

A study of interstellar aldehydes and enols as tracers of a cosmic ray-driven nonequilibrium synthesis of complex organic molecules

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Edited by R. D. Levine, The Fritz Haber Research Center, Jerusalem, Israel, and approved May 20, 2016 (received for review March 17, 2016)

Complex organic molecules such as sugars and amides are ubiquitous in star- and planet-forming regions, but their formation mechanisms have remained largely elusive until now. Here we show in a combined experimental, computational, and astrochemical modeling study that interstellar aldehydes and enols like acetaldehyde (CH₃CHO) and vinyl alcohol (C₂H₃OH) act as key tracers of a cosmic-ray-driven nonequilibrium chemistry leading to complex organics even deep within low-temperature interstellar ices at 10 K. Our findings challenge conventional wisdom and define a hitherto poorly characterized reaction class forming complex organic molecules inside interstellar ices before their sublimation in star-forming regions such as SgrB2(N). These processes are of vital importance in initiating a chain of chemical reactions leading eventually to the molecular precursors of biorelevant molecules as planets form in their interstellar nurseries.

astrochemistry | suprathreshold chemistry | photoionization | organics | low-temperature kinetics

For more than half a century, gas-phase reaction networks of rapid ion–molecule (1) and neutral–neutral reactions (2) have played a fundamental role in aiding our understanding of the evolution of the interstellar medium (ISM). However, with about 200 molecules detected in interstellar and circumstellar environments (3), these models fail to explain the synthesis of ubiquitous complex organic molecules (COMs)—organics containing several atoms of carbon, hydrogen, nitrogen, and oxygen (Fig. 1)—predicting abundances which are lower by several orders of magnitude compared with observations toward hot molecular cores like Sagittarius B2(N) (4). Because COMs constitute more than one-third of all detected interstellar molecules—among them vital precursors to molecular building blocks of life such as the sugar glycolaldehyde (HCOCH₂OH) (5)—the elucidation of their formation routes will unravel the most fundamental processes that drive the hitherto poorly understood interstellar organic chemistry (6) and define the molecular complexity of organic molecules, which can be synthesized in our galaxy (7), thus ultimately predicting where else in the universe the molecular precursors to the origins of life might be synthesized (8). Origins of life can be summarized as the events producing living systems from nonliving systems (9).

Because gas-phase reactions hardly reproduce the number densities of observed COMs in the interstellar medium, COMs were proposed to be first synthesized on interstellar grains—silicate-based nanoparticles coated with a few hundred nanometers of water (H₂O), methanol (CH₃OH), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), formaldehyde (H₂CO), and ammonia (NH₃) ices (10)—in molecular clouds at 10 K and then suggested to sublime into the gas phase in star-forming regions once the temperature of the grains rises due to the “switch on” of the central star (4). However, even these gas-grain networks could not replicate the observed abundances of

COMs, implying that key production pathways to COMs are still elusive. The crucial drawback of existing models is the assumption of an ice mantle of which only the first few monolayers participate in an active chemistry via diffusion-limited thermal surface reactions (11). This conjecture limits the validity of preceding gas–grain reaction networks because laboratory studies provided compelling evidence that an interaction of ionizing radiation in the form of cosmic rays and their secondary electrons with interstellar ices forms COMs as complex as sugars (12), amino acids (13), and dipeptides (14). Therefore, these considerations imply that the key reaction class—a cosmic-ray-induced nonequilibrium chemistry—has been overlooked for the last decades as a source of COMs deep within interstellar ices and that an intimate understanding of the underlying pathways to form COMs in the ISM on icy grains is still in its infancy.

Here, we report that interstellar aldehydes and enols such as the acetaldehyde (CH₃CHO)–vinyl alcohol (C₂H₃OH) and propanal (C₂H₅CHO)–1-propenol [CH₃CHCH(OH)] isomer pairs (6) act as fundamental tracers of a vigorous cosmic-ray-driven nonequilibrium chemistry transpiring throughout low-temperature ices in cold molecular clouds (reactions 1 and 2; Fig. 1). By combining our experimental results with novel astrochemical models, we expose that these processes operate even at temperatures as low as 10 K within interstellar ices and represent the key reaction class resulting in a facile synthesis of COMs via previously poorly explored cosmic-ray-triggered reaction pathways. Interstellar aldehydes and their enol tautomers exemplify the

Significance

Since the detection of the methylidyne radical (CH) in the interstellar medium nearly 80 y ago, about 200 molecules ranging from molecular hydrogen to fullerenes have been identified in interstellar and circumstellar environments, but the synthesis of complex organic molecules (COMs)—organics containing several atoms of carbon, hydrogen, nitrogen, and oxygen—has remained elusive to date. Here, we provide compelling evidence via laboratory experiments, computations, and modeling that the synthesis of COMs is driven by a cosmic-ray-triggered nonequilibrium chemistry within interstellar ices at temperatures as low as 10 K. These fundamental reaction mechanisms are of major significance to facilitate an understanding of the origin and evolution of the molecular universe.

Author contributions: R.I.K. designed research; M.J.A. performed research; S.G., A.I.K., C.N.S., and E.H. contributed new reagents/analytic tools; M.J.A., S.G., A.I.K., C.N.S., E.H., and R.I.K. analyzed data; and M.J.A., S.G., A.I.K., C.N.S., E.H., and R.I.K. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1604426113/-DCSupplemental.

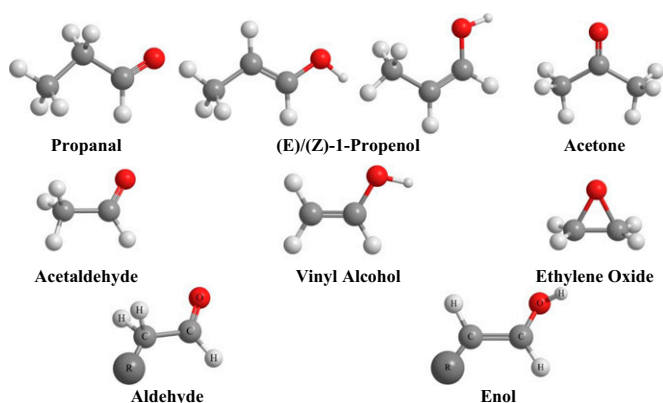
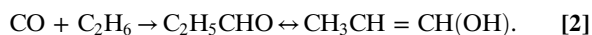
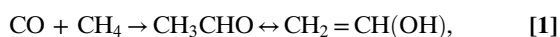


Fig. 1. Structures of two sets of structural isomers (C_3H_6O , C_2H_4O) of COMs. All molecules shown, except propenol, have been detected toward Sagittarius B2. A generic representation of the aldehyde–enols tautomer pair is shown at the bottom with “R” denoting an organic side group.

simplest members of a whole class of COMs, even including biorelevant molecules such as sugars, first synthesized via non-traditional chemistry deep within interstellar ices in molecular clouds and then released by sublimation in star-forming regions such as Sagittarius B2 ultimately unraveling how and where in the universe the molecular precursors to the origins of life might have been synthesized.



The experiments were conducted in an ultrahigh-vacuum (UHV) surface-science chamber at pressures of a few 10^{-11} torr (15) by exposing ices of carbon monoxide (CO) and methane (CH_4) or carbon monoxide and ethane (C_2H_6) to energetic electrons at 5 K. This mimics the processing of apolar interstellar ices via secondary electrons that are generated by galactic cosmic rays for a few 10^6 years (16), which represents the typical lifetime of interstellar ices in cold molecular clouds (*SI Appendix, Experimental Approach*). The chemical modifications of the ices and the development of functional groups were probed online and in situ via Fourier transform infrared spectroscopy (FTIR; Nicolet 6700) (*SI Appendix, Fig. S1 and Table S1*). After the irradiation the ices were heated to 300 K, via temperature-programmed desorption (TPD), to release the molecules into the gas phase. During the TPD process, individual subliming molecules were ionized via single vacuum UV (VUV) photon ionization and mass-resolved in a reflectron time-of-flight mass spectrometer. These apolar interstellar model ices composed of carbon monoxide with methane or ethane under anhydrous conditions were chosen to explore the proof of concept that enols along with their keto tautomers can be formed via interaction with ionizing radiation. Accounting for data from the Spitzer space telescope, ices containing CO at levels of up to 50% were observed toward high-mass star-forming regions (17). Apolar mixtures with methane (CH_4) at levels of up to 11% were also confirmed (17). It should be noted that ethane (C_2H_6) has not yet been detected on interstellar grains, but laboratory experiments verify that ethane can be formed easily by subjecting methane-bearing ices to ionizing radiation. The use of interstellar analogue ices presents a validated approach and very first step as verified by Ehrenfreund et al. (18).

Results

Laboratory Experiments: Mass Spectrometry. The mass spectra of the subliming molecules are recorded as a function of temperature

exploiting photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) (Fig. 2). The TPD profiles relevant to the acetaldehyde–vinyl alcohol ($C_2H_4O^+$; $m/z = 44$) and propanal–1-propenol ($C_3H_6^{18}O^+$; $m/z = 60$) tautomers are compiled in Fig. 3 for the CO– CH_4 and ^{18}CO – C_2H_6 systems. Note that n-butane (C_4H_{10} ; 58 amu) represents a major product in ethane-irradiated ices. Because n-butane can also be ionized under our experimental conditions, the $C_4H_{10}^+$ ion counts would interfere with those from the ionized C_3H_6O isomers (58 amu). Therefore, experiments were conducted with $C^{18}O$ instead of $C^{16}O$ to shift the masses by 2 amu to 60 amu ($C_3H_6^{18}O$). The ionization energies (IEs) of acetaldehyde (IE = 10.23 eV) (19) and of vinyl alcohol (IE syn = 9.17 eV; IE anti = 9.30 eV) (20) allow the distinction of both species by conducting two experiments and recording the TPD profiles of $m/z = 44$ at photoionization energies of 10.49 and 9.80 eV. Carbon dioxide (CO_2 ; IE = 13.77 eV) (21) and propane (C_3H_8 ; IE = 10.94 eV) (22) cannot be photoionized at 10.49 eV; this results in a contamination-free TPD profile. A third C_2H_4O isomer, ethylene oxide, has an ionization energy of 10.56 eV (23) and, hence, cannot contaminate the signal at $m/z = 44$. The TPD profile at 10.49 eV, which results from photoionization of both acetaldehyde and vinyl alcohol, exhibits a bimodal structure peaking at 117 and 147 K (Fig. 3A); in contrast, the TPD profile collected at 9.80 eV (Fig. 3B), at which energy only vinyl alcohol can be photoionized, depicts a single maximum at 147 K. We also conducted a separate calibration experiment by subliming carbon monoxide–methane ices doped with acetaldehyde without prior radiation exposure (Fig. 3C), suggesting that acetaldehyde can be attributed to the early sublimation event. A calibration experiment using vinyl alcohol is not possible as it is unstable and not commercially available, and therefore the only way to definitively determine if vinyl alcohol was present is to conduct a tunable photoionization experiment. To summarize, our findings indicate that the irradiation of the carbon monoxide–methane ices leads to the formation of both acetaldehyde and vinyl alcohol.

The TPD profiles of the irradiated carbon monoxide–ethane system depict an equivalent trend (Fig. 3 D–F) to the carbon monoxide–methane ices, revealing that both the aldehyde (propanal) and the enol [(E)/(Z)-1-propenol] are formed. No attempt was made to discriminate between the Z and E isomers.

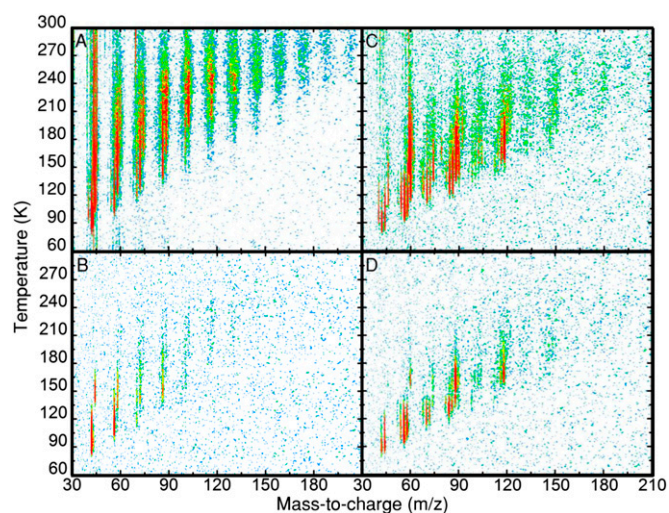


Fig. 2. PI-ReTOF-MS data recorded at photon energies of 10.49 and 9.80 eV as a function of temperature of the newly formed products subliming into the gas phase from the irradiated carbon monoxide–methane [(CO– CH_4): (A) 10.49 eV; (B) 9.80 eV] and carbon monoxide–ethane ices [$C^{18}O$ – C_2H_6): (C) 10.49 eV; (D) 9.80 eV].

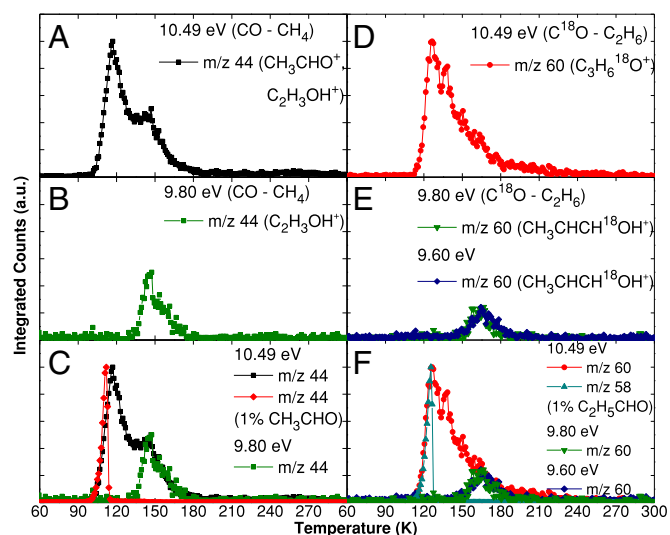


Fig. 3. (Left) PI-ReTOF-MS data at $m/z = 44$ for the CO-CH₄ system recorded at (A) 10.49 eV (black), (B) 9.80 eV (green), and (C) overlay of 10.49 eV (irradiated sample, black; 1% calibration, red) and 9.80 eV (green). (Right) PI-ReTOF-MS data at $m/z = 60$ for the C¹⁸O-C₂H₆ system recorded at (D) 10.49 eV (red), (E) 9.80 eV (green), and 9.60 eV (blue), and (F) overlay of 10.49 eV (irradiated sample, red; 1% calibration, cyan), 9.80 eV (green), and 9.60 eV (blue).

To discriminate between propanal (IE = 9.96 eV) (24), acetone (IE = 9.70 eV) (25), 2-propenol (IE = 9.67 eV) (26), and (E)/(Z)-1-propenol (IE = 8.64 eV/8.70 eV) (27), experiments at four photoionization energies (10.49, 9.80, 9.60, and 8.40 eV) were conducted. The experiment at 10.49 eV should photoionize all isomers if present; the photoionization energy of 9.80 eV could only lead to ion counts from acetone, 2-propenol, and (E)/(Z)-1-propenol; 9.60-eV photons only ionize (E)/(Z)-1-propenol, whereas 8.40-eV photons should not yield any signal. The TPD profile of 10.49 eV (Fig. 3D) displays a broad sublimation event peaking at 127 K. A reduction of the photoionization energy to 9.80 and 9.60 eV (Fig. 3E) results in identical TPD profiles peaking at a higher temperature of about 165 K. Also, there is no signal in the range from 110 to 150 K. Because the 9.80- and 9.60-eV experiments were conducted at energies below the ionization energy of propanal, the sublimation event in the 10.49-eV experiment from 110 to 150 K must be attributed to propanal. Further, because the TPD patterns at 9.80 and 9.60 eV are identical and hence overlap, we can conclude that the acetone/2-propenol isomers, which cannot be ionized with 9.60-eV photons, were not formed, and signal at 9.60 eV can be attributed solely to the (E)/(Z)-1-propenol tautomers. The experiment conducted with an energy of 8.40 eV resulted in no signal at the mass of interest, showing that there were no other contributors to the signal at $m/z = 60$. We also carried out a calibration experiment by subliming carbon monoxide-ethane ices doped with propanal (Fig. 3F), revealing that the onset of the propanal sublimation at 110 K agrees nicely with the start of the sublimation profile in the irradiation experiment. Consequently, the overlay of the tunable experiments (10.49, 9.80, and 9.60 eV) and the calibration study depicts a nice match between the experiments (Fig. 3F), demonstrating that both the aldehyde (propanal) and the enol [(E)/(Z)-1-propenol] are formed.

Therefore, the PI-ReTOF-MS data provide conclusive evidence on the detection of two keto-enol tautomer pairs: acetaldehyde-vinyl alcohol and propanal-(E)/(Z)-1-propenol. Because the photoionization cross-sections of these molecules at 10.49 eV are available, we can also determine their branching ratios to be 2.68 ± 1.02 (acetaldehyde versus vinyl alcohol), 3.20 ± 0.80

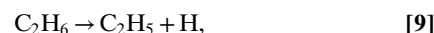
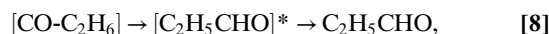
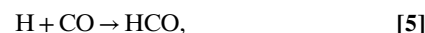
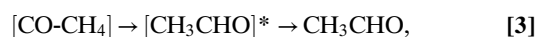
[propanal versus (E)-1-propenol], and 4.23 ± 0.96 [propanal versus (Z)-1-propenol], i.e., a dominating formation of the thermodynamically favorable aldehyde compared with the enol (SI Appendix, Determination of Keto-Enol Branching Ratios and Tables S2 and S3).

Laboratory Experiments: Infrared Spectroscopy. After the acetaldehyde-vinyl alcohol and propanal-(E)/(Z)-1-propenol tautomer pairs were identified, the focus was shifted to the potential formation pathways. This was accomplished by analyzing the absorption features of the newly synthesized molecules in the ices during and after the irradiation qualitatively and quantitatively. During the radiation exposure of the ices, several new absorption features emerged (SI Appendix, Fig. S1 and Table S1). In both systems, the formyl radical (HCO; HC¹⁸O), the main building block of the aldehydes of interest, was traced via the ν_3 fundamental centered at 1,853 and 1,811 cm⁻¹, respectively. Likewise, the methyl (CH₃) and ethyl (C₂H₅) radicals, which represent the alkyl moieties of acetaldehyde (CH₃CHO) and propanal (C₂H₅CH¹⁸O), respectively, were detected via their ν_2 and ν_{10} modes at 613 cm⁻¹ and 3,105 cm⁻¹, respectively, in the methane- and ethane-bearing ices. Besides these radicals, the carbonyl functional group (C=O) was monitored in the range of 1,790–1,600 cm⁻¹ and 1,740–1,600 cm⁻¹ for the methane- and ethane-bearing systems, respectively. The deconvolution of these features suggest that the absorptions at 1,728 cm⁻¹ and 1,715 cm⁻¹ can be attributed to the carbonyl stretching modes of acetaldehyde (CH₃CHO) and propanal (C₂H₅CH¹⁸O) synthesized during the exposure to ionizing radiation at 5.5 K. Further fundamentals associated with acetaldehyde were monitored at 1,427 cm⁻¹, 1,350 cm⁻¹, and 1,120 cm⁻¹ in the carbon monoxide-methane ices (16). Fundamentals which can account for vinyl alcohol arose at 3,239 cm⁻¹, 1,635 cm⁻¹, and 1,130 cm⁻¹ as well (28–30). Moreover, within the irradiated carbon monoxide-ethane ice, absorptions emerged at 1,715 cm⁻¹ and 1,693 cm⁻¹ for propanal (31) and at 1,435 cm⁻¹ and 1,340 cm⁻¹ for (E)/(Z)-1-propenol (32) (SI Appendix, Table S4). However, although possible fundamentals of acetaldehyde-vinyl alcohol and propanal-(E)/(Z)-1-propenol were observed, it should be stressed that these features and the carbonyl stretches in particular might also have contributions from higher molecular weight aldehydes with similar group frequencies as the molecules of interest (33).

The development of the infrared intensities at 1,728 cm⁻¹ and 1,715 cm⁻¹ versus temperature in the warm-up phase validated to what extent the carbonyl stretches were associated with acetaldehyde and propanal along with higher members of the aldehydes. Therefore, a decrease in the respective infrared intensities correlated with the rise of signal at $m/z = 44$ (CH₃CHO⁺) and $m/z = 60$ (C₂H₅CH¹⁸O⁺) as traced via PI-ReTOF-MS (SI Appendix, Figs. S2 and S3). This method is also applied for the enol tautomer of vinyl alcohol (1,635 cm⁻¹; $m/z = 44$, C₂H₃OH⁺) and (E)/(Z)-1-propenol (1,340 cm⁻¹; $m/z = 60$, CH₃CHCH¹⁸OH⁺). Once TPD started, the integrated area of the methyl and formyl radical absorptions remained constant until 10 K in the carbon monoxide-methane samples; the ethyl and formyl radical concentrations were unchanged until 15 K in the carbon monoxide-ethane experiments. The further increase of temperature resulted in diminished intensities of the methyl, ethyl, and formyl radical absorptions. However, as these intensities decreased, the infrared absorptions associated with acetaldehyde (CO-CH₄; 1,728 cm⁻¹) and propanal (C¹⁸O-C₂H₆; 1,715 cm⁻¹) increased by 15% and 27% until the temperature reached 16 K and 28 K, respectively (SI Appendix, Figs. S2 and S3). Therefore, we concluded that the majority of the aldehydes were synthesized during the radiation exposure via non-equilibrium chemistry and only a minor amount was formed during the warm-up phase of the experiment. The absorptions associated with acetaldehyde and propanal decreased thereafter and were no longer detected at 275 K and 168 K,

respectively. It is important to stress that the enol infrared bands showed no increase in signal once TPD was started though; this finding supported the conclusion that the enol production was due to nonequilibrium chemistry, but not via thermal (radical–radical recombination) reactions. The continuous in situ monitoring of the ice during the TPD protocol enabled the determination of what portion of the FTIR bands of the closed shell products correlated with the PI-ReTOF-MS mass signal at $m/z = 44$ and 60 . However, there was still an infrared signal at $1,728\text{ cm}^{-1}$ and $1,715\text{ cm}^{-1}$ detected after the sublimation of acetaldehyde and propanal, respectively (SI Appendix, Figs. S2 and S3). Therefore, the subtraction of signal due to higher molecular weight molecules contributing to the infrared band provided a correction factor so that the actual abundances of the molecule of interest could be constrained. Under the assumption that the change in the associated infrared band was due to the corresponding sublimation event, acetaldehyde (101–144 K), vinyl alcohol (132–174 K), propanal (113–164 K), and (E)/(Z)-1-propenol (146–185 K) were determined to contribute 19%, 9%, 7%, and 5%, respectively, to their infrared bands (SI Appendix, Figs. S2 and S3).

It is crucial to highlight that the FTIR spectroscopy of the ices during the irradiation and the TPD phase coupled with the PI-ReTOF-MS analysis of the subliming molecules reveal that the aldehydes and enols are synthesized essentially during the radiation exposure within the ices at 5 K without the requirement of previously speculated diffusion-limited reactions of thermalized radicals. The formation of the acetaldehyde was rationalized by the pseudo-first-order decomposition of a methane–carbon monoxide complex in the ice via formation of internally excited acetaldehyde $[\text{CH}_3\text{CHO}]^*$, which was stabilized by the matrix via phonon interaction to acetaldehyde (CH_3CHO) (reaction 3) (16). Alternatively, there is the formation of a methyl radical (CH_3) and a suprathermal hydrogen atom (H), triggered by the carbon–hydrogen bond rupture within the methane molecule. The latter can then overcome the barrier of addition (11 kJ mol^{-1} ; reactions 4 and 5) to add to the carbon monoxide molecule which will form the formyl radical (HCO). When the formyl radical resides in a proper recombination geometry with the methyl radical (CH_3), they can recombine to internally excited acetaldehyde $[\text{CH}_3\text{CHO}]^*$ within the matrix cage (reaction 6). If the recombination geometry is not favored, they reside in the ice matrix as evident from their infrared detection via their ν_3 and ν_2 fundamentals. Once stabilized, acetaldehyde could isomerize via hydrogen shift to vinyl alcohol ($\text{C}_2\text{H}_3\text{OH}$) with the energy supplied from the energetic electrons (reaction 7). In an analogous reaction sequence, the propanal ($\text{C}_2\text{H}_5\text{CHO}$)–(E)/(Z)-1-propenol $[\text{CH}_3\text{CHCH}(\text{OH})]$ tautomer could be synthesized (reactions 8–12). It should be noted that previous experiments demonstrated that the interaction of energetic electrons with ethane led to a carbon–hydrogen bond rupture, but not carbon–carbon bond cleavage (34). Recall that although acetaldehyde and propanal may have some thermal contributions due to their signals, it is important to point out that the enol isomers did not show any increase in intensity during TPD, which reinforces that the enol isomers are formed solely via nonequilibrium pathways during the irradiation phase of the experiment. Finally, it shall be highlighted that the involvement of cosmic-ray-triggered nonequilibrium processes within the ices is also documented by the energetics of the reactions to form acetaldehyde and vinyl alcohol from methane and carbon monoxide with the overall reactions being endoergic by 20 and 52 kJ mol^{-1} , respectively, thus excluding exoergic thermal reaction mechanisms as their source of formation. The associated rate constants are derived in SI Appendix, Experimental Approach and Fig. S4.



Astrochemical Modeling. Having established that acetaldehyde–vinyl alcohol and propanal–1-propenol are formed in interstellar analogue ices during the radiation exposure via nonequilibrium chemistry, astrochemical models were used to transfer these findings from the laboratory to the “real” interstellar medium. This was essential because experiments under laboratory conditions can hardly mimic all chemical and physical conditions in the interstellar medium simultaneously, where both the ice mantles contain large numbers of molecules and where the bombardment of dust grains occurs via cosmic rays followed by secondary electrons generated within the ices with a wide range of high energies (35) (SI Appendix, Experimental Approach). Further, the time the ices were processed in laboratory simulation experiments will always be faster than in the real interstellar medium; this was also accounted for in the simulations. The efficiency of the cosmic-ray-induced chemistry was determined in these simulations by exploiting a network of gas-phase and novel reactions within the ices including cosmic-ray-triggered acetaldehyde and vinyl alcohol formation (36, 37) (SI Appendix, Tables S5–S7). The models were limited to this isomer pair because 1-propenol has not been observed in the interstellar medium and hence a comparison of the models with astronomical observations would be hindered. Because acetaldehyde is observed over such a wide area in SgrB2(N), where vinyl alcohol has also been detected, the physical conditions were chosen such that they represent the average of conditions pertinent to these isomers covering both low- and high-temperature (star-formation) regions (38, 39). First, networks mimicking quiescent isothermal average conditions with a gas density of 10^4 cm^{-3} without the incorporation of the nonequilibrium ice chemistry via reactions 3–7 underproduced acetaldehyde and vinyl alcohol by up to 4 orders of magnitude. The models produced column densities of $5.6 \times 10^{11}\text{ molecules cm}^{-2}$ compared with observed values toward SgrB2(N) of $2.2 \pm 1.1 \times 10^{14}\text{ molecules cm}^{-2}$ for acetaldehyde and $1.7 \times 10^{10}\text{ molecules cm}^{-2}$ compared with observed column densities of $2.2 \pm 0.8 \times 10^{14}\text{ molecules cm}^{-2}$ for vinyl alcohol, respectively, at an age of 10^6 years—a typical age for dense clouds (39) (Fig. 4). In these models, acetaldehyde was mainly produced via the gas-phase reaction of ground-state atomic oxygen with the ethyl radical (C_2H_5) (40). Second, models that incorporated the novel nonequilibrium chemistry (reactions 3–7) provided an exceptional agreement between the theoretically predicted ($2.75 \pm 0.06 \times 10^{14}\text{ cm}^{-2}$) and observed values toward SgrB2(N) of $2.2 \pm 1.1 \times 10^{14}\text{ molecules cm}^{-2}$ for

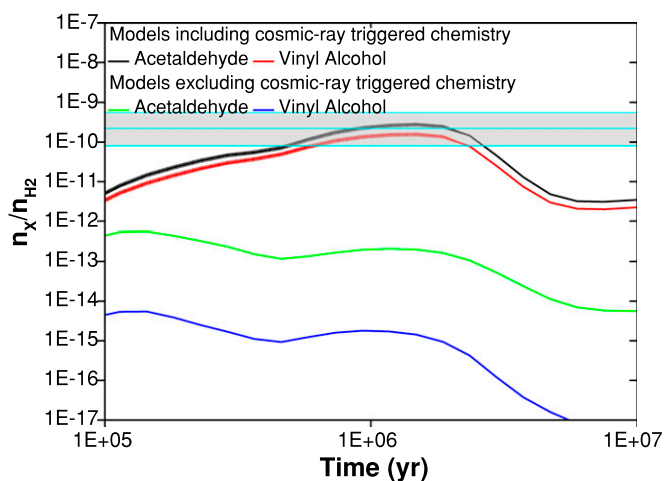


Fig. 4. Astrochemical models predicting the fractional abundances of acetaldehyde and vinyl alcohol in SgrB2(N). The models were operated with and without a cosmic-ray-triggered chemistry and provide compelling evidence of the essential role of a cosmic-ray-driven formation of acetaldehyde and vinyl alcohol. The cyan lines define the observed astronomical abundances in SgrB2(N) along with the error limits, thus establishing a remarkable match to the predicted data.

acetaldehyde and $1.55 \pm 0.03 \times 10^{14}$ molecules cm^{-2} compared with $2.2 \pm 0.8 \times 10^{14}$ molecules cm^{-2} for vinyl alcohol (*SI Appendix, Table S5*) once again at an age of 10^6 years. The abundance ratio of $1.8 \pm 0.2:1$ not only agrees nicely with the data reported in the literature (38), but also compares well with the experimentally derived ratio of $2.68 \pm 1.02:1$, i.e., a preferential formation of acetaldehyde compared with vinyl alcohol. Because acetaldehyde and vinyl alcohol were essentially formed within the ices during the radiation exposure, the results are insensitive to the gas temperature of SgrB2 varying from 300 K in dense star-forming regions to 40 K in the surrounding envelopes. Therefore, the modeling reveals that cosmic-ray-triggered nonequilibrium chemistry, which is efficient throughout the mantle at low grain temperatures, was essential to reproduce the abundances of COMs like acetaldehyde and its enol tautomer. These reactions do not require diffusion-limited radical-radical reactions in the warm-up processes as speculated previously.

Interstellar Chemistry and Conclusions

To conclude, our study identified two keto-enol tautomer pairs, acetaldehyde-vinyl alcohol along with propanal-(E)/(Z)-1-propenol, synthesized upon interaction of ionizing radiation with ices of carbon monoxide-methane and carbon monoxide-ethane ices representing interstellar analogue ices toward high-mass star-forming regions (10, 17). The aldehydes along with their enol tautomers are formed via a vigorous cosmic-ray-driven chemistry inside the ices at ultralow temperatures before their sublimation into star-forming regions, but not through traditional radical-radical recombination in the warm-up phase of the irradiated ices as postulated for the last decades. This classifies aldehydes and enols like acetaldehyde and vinyl alcohol detected with fractional abundances of a few 10^{-10} toward Sgr B2(N) as key tracers of an exotic nonequilibrium chemistry operating throughout low-temperature icy grains. The merged experimental and modeling data further rationalize for the first time, to our knowledge, quantitatively the previously unexplained fractional abundances of acetaldehyde and vinyl alcohol toward Sgr B2(N) (5), which have formerly neither been reproduced by gas-phase processes nor diffusion-limited radical-radical reactions on grain surfaces. This highlights the predictive nature of novel

astrochemical models toward the presence of COMs in the interstellar medium, once their nonequilibrium formation rates have been incorporated, thus providing a unique synergy between laboratory experiments, modeling, and validation via astronomical observations.

This present work reported here represents the first step toward a systematic understanding of the formation of a key class of interstellar molecules: COMs. Whereas gas-phase reactions can rationalize the formation of often highly unsaturated organic molecules such as polyacetylenes and cyanopolyacetylenes along with their radicals (1, 2) in interstellar and circumstellar environments, the synthesis of keto-enol isomer pairs via nonequilibrium processes opens up a hitherto overlooked versatile route to build up interstellar COMs, especially those which cannot be synthesized by classical bimolecular gas-phase reactions or thermal ice chemistry (37). The basic concept of the exotic nonequilibrium chemistry may also be expanded from aldehydes to synthesize ketones, carboxylic acids, carbon hydrates, amines, and amides—key classes of COMs in the interstellar medium—on interstellar grains. Formed in cold molecular clouds, this matter enters circumstellar disks in star-forming regions, where formation of planetary bodies takes place, thus providing the raw material for solar systems and (extrasolar) Kuiper Belts (7). It should be noted that each of these different environments can introduce further chemical modifications as each has a unique radiative, temporal, and chemical environment, i.e., aqueous alteration (41). Considering that comet 67P/Churyumov-Gerasimenko, which was recently visited within the framework of the Rosetta mission (42), originates from the Kuiper Belt and hence was formed (partly) from this presolar system material, the detected COMs carrying carbonyl functional groups such as acetaldehyde, acetone, propanal, and glycolaldehyde were also likely formed by these nonthermal processes, thus completing the full cycle from interstellar clouds via star-forming regions to our solar system eventually predicting where in the galaxy the molecular precursors to the origins of life might have emerged.

Materials and Methods

Experimental. The experiments used a contamination-free UHV chamber (10^{-11} torr) (15). The substrate consisted of a 1-cm^2 silver mirror interfaced to a cold finger and cooled to 5.5 ± 0.1 K. The processing of the ices and the infrared changes were probed online and in situ via FTIR spectroscopy. After the irradiation (*SI Appendix, Experimental Approach*), the sample was kept isothermal for 1 h and then the ices were heated to 300 K via TPD to sublime both the products and reactants for detection via PI-ReTOF-MS. The subliming molecules were analyzed via single-photon ionization by using coherent VUV light pulsed at 30 Hz. To produce VUV energies of 10.49, 9.80, 9.60, and 8.40 eV, see *SI Appendix, Experimental Approach*.

Theoretical. Photoionization cross-sections of acetaldehyde, vinyl alcohol, propanal, and (E)/(Z)-1-propenol were computed using the protocol reported by Gozem et al. (43) (*SI Appendix, Theoretical Approach and Table S2*). First, structures are optimized using density functional theory with the ω B97X-D functional and the augmented correlation-consistent triple-zeta (aug-cc-pVTZ) basis set (44). Dyson orbitals and ionization energies are computed in Q-Chem (45) using the equation-of-motion coupled-cluster (EOM-CC) approach (46–48). The photoionization cross-sections are computed by ezDyson Version 3.0 (43, 46, 49). In addition to the Dyson orbitals, which contain all of the necessary information about the molecular system (46–48), cross-section calculations also need the photoelectron wave function which can be described by using Coulomb waves with a partial (effective) charge Z that is between 0 and 1 (43). Zero-point energy corrections to the ionization energies are computed at the ω B97X-D/aug-cc-pVTZ level of theory. Upon computing the electronic contribution to the photoionization cross-sections, the Franck-Condon factors were accounted for by using S_0 and D_1 structures and frequencies computed with ω B97X-D/aug-cc-pVTZ (50) (*SI Appendix, Theoretical Approach and Table S4*).

Astrochemical Modeling. Astrochemical networks were used to explore the impact of the nonequilibrium chemistry on the production of these

complex molecules (*SI Appendix, Tables S5–S7*). The rate-limiting step in these models was the formation of the energetic hydrogen atom from the dissociation of methane (reaction 4). The rate coefficient, $JCH_4(s^{-1})$, for this process was calculated using the equation

$$JCH_4 = S_e G_{tot} \varphi, \quad [13]$$

where φ is the radiation flux, S_e is the electronic stopping cross-section of electrons in the medium (51–53), and G_{tot} is the total geminacy factor, i.e., the number of species produced per electron volt of energy deposited by the incoming particle summed over all product channels (54). This can be considered to be a first-order approximation of the efficiency of the radiation chemistry of carbon monoxide and methane; however, interstellar grains would have an amorphous solid water matrix (*SI Appendix, Astrochemical Modeling*) (55). Also, the models calculate rate coefficients for

diffusive grain–surface reactions using the diffusion energy barrier, E_d , using the diffusion formula $k_{diff} = \nu \exp(-E_d/T)$ and k_d determined from the experimental results (*SI Appendix, Astrochemical Modeling*). To use the laboratory data of the rate coefficient for reaction 6 in the models as a function of temperature, the reaction was treated as a diffusive one with a first-order rate coefficient for hopping from one potential well to an adjacent one.

ACKNOWLEDGMENTS. We acknowledge the W. M. Keck Foundation for financing the experimental setup. R.I.K. and M.J.A. thank the US National Science Foundation (AST-1505502) for support to conduct the experiments and data analysis. S.G. and A.I.K. thank the US Department of Energy, Basic Energy Sciences through DE-FG02-05ER15685 (A.I.K.) for support. C.N.S. and E.H. thank the US National Science Foundation for support of the astrochemistry program at the University of Virginia.

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