

Singlet Oxygen Insertion into Hydrocarbons: The Role of First- and Second-Generation Pathways in Astronomically Relevant Ices

Amit Daniely^{1†}, Alon Zamir^{1†}, Helen R. Eisenberg¹,
Ester Livshits¹, Elettra Piacentino², Jennifer B. Bergner³,
Karin I. Öberg², Tamar Stein¹

¹Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem, 9190401, Israel.

²Harvard-Smithsonian Center for Astrophysics, Harvard, Cambridge, 02138, MA, USA.

³UC Berkeley, Department of Chemistry, Berkeley, 94720, California, USA.

†These authors contributed equally to this work.

Abstract

Complex organic molecules are widespread in different areas of the interstellar medium, including cold areas such as molecular clouds where chemical reactions occur in ice. The underlying molecular mechanisms responsible for the observed rich chemistry are still not understood. O(¹D) atom reactions provide a pathway for chemical complexity even in cold areas, as the reactions are typically barrierless, and O(¹D) is a photofragmented product of astronomically relevant ices such as CO₂. In this work, we use quantum chemistry methods to model reactions in astronomical ices containing oxygen with small C1 and C2 hydrocarbons in the presence of UV radiation. Our results demonstrate that the underlying molecular mechanism of reactions in ice includes the oxygen insertion reaction (first-generation reactions), photofragmentation of products and radical recombination reactions (second-generation reactions). The mechanism explains the formation of formaldehyde in methane ice, acetaldehyde in ethane ice, CO in acetylene ice and the consumption of alcohol in all systems. This work demonstrates the important role of first- and second-generation reactions in the unique chemical processes in astronomical ices; where basic molecular building blocks are fragmented and recombined into new molecules resulting in enhanced chemical complexity.

Keywords: Astrochemistry, Ab initio molecular dynamics, oxygen insertion

1 Introduction

Molecules, including many polyatomic and complex organic molecules, are widespread throughout our universe and are observed in all stages of star and planet formation including pre-stellar cores, protostars and protoplanetary disks [1–7]. Molecules formed in these stages are incorporated in solid bodies that can be delivered to newly formed planets, providing an inventory of available complex organic molecules. Thus, understanding the rich chemistry that occurs at these stages is crucial to identifying the molecules available for prebiotic chemistry and is highly important to the field of astrobiology[8].

Molecular clouds, the birthplace of stars, are shielded from external UV radiation as they contain dust particles that efficiently absorb UV radiation and thus provide a shielded environment for molecular formation. The variety of molecules observed includes complex organic molecules such as formaldehyde, acetaldehyde, methanol, vinyl alcohol, ethylene oxide, ethenone [9–14] and many more[15–21]. Molecular clouds are characterized by low temperatures and contain icy grain mantles. They also have relatively high densities in comparison to the general conditions in the diffuse interstellar medium (ISM)[8, 22]. Despite the rich chemistry occurring in molecular clouds, the underlying molecular mechanisms responsible for molecular formation in such cold dilute areas are still not understood.

In the cold cloud cores, icy grains are the major reservoir of molecules as a result of the short freeze-out time scale. Among the observed ices, water ice is the most abundant followed by carbon monoxide (CO) and carbon dioxide (CO₂), as well as smaller amounts of organic molecules such as methane (CH₄) and methanol (CH₃OH)[23]. Gas-phase chemistry (including barrierless ion-molecule[24] and radical-molecule reactions) and gas-grain chemistry are possible pathways for the production of many of the observed species[8, 25–28]. The formation of different organic molecules in environments where temperatures are greater than 30 K can be explained via radical recombination mechanisms; the formation of radicals is followed by diffusion and recombination into larger molecular species[5, 29, 30].

At very low temperatures (< 20 K), diffusion of some of the radical species may be limited and different low-temperature channels for organic-molecule formation are expected. In cold shielded regions such as molecular clouds, external UV photons are shielded; however, the interaction of H₂ with cosmic rays results in secondary UV photons from the deexcitation of H₂ molecules (Ly- α radiation) [31]. As a result, Ly- α radiation is a dominant source of energy and the photochemical processing of ice is hypothesized to play an important role in the large variety of organic molecules observed in these areas [8, 23].

An important example is the formation of O(¹D) as a result of photolysis of water (H₂O) and carbon dioxide (CO₂) ice (with efficiencies of 10% and 100%, respectively.) Thus, the chemistry of O(¹D) insertion reactions is a possible source of many organic

reactions and provides a low-temperature pathway for organic-molecule formation in those ices. Moreover, $O(^1D)$ is metastable with a lifetime of ~ 110 s measured[32] in the gas phase and 32 s and ~ 1 s in neon and SF_6 matrices, respectively[33, 34]. Thus, $O(^1D)$ can efficiently diffuse in the ice before reacting and provide an efficient pathway for molecular formation in colder environments.

The gas-phase insertion reaction of $O(^1D)$ has been widely studied. It has been demonstrated that the insertion of $O(^1D)$ into methane is essentially barrierless and that CH_3OH is formed; at sufficiently high pressures, it is stabilized through collisions. At lower pressures, without an efficient way to dissipate the excess energy, the molecule fragments into $CH_3 + OH$ species [35–38].

Similar results were obtained in gas-phase experiments of oxygen insertion into C2 hydrocarbons[39–42]. In general, the highly reactive oxygen is inserted into the hydrocarbons followed by fragmentation into radical species to dissipate the excess energy. Recently, Bergner et. al. [43, 44] studied oxygen insertion reactions in ices of astronomical relevance to obtain insights into processes occurring in ice environments under constant radiation. The ice contained CO_2 (or O_2 in the case of CH_4) with different hydrocarbons, and $O(^1D)$ was produced by the photolysis of CO_2 . Products obtained in ice were different from the ones obtained in the gas-phase experiments, suggesting different mechanisms are responsible for product formation in the gas-phase or ice environment. Knowledge of the underlying molecular mechanism is crucial for the incorporation of the relevant reactions in astrochemical models.

In this manuscript, we model the underlying molecular pathways responsible for the rich molecular inventory of products resulting from the irradiation of ices containing different hydrocarbons and CO_2 using quantum chemistry methods. The reaction of oxygen with different hydrocarbons has been previously studied in its triplet form[41, 45–49]. Here, we focus on reactions of hydrocarbons with oxygen in its singlet form, $O(^1D)$. A possible explanation for the difference in the products in the gas phase and the ice environment is that the molecules in the ice alter the potential energy surfaces (PES) as observed previously in the case of molecular clusters [25, 26, 50, 51]. However, stability analysis of the different products on the PES reveals that while changes in stability were observed, they do not significantly alter the PES, as demonstrated in Appendix A.

Alternatively, as we demonstrate in this work, $O(^1D)$ reacts directly with the available hydrocarbons (as in the gas phase). These reactions are referred to as first-generation reactions; unlike the gas phase, the ice environment provides a way to dissipate the excess energy, and stabilization of the products is expected. Due to the constant irradiation of the ice, these products (as well as the C2 ice components) can further photofragment due to the interaction with UV radiation. The highly reactive radicals can further recombine, leading to new molecular species. These reactions are referred to as second-generation reactions and are demonstrated to play a role in the resulting products and their branching ratio. Thus, the observed laboratory ice chemistry is the result of a combination of O-insertion reactions, product fragmentation, and recombination of radicals, and the relative contributions of each are key to explaining

and predicting astrochemical observations. Our results shed light on processes occurring in astronomical ices, where basic molecular building blocks are fragmented and recombined into new, more complex molecules.

To model first- and second-generation reactions, we studied the dynamics of both the ground and excited electronic states. We considered possible spin-allowed internal conversion between different electronic states and neglected the spin-forbidden inter-system crossing.

The manuscript is organized as follows: In Section 2.1, we present the ground-state PESs of possible insertion reactions of O(¹D) with different hydrocarbons, namely, methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄) and acetylene (C₂H₂), studying possible products resulting solely from O(¹D) reaction with a hydrocarbon. By performing *ab initio* molecular dynamics (AIMD) simulations on the ground electronic state, we demonstrate the possible products of the reactions.

We then continue to study the excited state dynamics of the available building blocks in Section 2.2. The products of the insertion reactions and the building blocks of the ice can both form radicals that are recombined to form new secondary products. Recombination products are also presented. As the reaction occurs in an ice environment, we further studied the effect of the ice on the stability of the products, as reported in Appendix A. The details of all the performed calculations are given in Section 3

2 Results and Discussion

2.1 Ground-state potential energy surfaces

The PESs of methane, ethane, ethylene and acetylene, with singlet oxygen, were calculated using density functional theory (DFT) (see Section 3 for details) and are shown in Figure 1. In all cases (except insertion of O(¹D) into the acetylene σ bond, which is discussed below), the molecular geometry optimization of the hydrocarbon in the vicinity of O(¹D) (starting from a distance of 4.9 Å) resulted in an insertion reaction of the oxygen into the hydrocarbon. The fact that the reactions were observed from optimization demonstrates that they are barrierless. To further verify that the reactions are indeed barrierless, we performed frozen PES scan calculations, changing the distance between the O(¹D) and the hydrocarbons. The results shown in the supplementary material (SI) (Figure S1-S4), indicate that there is no barrier along the reaction coordinate at the first stage of the O(¹D) insertion. The insertion can take place via σ or π bonds. Insertion via σ bonds resulted in alcohols, as was observed for all the systems. In cases of hydrocarbons with π bonds, namely ethylene and acetylene, barrierless formation of ethylene oxide (C₂H₄O) and oxirene (C₂H₂O) were observed, respectively. For acetylene, the frozen-scan calculations exhibited a small and negligible barrier (~ 2 kcal/mol) in the insertion to the σ bond, forming alcohol at a distance above 2 Å and an angle of 180° as can be seen in Figure S4.

Figure 1 Panel A shows the PES of O(¹D) insertion into methane. The insertion occurred via a σ bond and the resulting product was methanol (Structure b). To study the evolution of the system over time, we performed AIMD simulations using

XMS-CASPT2[52, 53]; details of the simulations are given in Section 3 below. The simulations exhibited a fast formation of methanol in all trajectories, indicating that this is the expected product and is expected to stabilize in the ice environment. In the gas phase, fragmentation is expected and, indeed, within the time frame of the simulations (0.5 ps), 38% of the trajectories resulted in fragmented products, namely CH₃ and OH radicals, which is in agreement with previous studies[35, 54, 55]. Gas-phase and liquid argon experiments identified methanol as a major product[56]. Experiments in ice, however, resulted only in 65% methanol with the reminder as formaldehyde (CH₂O). The fact that a relatively large amount of formaldehyde was detected, which was demonstrated to be a minor channel in gas-phase experiments, implies the importance of secondary reactions occurring in the ice.

System	Product	Ice experiment (%)	Estimation from gas-phase ground-state simulations (%)
Methane	methanol	65	100 ¹
	formaldehyde	35	0
Ethane	ethanol	74	100 ¹
	acetaldehyde	26	0
Ethylene	acetaldehyde	53	18
	ethylene oxide	47	33
	vinyl alcohol	0	49 ¹
Acetylene	ethenone	100	98 ² ³
	ethynol	0	2 ³

¹Includes fragmented trajectories, which are expected to stabilize in an ice environment.

²Includes fragmented trajectories and trajectories resulting in oxirene (which are expected to form ethenone over longer simulation times).

³Percentage from reactive trajectories.

Table 1 Comparison of branching ratio obtained by Bergner et al. and by estimation from gas-phase ground-state simulations.

Figure 1 Panel B shows the PES of O(¹D) insertion into ethane. Here as well, only one barrierless product was observed; namely, ethanol (Structure b). Other products on the PES were acetaldehyde (Structure c), formaldehyde (Structure d) and dimethyl ether (Structure e). AIMD simulations employing XMS-CASPT2 resulted in the formation of ethanol in all trajectories. In 5% of the trajectories, we observed fragmentation of ethanol into C₂H₅ and OH radicals. The small fraction of simulations that resulted in fragmentation was likely due to the short simulation time (0.5 ps). The results are in agreement with reported gas-phase experiments, in which the insertion occurred and then was followed by unimolecular fragmentation channels of ethanol[42, 57, 58], and with experiments in liquid argon in which alcohol was the major product [56]. H₂ or H formation channels (in which acetaldehyde was formed) have been demonstrated to be minor channels[58]. The experiments in ice resulted in the formation of both ethanol and acetaldehyde with a branching ratio to ethanol of 74%, which again indicates that additional secondary processes took place.

Figure 1 Panel C shows the PES of O(¹D) insertion into ethylene. Here, there were two barrierless products resulting from the insertion reaction either from the π or

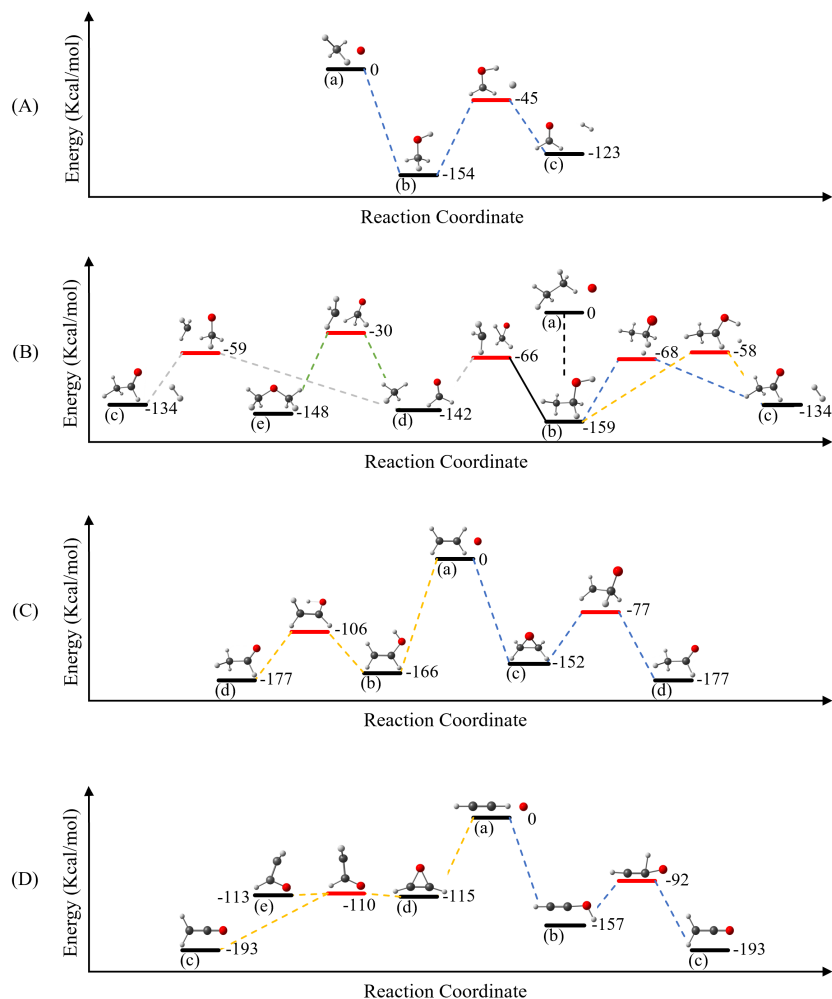


Fig. 1 PES of O(¹D) with (A): Methane, (B): Ethane, (C): Ethylene, and (D): Acetylene. Black lines represent structures that are minima on the PES, and red lines represent transition-state structures. Different colors of the broken lines represent different pathways to the products on the PES.

the σ bonds. Reaction from the π system resulted in the formation of ethylene oxide (Structure c) and reaction via the σ bond resulted in vinyl alcohol (Structure b). Both structures can lead to acetaldehyde (Structure d) with barriers of 75 kcal/mol from ethylene oxide and 60 kcal/mol from vinyl alcohol. XMS-CASPT2 AIMD simulations resulted mostly in barrierless products; namely, ethylene oxide (33%) and vinyl alcohol (46%). Acetaldehyde was observed in 18% of the simulations and 3% of the trajectories resulted in fragmentation into CH₂CH and OH radicals. Experiments in ice showed the formation of ethylene oxide and acetaldehyde with a branching ratio to ethylene oxide of 47%. Vinyl alcohol was not observed, which may be attributed to secondary

reactions in which it was further photofragmented as a result of the available UV radiation.

Figure 1 Panel D shows the PES of O(¹D) insertion into acetylene. As in the previous system, insertion can occur via the σ or π bond to form ethynol (Structure b), oxirene (Structure d) or formyl carbene (Structure e), which can further react to form ethenone (Structure c), with a negligible barrier from oxirene. The PES was also explored in the ice environment (see Appendix A for details). AIMD simulations employing XMS-CASPT2 resulted in the formation of ethenone in 58% of the simulations; among these simulations, 22% dissociated into CH₂ and CO radicals and 5% dissociated into CHCO + H. Eighteen percent of the simulations resulted in oxirene, which is likely to further react to form ethenone, as was seen in trajectories in which ethenone was produced by passing through an oxirene product. We observed a free transition in the simulations between oxirene and formyl carbene, which is oxirene in an open form. Two percent of the simulations (1 trajectory) resulted in alcohol; however, the reaction did not occur through σ insertion, but through the π system via oxirene and formyl carbene. In 22% of the simulations, we did not observe any reaction taking place within the time frame of the simulations; all these trajectories occurred when the simulation starting point was from a "side" orientation, not directly above the π system. In general, in the case of ethylene and acetylene systems, reactions from the π were much favored relative to those from the σ . This point was also demonstrated within the ice environment. Both for acetylene and ethylene, even when the oxygen was placed close to a hydrogen atom, the reaction occurred via the π system of the adjacent molecules, even though it was distant, as can be seen in Figure 2.

Table 1 summarises the difference in branching ratio obtained by Bergner et al. or the estimated one from gas-phase ground-state simulations, demonstrating that first-generation reactions alone cannot explain experimental observations.

2.2 Excited states dynamics

The ice experiments performed by Bergner et al [43, 44] were performed using an ultra-high-vacuum chamber in which ices were grown by introducing gases deposited on a cooled substrate (9 K) through a dosing pipe. The ice samples were irradiated using a H₂D₂ lamp for 2-3 hours at different temperatures.

As the ice was under constant radiation, secondary products may have been formed. The hydrocarbons that constitute the ice (except methane) could absorb Ly- α radiation available in the experiment and photofragment, adding to the available collection of radicals in the ice. This is evident from the experimental results of the pure ices: irradiation of ethane led to the formation of methane, ethylene and acetylene hydrocarbons. Irradiation of ethylene led to the formation of ethane and acetylene, and irradiation of pure acetylene resulted in its consumption[44]. These results indicate that in the conditions of the experiments, other components of the ice besides the CO₂ could also photofragment to form radicals and recombine to form a variety of organic species. To explore possible mechanisms, we calculated the energies of excited electronic states of the different hydrocarbons. Figure 3 shows the singlet energy levels of each hydrocarbon. As can be seen from the figure, all the low-lying excited states of the C2 hydrocarbons were accessible (Figure 3 Panels B-D) and could take part in

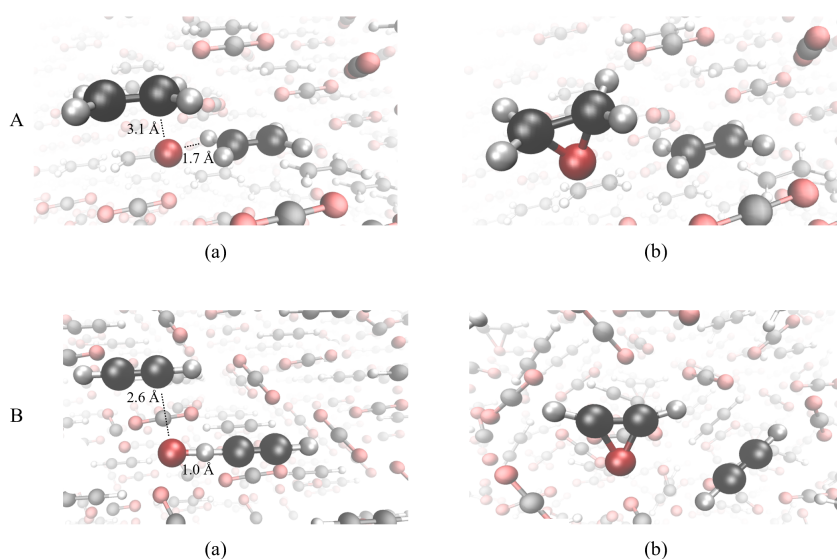


Fig. 2 Top Panel (A): (a) Initial structure of C₂H₄ with O(¹D) in CO₂/C₂H₄ ice. The O(¹D) is located closer to the hydrogen atom (1.7 Å) than to the carbon on the neighboring C₂H₄ molecule (3.1 Å). (b): Final structure after geometric optimization: despite the proximity to the hydrogen, the reaction occurred via the π bond on the neighboring molecule. Bottom Panel (B): (a) Initial structure of C₂H₂ with O(¹D) in CO₂/C₂H₂ ice. The O(¹D) is located in close proximity to the hydrogen (1.0 Å) relative to the carbon on the neighboring C₂H₂ molecule (2.6 Å). (b): Final structure: despite the proximity to the hydrogen, the reaction occurred via the π bond on the neighboring molecule.

the observed chemistry. Moreover, the products of the O(¹D) insertion reaction could also further photofragment and lead to secondary reactions that contributed to the chemical complexity.

In the following sections, we explore the possible products as a result of the photofragmentation of each of the hydrocarbons and the O(¹D) insertion products, employing Non-Adiabatic AIMD (NA-AIMD) calculations using XMS-CASPT2 method. Recombination processes were calculated using DFT.

2.2.1 CH₄ + O(¹D) system

Unlike the other hydrocarbons, in methane, the lowest-lying excitation is above 10 eV, which is not accessible within the energy range of the experiment; thus, contributions due to methane excitations were not considered. In the presence of O(¹D), methane will react to form methanol in which the ice provides an efficient way to dissipate the excess energy; thus, no fragmentation products are expected. Indeed, Bergner et al. did not observe any CH₃ or OH radicals[44].

In the presence of UV radiation, the formed methanol can be excited, as is evident from its energy-level diagram (shown in SI Figure S5) with the lowest excited state at 6.7 eV. To study the outcome of the system upon excitation, we performed NA-AIMD simulations on the first excited electronic state. Details of the calculations are given in Section 3.2. The dynamic simulations demonstrated a quick photodissociation (within

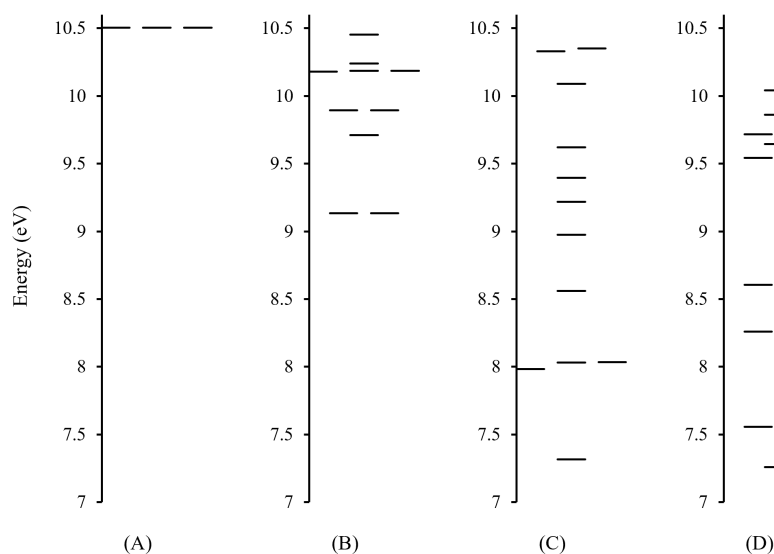


Fig. 3 Electronic excited states of (A): Methane, (B): Ethane, (C): Ethylene, and (D) Acetylene calculated using EOM-CCSD/aug-cc-pVDZ.

60 fs in all 50 trajectories) of the methanol to form a methoxy radical (CH_3O) and H radical. Such fragmentation of the alcohol is typical in all the systems that we have studied and is in agreement with the literature[38].

As a result of the secondary reactions, H radicals are also available in the ice in addition to the $\text{O}(^1\text{D})$ atoms. The oxygen and hydrogen atoms are expected to efficiently diffuse even in such cold environments and to further react and recombine with other available radicals.

To study the possible recombination paths of $\text{CH}_3\text{O} + \text{H}$, we performed ground-state AIMD simulations using DFT, as detailed in Section 3.1. The recombination resulted in either formaldehyde (87% of the simulations) or methanol (13% of the simulations) and depended on the starting orientation of the radicals, as shown in Figure S6 in the SI. An example of the trajectories is shown in Figure 4.

The results explain the molecular pathway for the formation of formaldehyde, which is a result of the photofragmentation of methanol, produced when methane reacts with $\text{O}(^1\text{D})$, followed by the recombination of the radicals formed.

2.2.2 $\text{C}_2\text{H}_6 + \text{O}(^1\text{D})$ system

Bergner et al.[44] found that oxygen atoms react with ethane to form ethanol and acetaldehyde, with a branching ratio to ethanol of 74%, while ground-state dynamics demonstrate solely the formation of ethanol. Unlike the gas phase, in the ice environment, the ethanol can be stabilized and not fragmented. The calculation of excited state energies of ethanol, shown in Figure S7 in the SI, demonstrates that ethanol can be excited under experimental conditions. To study the results of its photoexcitation, we performed NA-AIMD simulations on the first excited electronic state. Ethanol in

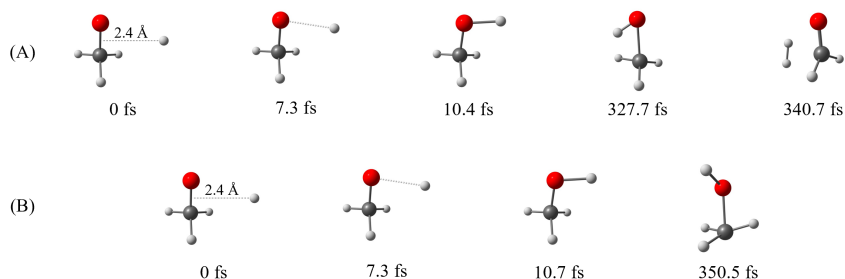


Fig. 4 Examples of the recombination between a CH_3O radical and H radical. Panel A demonstrates the formation of formaldehyde and H_2 . Panel B demonstrates the formation of methanol.

the first excited state fragmented very quickly into an ethoxy radical ($\text{CH}_3\text{CH}_2\text{O}$) and H radical in all 50 trajectories.

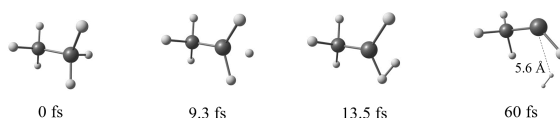


Fig. 5 Example of a trajectory starting from the second low-lying excited state of ethane, resulting in ethylidene + H_2

Ethane, the main component of the ice, can also photofragment under the experimental conditions, as is evident from its energy level diagram in Figure 3 Panel B. For ethane, we performed NA-AIMD simulations on the two lowest-lying excited electronic states. Starting from each state, namely S1 or S2, we ran 50 trajectories for 60 fs, as by this time, all the trajectories resulted in fragmented products. The statistics were similar for both initial states and were, therefore, independent of the starting electronic state, as demonstrated in Figure S8 in the SI. The reason for this is that when starting on S2, the system rapidly crossed to S1, in which ethylidene (CH_3CH) was formed. In total, 96% of the trajectories resulted in ethylidene (CH_3CH) and H_2 and 4% resulted in ethyl radical (CH_3CH_2) + H radical. An example trajectory is shown in Figure 5. Both H and H_2 loss have been reported as possible fragmentation pathways of ethane[59–61], and the formation of ethylidene has been previously discussed[62, 63]. It has been suggested that it forms through the reaction between $\text{C}(^1\text{D})$ and methane [64], as well as from the reaction between $\text{O}(^3\text{P})$ and propene during combustion[65]. Additionally, ethylidene has been observed as a bound species on the surface of platinum [66] and as part of transition metal complexes[67]. Free ethylidene has recently been produced in the photodissociation of gaseous methylketene and propenal, while the triplet form of ethylidene has been demonstrated as stable in the absence of collisions; the singlet form undergoes isomerization by a 1,2-hydrogen atom shift producing vibrationally excited ethylene[68]. In the ice experiment, the irradiation of pure ethane ice resulted in ethylene, as well as other products. The route was likely through the

singlet ethylidene product, which was the main product of the photofragmentation of ethane, which underwent a fast H atom migration, forming ethylene [68].

In addition to the presence of O(¹D) in the ice, photofragmentation of both ethanol and ethane results in highly reactive species in close proximity to each other. Their high reactivity can lead to the recombination of radical species, especially in the presence of oxygen and hydrogen that can effectively diffuse in the ice even at low temperatures.

To study the recombination processes of the ethoxy radical (CH₃CH₂O) and H radical, we performed DFT AIMD simulations, sampling different initial orientations of the radicals, with the final result depending on the initial orientations. Interestingly, the major product of the recombination was acetaldehyde (53.7%), followed by the formation of formaldehyde (31.7%) and ethanol (14.6%), as can be seen in Figure S9 in the SI. The recombination processes can explain the pathway for acetaldehyde formation, which was the second major product observed in the experiment.

2.2.3 C₂H₄ + O(¹D) system

Ground-state simulations of O(¹D) reacting with ethylene predicted 45% formation of vinyl alcohol, 33% formation of ethylene oxide and only 18% formation of acetaldehyde; while Bergner et al[44] observed the formation of acetaldehyde (53%) and ethylene oxide (47%) with no observation of vinyl alcohol. Vinyl alcohol was, however, observed in different experiments; thus, it is possible that vinyl alcohol was formed in the ice, and further photofragmented as a result of the available UV radiation[69]. Electronic energy levels of vinyl alcohol are presented in Figure S10 in the SI, demonstrating that, like the other alcohols under study, excited electronic states are accessible within experimental conditions.

To study the fate of vinyl alcohol as a result of interaction with radiation, we performed NA-AIMD simulations on its first excited state. In all of the simulations, we observed a quick fragmentation of excited vinyl alcohol into a vinyloxy radical (CH₂CHO) and H radical.

To model the recombination of the radicals, we performed a DFT AIMD simulation, starting from different orientations on the ground state. The majority of trajectories (70.8%) resulted in the formation of the observed product, namely acetaldehyde. The rest of the simulations resulted in vinyl alcohol (12.9%) or ethenone (14.6%), as shown in Figure S11 in the SI. While ethylene oxide was formed on the ground state, second-generation reactions are needed to explain the formation route of acetaldehyde via the consumption of vinyl alcohol.

The ice components can also absorb radiation, as is evidenced by the electronic energy levels in Figure 3 Panel C. To study possible fragmentation paths due to radiation, we performed NA-AIMD simulations on the first and second excited electronic states of the hydrocarbon. The photodynamics of ethylene have been well-studied[70–73]. The S1 state, the Rydberg state, was not reactive and all simulations resulted in a distorted form of ethylene. In S2, the ππ* state, 48% of the simulations resulted in a chemical change in the time frame of the simulations: 18% resulted in the formation of ethylidene (CH₃CH), 8% resulted in acetylene + H₂ which fragmented from ethylidene, 16% of the simulations resulted in the dissociation into a vinyl radical

(CHCH₂) and H radical and 3% resulted in vinylidene (H₂CC) + H₂. These trajectories demonstrate the formation of acetylene from ethylene, which was observed in the pure ice experiments and is consistent with the observation that, upon irradiation of ethane and ethylene ice, acetylene was formed. In the rest of the simulations (52%), S2 remained as C₂H₄ and rotated around the π bond during the simulations. We observed hopping between S2/S1 states in a twisted geometry of ethylene, and between S1/S0 in twisted-pyramidalized ethylene, which is in agreement with the literature[70–72]. In its rotated form, ethylene is more stable in the triplet state, and inter-system crossing may also take place [74].

2.2.4 C₂H₂ + O(¹D) system

From the ground-state dynamics of acetylene and oxygen, we expect ethenone to be the major product. Bergner et al [44] observed ethenone and CO as the reaction products. While ethenone is directly formed from the reaction between acetylene and O(¹D), the pathway to form the large quantities of the observed CO was not clear. One of the possible suggested explanations was that it resulted from second-generation reactions of the hydrocarbon fragments and O(¹D).

To study possible second-generation reactions, we performed NA-AIMD simulations starting from the S1, S2 and S3 low-lying excited electronic states of acetylene. We ran 50 trajectories, each for 300 fs. The product distribution is presented in Figure 6.

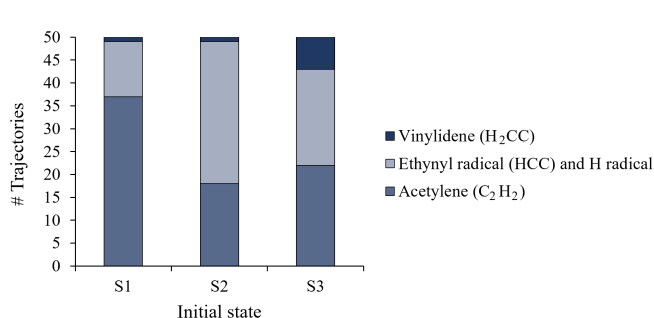


Fig. 6 Product distribution calculated from NA-AIMD simulations of photoexcited acetylene, starting from different electronic states.

In the starting structure of linear acetylene, the three states are very close in energy, as is demonstrated in Figure 3 Panel (D). We allowed crossing between all three excited states and the ground state, and indeed observed crossing between all the excited states. In the excited states, the structure of acetylene was distorted and we observed the cis and trans isomers, which have been previously identified [75, 76]. We observed the photodissociation channel of acetylene into an ethynyl radical (HCC) and H radical, which occurred mainly in the S1 and S2 states. This channel has been previously reported as a fragmentation channel of acetylene [59, 77–81]. Additionally, we observed the formation of the vinylidene (H₂CC) product in 6% of all simulations.

This structure has been identified as the minimum on the S1 PES [76]. The formation of this product is obtained via two possible pathways. In the first pathway, the system crosses back to the ground state in a distorted form in which the acetylene is no longer linear. The distortion enables hydrogen transfer from one carbon to the other on the ground state leading to vinylidene (H_2CC) formation. As the product is vibrationally excited when crossing back to the ground state, the hydrogen can also move back to reform acetylene and the transition between acetylene to vinylidene (H_2CC) is observed through the rest of the dynamics. In the second pathway, the formation of vinylidene (H_2CC) occurs in the S1 state and the product is stable: No reformation of acetylene is observed.

The available radicals in the ice can further react with $\text{O}(^1\text{D})$. We studied the recombination process of an ethynyl radical (HCC) with $\text{O}(^1\text{D})$ using DFT AIMD simulations, as in the previous systems. The majority (95%) of the simulations resulted in fragmentation to HC and CO radicals, explaining the formation path of CO observed in the experiment. Examples of trajectories are shown in Figure 7.

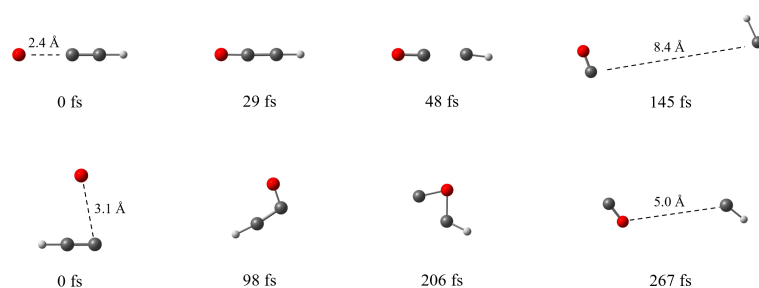


Fig. 7 Examples of AIMD simulations of the reaction between HCC and oxygen (^1D).

3 Methods

3.1 Ground state

PES of the $\text{O}(^1\text{D})$ insertion reactions into different hydrocarbons were performed using DFT with the Q-Chem 5 software package [82]. The different structures on the PES were optimized using the $\omega\text{B97X-V}$ functional [83] with an aug-cc-pVDZ basis set [84]. Transition state structures were studied by using the freezing string method (FSM) [85] and intrinsic reaction coordinate (IRC). Frequency calculations were performed to verify that all the structures on the PESs were indeed minimum points or saddle points. For more accurate energies, we performed single-point calculations on all the optimal structures on the PESs using the $\omega\text{B97X-V}$ functional [83] with an aug-cc-pVTZ basis set.

To study the evolution of the systems over time, we performed AIMD simulations of the $\text{O}(^1\text{D})$ insertion reactions into the different hydrocarbons in the study. AIMD simulations were performed with the extended multi-state complete active

space second-order perturbation theory (XMS-CASPT2) method [52, 53] within the so-called “left SS-SR” [86] contraction scheme for internally contracted basis functions in which a vertical shift set to $0.2 E_h$ was used.

The dynamic simulations on the ground-state surface were performed using the BAGEL electronic structure package[87] interfaces with the Newton-X (v2.2.0) program.[88] The simulations ran for 500 fs using a time-step of 0.3 fs.

1. Methane: For the CH_4 system, we used a (10e,8o) active space. We ran 60 trajectories starting from two possible initial positions; 30 trajectories started from an orientation in which the $\text{O}(^1\text{D})$ was located in front of a hydrogen atom and the other 30 trajectories started with the oxygen positioned between two hydrogen atoms.
2. Ethane: For the C_2H_6 system, we used a (12e,8o) active space. We ran 60 trajectories starting from two different initial positions; 30 trajectories started from an orientation in which the $\text{O}(^1\text{D})$ was located on the side of the molecule, facing a hydrogen atom. The other 30 trajectories started with the oxygen positioned above the two carbon atoms.
3. Ethylene: For the CH_2CH_2 system, we performed AIMD simulations on the ground state using a (10e,8o) active space. We started the simulation from two starting points: with the $\text{O}(^1\text{D})$ in front of the π bond in the molecular plane and perpendicular to the molecular plane. Additionally, we started the simulations from a σ direction in which the $\text{O}(^1\text{D})$ was located between two hydrogen atoms.
4. Acetylene: For the acetylene system, we performed AIMD simulations on the ground state using a (10e,7o) active space. To model the insertion reaction from the π direction, we started the simulation with the $\text{O}(^1\text{D})$ located in front of the middle of the π bond perpendicular to the molecular plane. Alternatively, we modelled the reaction starting from the σ direction. When $\text{O}(^1\text{D})$ was placed along the axis of the acetylene molecule (i.e., the CH-O angle was 180° degrees), we observed distancing of $\text{O}(^1\text{D})$ at the time scale of the simulations. We then sampled this direction by placing the $\text{O}(^1\text{D})$ at different angles from the acetylene molecule (specifically, the CH-O angle), varying from 100° to 170° .

In all systems, the nuclear velocities were randomly sampled from the Maxwell–Boltzmann distribution according to the temperature, which varied between 30 K and 80 K in all trajectories.

3.2 Excited-states

Excitation energies were calculated using the equation of motion Coupled-Cluster singles doubles (EOM-CCSD)[89–92] method and XMS-CASPT2[52, 53]. To study different reactions in excited electronic states and their propagation in time, we performed NA-AIMD simulations using the XMS-CASPT2 method [52, 53] within the so-called “left SS-SR” [86] contraction scheme for internally contracted basis functions in which a vertical shift set to $0.2 E_h$ was used, which was similar to the ground-state calculations. We performed XMS-CASPT2 NA-AIMD with an aug-cc-pVDZ basis set utilizing the BAGEL electronic structure package[87] interfaced with the Newton-X (v2.2.0) program[88]. In the excited state dynamics, we took into account

non-adiabatic transitions between different states by allowing surface hopping[93]. The initial conditions of each trajectory (namely, geometry and velocity) were generated from a DFT AIMD simulation on the ground state of each system at 30 K. We sampled initial conditions every 40 steps starting from Step 580 fs, assuming that by this time, the system had reached thermalization. For each state, we ran 50 trajectories each for 300 fs or until fragmentation occurred, using a 0.3 fs time step.

1. Ethane: we performed XMS-CASPT2 calculations with a (6e,8o) active space. Simulations were performed starting on the first two excited states, namely S1 and S2, allowing non-adiabatic transitions only between sequential states.
2. Ethylene: we performed XMS-CASPT2 calculations for the first two excited states, namely S1 and S2. We used a (8e,6o) active space when performing dynamic simulations on the first excited state, taking into account non-adiabatic coupling between the ground state and the first excited state. On S2, we used a (8e,8o) active space while taking into account non-adiabatic transitions between sequential states S0, S1, S2 and S3.
3. Acetylene: we performed NA-AIMD simulations starting with the S1, S2 and S3 low-lying excited states employing XMS-CASPT2 with a (6e,6o) active space. Non-adiabatic coupling between all states (three excited states and the ground state) was allowed during the simulations.
4. Alcohols: namely methanol, ethanol and vinyl-alcohol. We performed NA-AIMD simulations on the S1 state and allowed surface-hopping back to the ground state. We observed a rapid fragmentation of the OH bond in all cases; thus, all the simulations ran for 60 fs. For methanol, we used XMS-CASPT2 with a (4e,6o) active space. For ethanol, we used XMS-CASPT2 with a (6e,8o) active space. For vinyl-alcohol, we used XMS-CASPT2 with a (4e,8o) active space.

3.3 Radical recombination

Due to the high computational cost of the XMS-CASPT2 method, we performed AIMD simulations to study the recombination processes using DFT, specifically with the ω B97X-V functional and an aug-cc-pVDZ basis set. We started with two species at a distance of at least 2.4Å from the center of the carbon bond and sampled different angles between the fragmented products. For each angle, we ran 30 trajectories with varying temperatures between 10 K and 40 K, and the velocities were randomly sampled from the corresponding Maxwell–Boltzmann distribution.

3.4 Ice environment

To study the effect of the ice environment on the stability of the different structures, calculations were performed within the DFT framework using the plane-wave-based Vienna *ab initio* simulation package (VASP)[94] with PAW[95, 96] pseudopotentials and the PBE0 [97–99] hybrid exchange-correlation functional. Due to significant van der Waals interactions between the molecules, van der Waals dispersion corrections were calculated using the many-body dispersion energy method of Tkatchenko et al. [100, 101] Results were converged to an accuracy of approximately 0.03 eV, in relation to the cutoff energy for the plane-wave basis (converged at 400 eV), the k-point mesh

density and the vacuum length in the calculations for isolated molecules. Structures were relaxed using ionic relaxation with the conjugate gradient algorithm.

4 Conclusion

The reaction of O(¹D) with different hydrocarbons is barrierless and results in the addition of oxygen to the π bond or in insertion into the CH bond. In the gas phase, without an efficient way to dissipate the excess energy, the products are mainly fragmentation products. In contrast, in an ice environment, the ice supplies an efficient way to dissipate the excess energy and stabilization of the products is obtained.

Our findings show that when the ice is subjected to UV radiation, as expected in environments like molecular clouds, second-generation reactions play a key role. In these reactions, the initial products further photodissociate into radicals and then recombine, significantly contributing to the chemical complexity. In the case of methane, we demonstrate that while methanol is formed in a direct insertion reaction, the formation of formaldehyde is a result of photofragmentation of the methanol into radicals; their recombination provides a path for formaldehyde formation. In the case of ethane and ethylene, second-generation reactions are responsible for the formation of acetaldehyde, and in the case of acetylene, the second-generation reactions lead to the formation of CO, which was observed in large quantities in the experiments.

Data Availability. All study data are included in the article SI.

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Appendix A The effect of the ice on the structure's stability

In order to understand and quantify the effect of the ice on the carbohydrate molecule of interest, calculations of energy and atomic configuration were performed for both the isolated molecule in a vacuum and the molecule within the hydrocarbon/CO₂ ice. All energies are given with reference to the isolated oxygen atom and the isolated hydrocarbon molecule or the hydrocarbon/CO₂ ice for the vacuum and ice calculations, respectively. All calculations were performed with spin polarization. The initial magnetization was set to zero in structures that otherwise reached the triplet state in order to ensure a singlet state, as this is the system of interest.

The ice was built for each hydrocarbon molecule by creating a small unit cell with the hydrocarbon molecule and two CO₂ molecules. The ice was then relaxed using ionic relaxation while allowing the cell volume and shape to also relax. A supercell was then created by replicating the small relaxed unit cell in the direction of each lattice vector, thereby creating a supercell of fixed dimensions with eight replicated hydrocarbon molecules and 16 CO₂ molecules. One hydrocarbon molecule in the supercell was then replaced by the carbohydrate molecule of interest and the ice was relaxed to obtain the energies and atomic configurations of the stable states. This was carried out for various orientations of the carbohydrate with the ice. The energies and atomic

configurations of the transition states were calculated by fixing the atomic positions of the transition state of the carbohydrate molecule of interest to those obtained in Section 2.1 and relaxing the rest of the ice. Binding energies were also determined by calculating the difference between the energy of the ice-carbohydrate complex and the single-point energy of the ice with the carbohydrate removed, plus the single-point energy of the carbohydrate with the ice removed. Additionally, the effect of having one CO₂ molecule per hydrocarbon, as opposed to two, was examined and determined to be insignificant. As can be seen, the ice always stabilizes the carbohydrate more than the vacuum, as a result of hydrogen bonding between the oxygen atom and the ice. Oxirene and ethynol are more stabilized by the ice than ethenone due to greater hydrogen bonding with the ice; however, this is not a significant effect. There were many metastable states observed for each carbohydrate molecule, depending on the initial orientation of the molecule within the ice. Note that the same effect was observed when an oxygen radical was introduced into the hydrocarbon/CO₂ ice and the system was relaxed, resulting in the oxygen atom bonding with a hydrocarbon. The resulting carbohydrate was orientated differently within the ice depending on the initial placement of the oxygen radical with the ice. The binding energy calculations show that most of the difference in energy of these metastable states results from the reorganization of the ice around the carbohydrate and not from significant differences in the bonding between the carbohydrate and the ice.

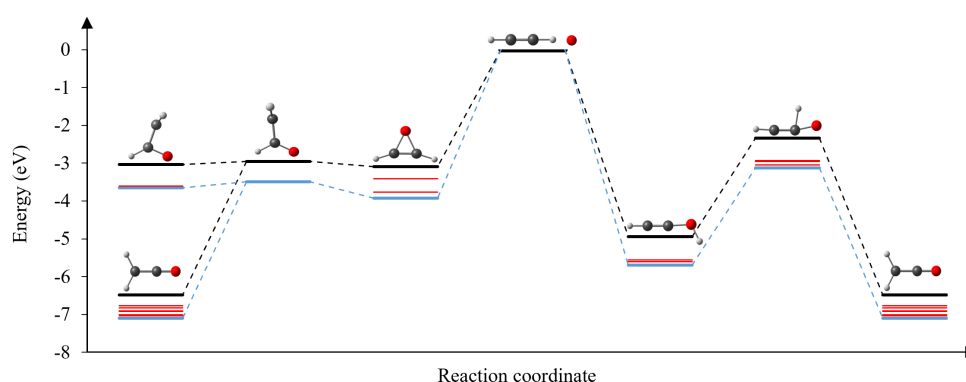


Fig. A1 Comparison of the stability of the different structures on the acetylene PES calculated in vacuum (black lines) and in different orientations of the ice (red lines); the most stable orientation in the ice is represented in blue.

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