The Case of H$_2$C$_3$O Isomers, Revisited: Solving the Mystery of the Missing Propadienone

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Abstract

To date, two isomers of H$_2$C$_3$O have been detected, namely, propynal (HCCCHO) and cyclopropenone (c-H$_2$C$_3$O). A third, propadienone (CH$_2$CCO), has thus far eluded observers despite the fact that it is the lowest in energy of the three. This previously noted result is in contradiction to the minimum energy principle, which posits that the abundances of isomers in interstellar environments can be predicted based on their relative stabilities and suggests, rather, the importance of kinetic over thermodynamic effects in explaining the role of such species. Here, we report results of ab initio quantum chemical calculations of the reaction between H and (a) HC$_2$O, (b) H$_2$C$_3$O (both propynal and propadienone), and (c) CH$_2$CHCO. We have found that, among all possible reactions between atomic hydrogen and either propadienone or propynal, only the destruction of propadienone is barrierless and exothermic. That this destruction pathway is indeed behind the nondetection of CH$_2$CCO is further suggested by our finding that the product of this process, the radical CH$_2$CHCO, can subsequently react barrierlessly with H to form propenal (CH$_2$CHCHO) which has, in fact, been detected in regions where the other two H$_2$C$_3$O isomers are observed. Thus, these results not only shed light on a previously unresolved astrochemical mystery, but also further highlight the importance of kinetics in understanding the abundances of interstellar molecules.

Key words: astrochemistry – ISM: abundances – ISM: clouds – ISM: molecules – molecular processes

1. Introduction

In a recent review by McGuire (2018), it was noted that, to date, approximately 200 different individual molecular species have been detected in either interstellar or circumstellar regions. As observing facilities and observational techniques have become more sophisticated, larger and more complex molecules have been detected, including a number of isomers—one of the most notable being the branched form of propyl cyanide (C$_3$H$_7$CN; Belloche et al. 2014).

Uncovering the chemical mechanisms behind the observed relative abundances of these isomers remains one of the major challenges in astrochemistry today, and as increasingly complex molecules are detected, this problem will only grow more acute. For example, the abundances of H$_2$C$_3$O isomers have posed a longstanding astrochemical conundrum. The first such species to be detected was propynal (HCCCHO), observed by Irvine et al. (1988) in the cold core TMC-1. The cyclic molecule cyclopropenone (c-H$_2$C$_3$O) was later seen by Hollis et al. (2006) toward Sgr B2(N) using the GBT. There is also a third form, propadienone (CH$_2$CCO), that was calculated to be the most stable of the three (Komornicki et al. 1981; Maclagan et al. 1995; Ekern et al. 1996; Scott & Radom 2000; Karton & Taibi 2014); however, this last form has thus far proven elusive.

One such attempt to detect propadienone was made by Loomis et al. (2015), who searched for isomers of H$_2$C$_3$O in archival data from the PRIMOS survey of Sgr B2(N). There, they reported detections of cyclopropenone and propynal but a nondetection of CH$_2$CCO. In that work, Loomis and coworkers interpreted their results as highlighting the influence of some as yet unknown reaction that favored either the production of propynal and cyclopropenone and/or the destruction of propadienone.

More recently, Loison et al. (2016) reported nondetections of propadienone toward a number of starless cores and molecular clouds, despite having detected both cyclopropenone and propynal. Based on these observational results, as well as those from detailed chemical modeling, they too concluded that the abundances of the H$_2$C$_3$O molecules were kinetically, rather than thermodynamically controlled. Loison and co-workers speculated that the primary contributing factor behind the observed abundances of these isomers were differing formation routes. However, the results of their simulations regarding propadienone were mixed, with its calculated abundance being within the observational error of their upper limit for at least sources with typical densities of $\sim 10^4$ cm$^{-3}$ at relevant timescales. Thus, despite evidence suggesting the impact of some key chemical reactions on the abundance of propadienone, their identities remained mysterious.

Here, we report the results of ab initio quantum chemical calculations of the reaction H + HC$_2$O, as well as hydrogen additions to a number of related species, including propynal and propadienone. Though this study was motivated by the recent detections of HC$_2$O (McGuire et al. 2017) and H$_2$C$_3$O (Ordiner et al. 2017; McGuire et al. 2017), in performing these calculations we have uncovered the likely chemical pathways responsible for the puzzling lack of CH$_2$CCO.

Secondarily, our findings shed additional light on the validity of using thermodynamics to predict molecular abundances in the ISM, more generally, and highlight the central importance of chemical activation energy barriers, i.e., kinetics. Such an attempt to make sense of observational results was made by Lattelais et al., who proposed a general rule based on a comparison between observational data and the results of quantum chemical calculations (Lattelais et al. 2009, 2010, 2011). This guideline, which they called the “minimum energy principle” (hereafter MEP), states that the relative abundances of different isomers in the same region could be estimated based on the energy differences between them, with the most stable being the most
abundant. However, even in their first work on the MEP, Lattelais et al. (2009) noted exceptions, for instance, species with the formula C₂H₄O₂. Thus, though the aim of this work is neither to further challenge the already dubious MEP nor to again demonstrate—as we have previously done in Loomis et al. (2015)—that the H₂C₅O isomers violate said principle, our results do provide further evidence for the centrality of kinetics in understanding the theoretical basis behind interstellar isomer abundances.

The rest of this work is as follows: in Section 2 we give an overview of the methods and tools used in this study. In Section 3 our results are presented, and their astrochemical implications are discussed in Section 4. Finally, our conclusions are summarized in Section 5.

2. Computational Details

We used unrestricted density functional theory (DFT) with the PW6B95 functional (Zhao & Truhlar 2005) and the def2-TZVP basis set (Schäfer et al. 1994). These calculations were done in Turbomole⁴ accessed via ChemShell (Sherwood et al. 2003; Metz et al. 2014). The geometry optimizations and instanton calculations were done in DL-Find (Kästner et al. 2009) through ChemShell. All molecular degrees of freedom were optimized in all cases. No symmetry was imposed on the molecules. For radical–radical reactions, like H + H₂C₅O, an unrestricted broken-symmetry wave function was used with overall as many spin-up as spin-down electrons, but finite spin density on both radicals. Although a gas-phase model was used, rate constants were as spin-down electrons, but symmetry wave function was used with overall as many spin-up

3. Results and Discussion

The results of our geometry optimizations of the molecule HC₅O show that it is not linear. Rather, in agreement with QCISD calculations by Wang & Cooksy (1996) and Cooksy et al. (1995), we found two main configurations, namely, one with a bend on the CO-end, and another with the bend on the CH-end, with the latter being more stable.

Minima and transition state structures were verified by frequency calculations from numerical Hessians in DL-Find. Energies are reported including the harmonic vibrational zero-point energy. Barrierless processes were identified by starting energy minimizations from the separated reactants. An optimization ending up in the product minimum demonstrates a barrierless path.

Bimolecular rate constants were calculated using instanton theory (Miller 1975; Coleman 1977) as implemented in DL-Find (Rommel et al. 2011) below the crossover temperature, 

\[ T_c = \frac{\hbar \omega_b}{2\pi k_b}, \]

with \( \hbar \) and \( k_b \) being the reduced Planck and Boltzmann constants, respectively, and \( \omega_b \) the absolute value of the imaginary frequency at the transition state. The instanton path was discretized with 40 replicas, except for the calculations at 55 and 50 K for the reaction H + HCCCHO \( \rightarrow \) HC₅O + H₂, where 78 replicas were used. Convergence with respect to the number of replicas was confirmed by using more replicas at one low temperature. Through the use of both a well-established correction (Kryvohuz 2013; McConnell & Kästner 2017) close to the crossover temperature and the use of reduced instanton theory (Kryvohuz 2013) above that temperature, a continuous curve over the full temperature range was achieved.

⁴ W7.1, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, http://www.turbomole.com.

Table 1: Overview of Reaction Energies (\( \Delta E \)) and Activation Barriers (\( \Delta E_a \)) in kJ mol⁻¹ of All Reactions Studied

| Label | Reaction | \( \Delta E \) | \( \Delta E_a \) |
|-------|----------|----------------|----------------|
| (R1)  | H + HC₅O \( \rightarrow \) CH₂CCO | −363.2 | 0.0 |
| (R2)  | H + HC₅O \( \rightarrow \) HCCCHO | −340.3 | 0.0 |
| (R3)  | H + CH₂CCO \( \rightarrow \) HCCCHO + H₂ | −58.2 | 18.4 |
| (R4)  | H + CH₂CCO \( \rightarrow \) CH₂CHCO | −246.5 | 0.0 |
| (R5)  | H + CH₂CCO \( \rightarrow \) CH₃CCOH | −117.2 | 38.1 |
| (R6)  | H + CH₂CCO \( \rightarrow \) CH₂CHCHO | −169.7 | 0.0 |
| (R7)  | H + CH₂CCO \( \rightarrow \) CH₃CCO | −205.4 | 6.2 |
| (R8)  | H + HCCCCO \( \rightarrow \) CCCHO + H₂ | 128.1 | 128.1 |
| (R9)  | H + HCCCCO \( \rightarrow \) HC₅O + H₂ | −76.5 | 11.7 |
| (R10) | H + HCCCCO \( \rightarrow \) CHCCCHOH | −168.8 | 26.9 |
| (R11) | H + HCCCCO \( \rightarrow \) CHCCCHOO | −74.6 | 23.8 |
| (R12) | H + HCCCCO \( \rightarrow \) CHCHCHO | −164.5 | 18.9 |
| (R13) | H + HCCCCO \( \rightarrow \) CH₂CCHO | −192.7 | 11.3 |

Thus, while both CH₂CCO and HCCCHO can be formed by hydrogenation of HC₅O, they show different stabilities with respect to further hydrogenation. Here, we have further studied the hydrogen addition reactions to all atoms of propadienone,
which is drawn orange in the right structure. Here potential energies without zero-point energy are shown.

An examination of the energetics of these processes, summarized in Table 1, shows that they are all exothermic. As with propadienone, hydrogen atoms can react with propynal, HCCCHO, leading to hydrogen additions and abstractions. However, unlike the case with CH$_2$CCO, the results of our calculations show that all of these reactions involving HCCCHO either have a barrier or (abstraction of the aliphatic H) are endothermic. Thus, at the low temperatures of molecular clouds, they will be significantly slower than the barrierless process destroying CH$_2$CCO. Of the six possible reactions, hydrogen abstraction leading back to HC$_3$O (R9) and hydrogen addition leading to CH$_3$CHO (R13) have the lowest barriers of 11.7 and 11.3 kJ mol$^{-1}$, respectively. Their rate constants are plotted in Figure 2, and are fairly similar, which can be expected from the similar barriers. Overall, the rate constants of both reactions are low: at 100 K they are $8.5 \times 10^{-16}$ and $2.4 \times 10^{-16}$ cm$^3$ s$^{-1}$ while at 50 K, the lowest temperature for which we performed instanton calculations, they are merely $1.1 \times 10^{-17}$ and $3.7 \times 10^{-18}$ cm$^3$ s$^{-1}$. In sum, our calculations reveal that propynal is rather stable against reaction with H atoms, unlike propadienone, which will be efficiently destroyed by atomic hydrogen on both grain surfaces and in the gas.

4. Astrochemical Implications

Atomic hydrogen is a known component of even dense molecular clouds, where it is produced mainly via the cosmic-ray-driven dissociation of H$_2$ (Padovani et al. 2018). Thus produced, these atoms can adsorb onto the surface of interstellar dust grains, where their high mobilities make reactions between them and other grain species one of the dominant formation routes for complex organic molecules in the ISM (Herbst & van Dishoeck 2009). Cosmic rays can also drive the formation of atomic hydrogen within interstellar ices via radiolytic dissociation (Shingledecker & Herbst 2018; Shingledecker et al. 2018). Therefore, given the ubiquity of H in the gas, as well as both on and in dust-grain ice mantles, our finding that H atom addition to CH$_2$CCO (R4) is barrierless and exothermic provides a compelling explanation as to why this most stable HC$_3$O isomer has remained undetected in sources over a wide range of physical conditions (Loomis et al. 2015; Loison et al. 2016).

Our hypothesis that reaction (R4) is indeed the long-sought process underlying the consistent nondetections of propadienone is further supported by both previous observational and experimental studies. For example, in Zhou et al. (2008) it was shown that, in a mixed CO:C$_2$H$_2$ ice at 10 K irradiated by high-energy electrons under ultra-high vacuum, the formation of both cyclopropenone and propynal could be observed, though interestingly, no firm detection of propadienone could be made. There, atomic hydrogen was efficiently destroyed by the dissociation of acetylene, which could then quickly destroy CH$_2$CCO even at the very low temperatures at which the experiment was carried out.

Another finding suggestive of the importance of reaction (R4) was the detection by Hollis et al. (2004) of propenal (CH$_3$CHCHO) in Sgr B2(N), where HCCCHO and c-H$_2$C$_3$O have been seen (Loomis et al. 2015). In the paper reporting their detection, Hollis et al. proposed the following formation route for CH$_3$CHCHO:

\[ \text{HCCCHO} + 2\text{H} \rightarrow \text{CH}_3\text{CHCHO}. \quad \text{(R15)} \]
However, as the results of our calculations show, a much more energetically favored precursor is in fact CH$_2$CCO. If reaction (R4) followed by (R14), as opposed to (R15) is the dominant formation route for CH$_2$CHCHO then, in a sense, propadienone might be hiding in plain sight as propenal, rather than missing.

More generally, our results support the claim made by Loomis et al. (2015) that molecular abundances in interstellar environments, even in hot cores like Sgr B2(N), are ultimately kinetically controlled, i.e., governed by reaction barriers rather than the thermodynamic stabilities of individual species. Moreover, as one can glean from an overview of the data in Table 1, it is often not possible to intuit the presence or size of such barriers, particularly for neutral–neutral reactions not involving two radicals. Thus, detailed quantum chemical calculations are essential astrochemical tools that can, as shown here, shed light on the underlying processes that give rise to seemingly perplexing observational results.

Finally, these data both strengthen the chemical connection between unsaturated carbon-chain species like HC$_3$O and nearly saturated organic molecules, such as CH$_2$CHCHO, and suggest that other members of the HC$_3$O ($n = 3\sim7$) family—as well as perhaps similar carbon-chain species like the ubiquitous cyanopolyynes—might likewise serve as backbones for more complex molecules (McGuire et al. 2018).

5. Conclusions and Outlook

We have carried out calculations of reactions between atomic hydrogen and HC$_3$O, CH$_2$CCO, and HCCCHO. Our main findings are the following:

1. that H + HC$_3$O, (R1) – (R2), is both barrierless and exothermic, and leads to either propadienone (CH$_2$CCO) or propynal (HCCCHO), with the orientation of the reactants being the main factor influencing which of these two products is formed;
2. that the reactivity of propynal and propadienone with H are starkly different, with only H + CH$_2$CCO → CH$_2$CHCO (R4) being both barrierless and exothermic;
3. that the above finding serves as a compelling explanation as to why attempts to detect propadienone have been consistently negative; and
4. that the subsequent barrierless exothermic reaction of CH$_2$CHCO with H, shown in (R14), yields propenal (CH$_2$CHCHO), which has been observed in Sgr B2(N).

These findings are in agreement with recent work by Garrod et al. (2017), who examined the formation mechanisms of both the branched (i-C$_3$H$_7$CN) and straight-chain (n-C$_3$H$_7$CN) forms of propyl cyanide in detail. As with propadienone, the more stable isomer (i-C$_3$H$_7$CN) was determined to be less abundant than n-C$_3$H$_7$CN (Belloche et al. 2014). Interestingly, it was found by Garrod et al. (2017) that kinetic factors—specifically, the rates of reaction with H and CN and the relative efficiencies of the addition of these radicals to either secondary or terminal carbon atoms—were essential for accurately reproducing the i:n ratio.

Thus, though the focus of this work was on explaining the consistent nondetections of propadienone and not on disproving the already questionable MEP, our results further reinforce the central role of kinetics in understanding the behavior of interstellar isomers, even in comparatively warm environments like star-forming regions. Unfortunately, this makes interpreting observed abundances more challenging since even similar species, like propynal and propadienone, can display quite different reactivities. Thus, as the variety and complexity of known interstellar molecules continues to increase, so too will the importance of detailed experiments or quantum chemical calculations in understanding the chemical basis underlying observational results.

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Software: Turbomole (http://www.turbomole.com), ChemShell (Sherwood et al. 2003; Metz et al. 2014), DL-Find (Kästner et al. 2009), Molpro (Werner et al. 2018).

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