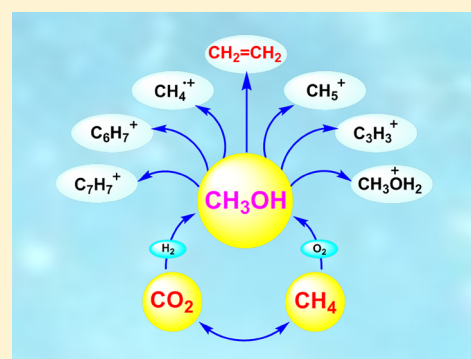


Chemical Aspects of Astrophysically Observed Extraterrestrial Methanol, Hydrocarbon Derivatives, and Ions

George A. Olah,* Thomas Mathew, G. K. Surya Prakash, and Golam Rasul

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, United States

ABSTRACT: Astrophysically observed extraterrestrial molecular matter contains, besides hydrogen and water, methane and methanol as the most abundant species. Feasible pathways and chemical aspects of their formation as well as of derived hydrocarbon homologues and their ions (carbocations and carbanions) are discussed on the basis of observed similarities with our studied terrestrial chemistry. The preferred pathway for converting extraterrestrial methane according to Ali et al. is based on CH_5^+ and Olah's related nonclassical carbonium ion chemistry. On the basis of the observed higher reactivity of methanol compared with methane in various chemical reactions, a feasible new pathway is proposed for the conversion of extraterrestrial methanol to hydrocarbons, their derivatives, and carbocations together with a possible connection with methonium ion-based chemistry.



■ INTRODUCTION

In our solar system and observable galaxies, besides dihydrogen and water (as water ice), methane^{1–5} and the recently discovered methanol^{6–12} constitute the major molecular matter. They were observed by astrophysical studies in large interstellar clouds as well as in the atmospheres of various planets, their moons (e.g., Titan, a moon of Saturn), nascent stars, and other celestial bodies (asteroids and comets). Recently, numerous organic hydrocarbon derivatives and their ions (carbocations and carbanions) have also been observed and reported by Ali et al.^{13,14} Larsson et al.,¹⁵ and Vuitton et al.¹⁶ Oka and co-workers^{17,18} pioneered the astrospectroscopic study of the parent carbonium ion (CH_5^+), which is fundamental to Olah's related nonclassical carbonium ion chemistry.^{19–24} Studies by Schlemmer and co-workers^{25,26} gave further evidence for the extraterrestrial persistence of CH_5^+ . Saladino et al.²⁷ as well as Miller and Cleaves²⁸ have investigated the formation of nucleosides, amino acids (building blocks for proteins), and other essential organic molecules under abiotic conditions. We would prefer not to use the term “organic chemistry” for abiotic hydrocarbon chemistry and astrochemistry. It was Berzelius who in 1807 first named compounds as organic or inorganic on the basis of their origin from living organisms or inanimate matter.²⁹ However, the development of extensive natural product chemistry made “organic” origin a significant part of carbon- and hydrogen-containing compounds (i.e., hydrocarbons).

Our paper deals with the abiological extraterrestrial chemical aspects of the formation and transformation (evolution) of molecular hydrocarbon matter containing the parent methane and its oxygenated analogue methanol. We further discuss feasible pathways for the chemical evolution of inanimate matter formed in space into more complex substituted

hydrocarbon molecules on the basis of comparisons with our studied terrestrial chemistry.

■ RESULTS AND DISCUSSION

Hydrocarbons and Derivatives, Carbocations, and Derived Carbanions. The elements carbon and hydrogen are needed to produce hydrocarbons. Hydrogen and helium were formed after the Big Bang that created our universe in accordance with Einstein's fundamental energy–mass interconversion relationship ($E = mc^2$). Other elements were formed by subsequent nucleosynthesis in the hot interiors of stars.^{30,31} Upon the supernova explosions of these stars, the elements were transported to Earth and other celestial bodies by asteroids and comets^{32–34} along with extraterrestrially formed molecular matter. By nuclear fusion, hydrogen was transformed into carbon, nitrogen, and oxygen and other elements.^{30,31} When oxygen was released by supernova explosions into interstellar space containing hydrogen, water was formed that is observed in major interstellar clouds. Our developing planet Earth received water from the clouds of interstellar space, transported to Earth by asteroids and comets. Over geological time, water filled up the oceans,^{32–34} as shown by Stanford University researchers on the basis of evidence from the recent studies of the Barbaton greenstone belt of South Africa.³⁴ All of our enormous amount of water thus was formed extraterrestrially and transported to earth. Similarly, molecular matter containing the essential elements C, N, O, and others was formed extraterrestrially and must have been transported by asteroids and comets to the prebiotic Earth and other planets.

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As widely discussed by astronomers, the formation of our universe happened, as generally accepted, after the Big Bang. Our study relates to the chemical aspects of the formation and evolution of hydrocarbon-based molecular matter, with its parent methane (CH_4) and its mono-oxygenated derivative methanol (CH_3OH), identified in the interstellar medium (ISM) in large quantities, as the main sources of hydrocarbon derivatives and ions (carbocations and carbanions).

The fast-developing astrophysical study of extraterrestrially observed molecules, those containing carbon and hydrogen (i.e., hydrocarbons) represent a major group of some 200 molecules (some also containing heteroatom (N and O) derivatives). In particular, significant and extensive spectroscopic data were obtained recently from the upper atmosphere of Titan (a moon of Saturn) by the Cassini spacecraft using its onboard instruments. They were studied and interpreted by Ali et al.^{13,14} and others. The analyzed data from the Ion Neutral Mass Spectrometer (INMS) and the Cassini Plasma Spectrometer (CAPS) instruments on board the spacecraft also showed the prevalence of a wide variety of carbocations similar to those studied by Olah et al.³⁵ under condensed-state terrestrial conditions in superacid media. As shown in Figure 1,

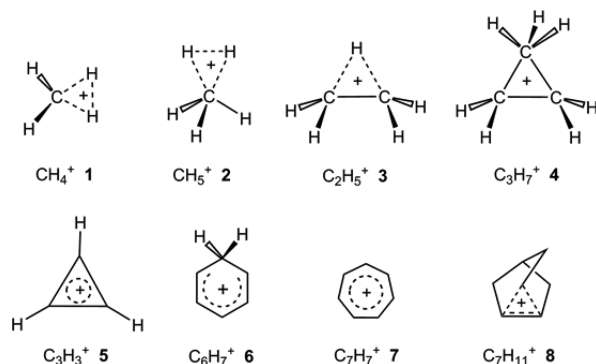


Figure 1. Plausible carbocations observed in the upper atmosphere of Titan by the analysis of data obtained from the Cassini spacecraft by Ali et al.¹⁴

they include, inter alia, alkyl cations ($\text{C}_n\text{H}_{2n+1}^+$), methane radical cation ($\text{CH}_4^{\bullet+}$), methonium ion (CH_5^+), corner-protonated cyclopropane (C_3H_7^+), cyclopropenium ion (C_3H_3^+), benzenium ion (C_6H_7^+), benzyl cation (C_7H_7^+), which could likely be the tropylium cation, and even norbornyl cation ($\text{C}_7\text{H}_{11}^+$), which besides CH_5^+ played a key role in the classical–nonclassical ion controversy and the development of carbonium ion chemistry.^{14,19,20} In their discussions, Ali et al. emphasized the role of Olah's derived nonclassical carbonium ion chemistry^{19–24} as the basis of the formation of similar “organic ions” in Titan's upper atmosphere. They also discussed the observation of simple aromatic molecules and ions (including cyclopropenium ion as the parent) and their transformation to complex bridged bi- and tricyclic hydrocarbon ions such as naphthalene and phenanthrene as well as tricyclic perinaphthenyl cations.

A significant number of related negatively charged molecular hydrocarbon ions (acetylene-based carbanions), similar to those studied by Cram and others,^{15,16,36} were also observed and discussed by Ali et al. They pointed out that the closed-shell complex carbocations can undergo electron recombination to form open-shell neutral radicals, which subsequently form carbanions via electron attachment at low temperatures with

thermal electrons. Even a series of nitrogen-containing hydrocarbon ions were observed, which included $\text{C}_{10}\text{H}_8\text{N}^+$, $\text{C}_{11}\text{H}_{10}\text{N}^+$, $\text{C}_{12}\text{H}_8\text{N}^+$, $\text{C}_{13}\text{H}_{10}\text{N}^+$, etc., and their derived anions attributable to polycyclic aromatic nitrogen-containing hydrocarbons formed via ammonia originating from N_2 and H_2 .

The astrophysical observation of large methanol clouds, not unlike methane clouds, and their derived hydrocarbon products in our solar system and galaxy^{5–11} inevitably proves their abiological origin and formation. The needed carbon, which was formed in the interiors of stars and released by supernova explosions, was dispersed into the surrounding space and combined with abundant hydrogen to form methane. Surface absorption of methane on space ice or dust facilitated the reactions in the otherwise extreme dilution of space. As oxygen was also formed in the interiors of stars, it was also dispersed together with carbon, forming carbon oxides (CO or CO_2), which with hydrogen were then able to form methanol. The conversion of carbon oxides and hydrogen to methanol takes place on the surface of space ice or dust³⁷ similar to terrestrial chemistry in Figure 2.



Figure 2. Conversion of carbon oxides to methanol.

Methanol is known as wood alcohol, which is of biological origin obtained by thermal distillation of wood. Industrially it has long been produced from syngas containing CO and hydrogen in the ratio of 1:2, now also called metgas, or by catalytic hydrogenation of CO_2 . Methane itself can also be oxygenated to methanol through metgas under recently discovered oxidative bireforming conditions, the overall process involving only the insertion of a single oxygen atom into a C–H bond of methane.^{38,39} The selective direct oxidation of methane to methanol, which was a long-attempted endeavor, can be achieved only in extremely low yields. When methanol is oxidized, it gets further converted to its thermodynamically preferred products formaldehyde, formic acid, and eventually carbon dioxide. Hydrogenation of carbon dioxide is readily achieved and is considered also to take place under extraterrestrial conditions.

The relationship of extraterrestrially observed molecules and ions with our hydrocarbon chemistry raised interest in whether studied terrestrial chemistry could also offer insight into the formation and persistence of the large interstellar clouds of methanol. In 1995, astronomers discovered a cloud of methanol (named the Sagittarius B2 cloud)^{7,12} spanning around a stellar nursery in our Milky Way galaxy. The very large cloud (288 billion miles wide) was calculated to hold more than 10 trillion trillion (10^{25}) tons of methanol! Numerous other methanol clouds have also been observed since, always close to nascent young stars.^{4–8} The formation of extraterrestrial hydrocarbons, derivatives, and ions must have taken place under abiological conditions, as to date no extraterrestrial biological life has been observed outside our planet Earth.

The question of how and through what possible pathways the observed varied hydrocarbons (including cyclic ones) as well as their carbocations and products were formed in our solar system and galaxies remains to be answered. On the basis of the analysis of the data obtained by the Cassini space mission to Titan, Ali et al. discussed their interpretation and views on

the formation of inanimate extraterrestrial molecular matter. By analogy to studied terrestrial chemistry, they suggested that methane formed in space from carbon and hydrogen was converted to its products and ions through protonation by H_3^+ , the core of hydrogen clouds (observed and studied by Oka⁴⁰), to the “nonclassical” carbonium ion CH_5^+ (methonium ion), also observed by Oka and studied through what is called “Olah’s related nonclassical carbonium ion chemistry”. This pathway is indeed reasonable by analogy with the studied related terrestrial chemistry. An additional possible pathway was considered to involve radiation-induced formation of methyl radical (CH_3^\bullet) as well as the formation of $\text{CH}_4^{+\bullet}$ and subsequent reactions to form observed products and carbocationic species.

Realizing the higher reactivity of methanol compared with methane in terrestrial chemical studies, we now suggest a new feasible pathway for the astrochemical formation of hydrocarbons, derivatives, and their carbocations from extraterrestrial methanol. As the conversion of methane to its products through carbocations according to studied chemistry is not a selective and efficient process, this can be overcome by using instead of methane a suitable derivative such as methanol. We carried out extensive studies on the development of what is now called the “methanol economy”^{41–43} and in general developed efficient methods for producing hydrocarbons and their products from CH_3OH and its protonated form, methyloxonium ion (CH_3OH_2^+). Extraterrestrial methanol clouds and methanol observed in the atmospheres of planets of the solar system and their moons, including the extensively studied Titan, indeed contain the CH_3OH_2^+ associated with excess methanol. Our chemistry has shown that under strongly protolytic conditions (i.e., in superacids), protonated methanol can be condensed to various alkyl cations, including the well-studied *tert*-butyl cation. Methanol can also form hydrocarbon analogues through an oligomerization mechanism of intermediately formed ethylene.⁴⁴

In the interstellar media, the formation of H_3^+ due to the interaction of high-energy cosmic rays with H_2 adsorbed on space dust or ice surfaces is well-recognized.^{40,45,46} This process is fast and energy-efficient (exothermic by ~ 39.2 kcal/mol). The H_3^+ associates with excess molecular hydrogen to form $\text{H}_3^+(\text{H}_2)_n$ adducts, making it persistent in interstellar hydrogen clouds.^{47,48} Methanol, being a strong n-donor nucleophile,⁴⁶ can then be readily protonated to give CH_3OH_2^+ , which associates with excess methanol to form $\text{CH}_3\text{OH}_2^+(\text{CH}_3\text{OH})_n$ adducts composing the methanol clouds. Observed extraterrestrial hydrocarbon products thus can be derived from methanol.

On the question of how methanol formation and conversion can take place in the extreme dilution of any molecular matter in cold space, science can provide the answer.⁴⁹ The reactions are not considered to take place as gaseous ion reactions with very low statistical probability of multibody collision but occur on the surface of space ice or dust particles, which allow surface accumulation, catalytic activation, and interaction using the energy of powerful space radiation.

The clouds of methanol^{6–12,50–52} (like those of methane⁵) show remarkable persistence despite being exposed to the energetic radiation in interstellar space. The remarkable resistance of methanol molecules to dissociative decomposition can be considered to be due to their existence not as “free” methanol but associated with the mentioned surfaces of space dust particles or methanol ice. The surface of the dust or ice

species is not smooth but contains imperfections that help association to take place, as shown in laboratory experiments approximating the composition of such systems. Stabilization against radiative dissociation also is assisted by the discussed presence of its protonated form CH_3OH_2^+ (not unlike CH_5^+) associated with neutral CH_3OH (H_2 or CH_4) via weak bonding interactions. This was experimentally shown by Kebarle and co-workers^{53–56} and others^{57–59} in their gas-phase ion cyclotron and vibrational spectroscopic experimental studies of such clusters (Figure 3). Eventually radiative dissociation of

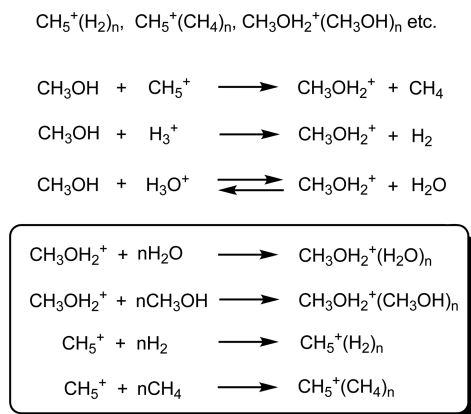


Figure 3. Stabilization of extraterrestrial methane and methanol by the formation of associated ion clusters.

methanol (even in its protected ion clusters) must take place, but continuing new formation compensates for this, maintaining the observed steady-state concentration.

As discussed above, numerous carbocations derived from various aliphatic hydrocarbons as well as a significant number of aromatic, polyaromatic, and heteroaromatic hydrocarbons have been discovered by astrophysical observations.^{12,13,60} This shows that under suitable extraterrestrial conditions, a single carbon-containing building block can produce a large variety of hydrocarbons and their heteroatom derivatives. A possible path for the astrochemical synthesis of ethylene and propylene from methanol is also suggested to involve coupling reactions by an “astrochemical methanol to olefins (MTO)” process under the influence of high-energy cosmic rays on suitable dust or ice particles prevalent in interstellar space (Figure 4). Radiation-

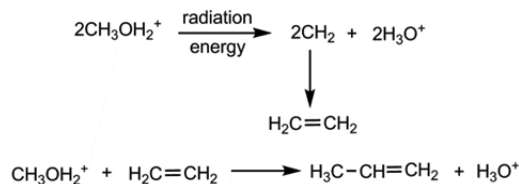


Figure 4. Astrochemical methanol to olefin (MTO) conversion.

induced monomolecular dehydration of methanol may also lead to singlet methylene, which can undergo dimerization to afford ethylene. Ethylene can then react further with singlet methylene to provide propylene through the cyclopropane intermediate.

Subsequent reactions of ethylene and propylene can give homologous acyclic and cyclic hydrocarbons and their carbocations. Such ions can also aromatize under high-energy radiation conditions and by subsequent protonation to give the

observed cyclic and polycyclic aromatic ions. In the studied hydrocarbon chemistry, such conversions were reported in the 1980s both over acidic zeolites (ZSM-5) by the Mobil research team^{61,62} (who developed it into a commercial process) and via bifunctional acid–base catalysis by Olah et al.^{44,63–65}

Interestingly, in our computational studies, we have found that the conversion of methanol to ethylene could also follow a pathway involving astrochemical protolytic cleavage of CH_3OH_2^+ to give CH_5^+ , which then would undergo radiation-induced cleavage to give singlet methylene, which can dimerize to afford ethylene. The reaction of CH_3OH_2^+ with H_3^+ to form CH_5^+ is computed to be exothermic ($\Delta H = -41.7$ kcal/mol; Figure 5, eq 2), making it a thermodynamically

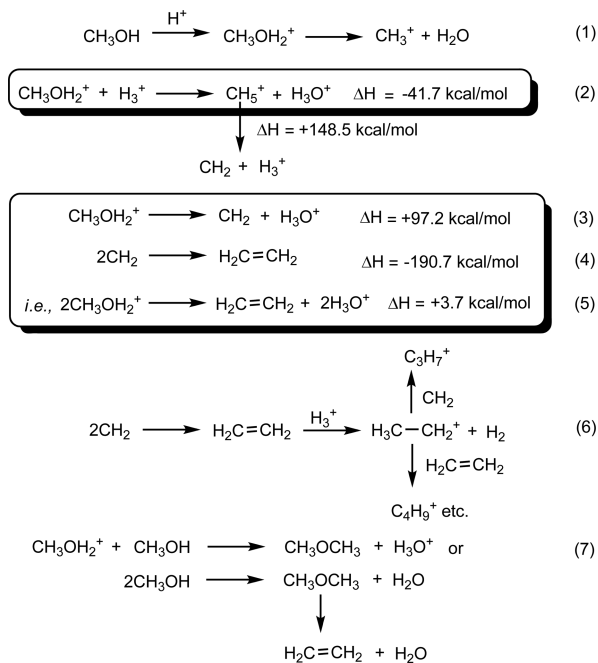


Figure 5. Plausible astrochemical pathways of methanol to ethylene conversion.

favorable process. Although cleavage of CH_3OH_2^+ to give singlet methylene is an endothermic process ($\Delta H = +97.2$ kcal/mol; Figure 5, eq 3), the subsequent dimerization to form ethylene is a highly exothermic process ($\Delta H = -190.7$ kcal/mol; Figure 5, eq 4) under terrestrial conditions. Although the feasibility of these reactions is low under extraterrestrial conditions such as varying temperatures (extremely low to high) and high-energy radiation, optimal circumstances may arise and lead to favorable conditions. The structures, energies, and zero-point vibrational energies (ZPEs) of the structures were computed at the CCSD(T)/cc-pVTZ + ZPE level.⁶⁶

Whereas this pathway (Figure 5, eq 2) is considered less probable than the direct conversion of methanol because of charge–charge repulsion, it points out a feasible connection of the methonium ion chemistry with methanol conversions. It is significant that extraterrestrial methane and methanol have been shown to be readily capable of undergoing thermodynamically feasible protolytic formation of CH_5^+ (and thus related carbonium ion chemistry). However, as shown in Figure 5, methanol can follow the favorable direct MTO conversion to its derivatives and carbocations through its protonated form, CH_3OH_2^+ . These pathways represent conversion based on

similarities to observed hydrocarbon products and ions under differing conditions.

The observation of extraterrestrial hydrocarbons and their heteroatom derivatives and ions is very significant.^{13–15} As mentioned above, besides carbocations they also include carbanions such as C_4H^- , C_6H^- , and C_8H^- involving polyalkyne-like structures, which are formed by electron attachment. Observed nitrogen-containing anions include CN^- and CCCN^- , the latter derived from cyanoacetylene by radiative electron attachment processes.^{13–15,67}

The conversion of energy released by the Big Bang into various subatomic particles, which through their combination subsequently formed hydrogen and, by eventual nucleosynthesis under suitable conditions in the hot interiors of stars, carbon and other elements. Upon their dispersion into the surrounding space following the supernova explosions of their stars' extinction, varied molecular matter including hydrocarbons was formed. Our discussions have centered so far on the simplest C_1 hydrocarbon molecule, methane, and its oxygen-containing analogue methanol. Through their abiobiochemical transformation, a plethora of hydrocarbons, their derivatives, and ions were formed, as recently detected most significantly by the Cassini–Huygens spacecraft orbiting Saturn's moon Titan since 2004.^{13–15}

In the interstellar clouds and the atmospheres of planets, comets, and asteroids, besides H_2O , CH_3OH , and CH_4 , carbon oxides (CO , CO_2), formaldehyde (CH_2O), ammonia (NH_3),⁶⁸ and other species, including significant amounts of formamide (NH_2CHO), the simplest amide and key building block for the synthesis of amino acids and peptides,^{26,68–70} have been detected. The Philae Lander of the remarkable Rosetta space mission of the European Space Agency even landed on a comet (67P/Churyumov-Gerasimenko) and sent back data from its on-board mass spectrometer on the analysis of sampled matter of the comet.⁷¹ These data revealed the presence of CHO-bearing organics consistent with their formation from formaldehyde and acetaldehyde.⁷² The data also showed the presence of some 16 other “organic” compounds, including formamide.⁷³ Even molecular oxygen was detected. From simulated laboratory experiments, Marcellus et al.⁶⁸ suggested that a mixture of CO , CO_2 , CH_3OH , NH_3 , and CH_4 mimicking a dense molecular cloud and its prevailing conditions produced a mixture with 10 analogue aldehydes, including sugar-related glycolaldehyde and glyceraldehyde, which are considered to be two key prebiotic intermediates in the first step toward the formation of ribonucleotides. Studies showed the formation of activated pyrimidine ribonucleotides from glycolaldehyde and glyceraldehyde under prebiotically plausible conditions.⁷⁴

Significant further experimental study under simulated conditions was carried out by Saladino et al.²⁷ mimicking the conversion of formamide under extraterrestrial conditions. When formamide was irradiated by a high-energy proton beam in the presence of various powdered meteorites and the products were analyzed by mass spectrometry, they found an extremely rich abiobiochemical mixture of products including amino acids, carboxylic acids, nucleobases, sugars, and, most significantly, all four nucleoside bases: cytidine, uridine, adenosine, and thymidine. They suggested that the mechanism for their formation involves the cyanide radical (CN^\bullet). Other studies showed the presence of extraterrestrial amino acids or even simple proteins as well as various carbohydrates,^{75,76} which are building blocks of life.

The detection of various “organic” molecules (or their precursors) in extraterrestrial molecular clouds, in the atmospheres of planets and their moons, and, even more significantly, on comets and meteorites shows that all of these extraterrestrial building blocks were abiologically formed in our solar system. They were transported to the favorable “Goldilocks” conditions of Earth, where they were able to undergo further evolutions into increasingly complex molecular systems forming biological life.

SUMMARY

The merit of advancing our knowledge of the composition and relevance of extraterrestrial molecular matter, including hydrocarbons, their derivatives, and ions, in our solar systems (and even in some of our observable galaxies) goes primarily to astrophysicists and their pioneering observations quoted in our paper. It is hoped that chemical interpretation based on similarities with our studied terrestrial chemistry as mentioned in this paper will significantly enhance the understanding of our universe.

METHODS

The results of our experimental work are discussed in our cited publications. Comparisons and conclusions were made by evaluating recently published and quoted astrophysical observations. Quantum-chemical calculations of structures, energies, and frequencies were carried out at the CCSD(T)/cc-pVTZ + ZPE level and show the feasible interconversion of the CH_5^+ -based and CH_3OH_2^+ -based chemical transformation pathways.

AUTHOR INFORMATION

Corresponding Author

*olah@usc.edu

Notes

The authors declare no competing financial interest.

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