI-Re-TOF-MS and a chemical understanding from the very first principles. The recent identification of the previously ‘non-existing’ methanetriol ($CH(OH)_3$) allows us further to contemplate even more exotic species, which might be one day detected in deep space by powerful radio telescopes.

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