January 10, 2024

Dear Associate Editor

Professor Luis Banares,

Article CP-ART-12-2023-005872

Enclosed please find our **revised** research article No. CP-ART-12-2023-005872 entitled ‘**Elucidating the Chemical Dynamics of the Elementary Reactions of the 1‑Propynyl Radical (CH3CC; X2A1) with 2-Methylpropene ((CH3)2CCH2; X1A1)**’ for the *Physical Chemistry Chemical Physics*. All changes made to the text during revision were highlighted in yellow.

We sincerely thank the editor and reviewers for taking the time to review our manuscript and providing constructive feedback to improve our manuscript. We have revised the manuscript accordingly by following the reviewers’ suggestions. Below are the original comments from the editor and reviewers (*italics*) and our point-by-point response:

**Referee 1:**

1. *The authors present a 1-propynyl radical and 2-methylpropene reaction study by combining experimental findings with ab initio and statistical calculations. In addition, although somewhat hidden, they also mention the reaction between the 1-propynyl radical and 2-butene in both cis and trans configurations. These reactions are of great importance to the astrochemistry area due to the presence of some of the molecules in interstellar clouds.*

*In the central part of the paper, the authors focus on the first reaction, 1-propynyl radical with 2-methylpropene. The experimental and main theoretical calculations are well presented and discussed.* ***The results show a primary channel for the H atoms, while the methyl radical loss is a minor channel. However, the authors mentioned that detecting the methyl radical co-fragment was not possible due to some contamination at the masses relevant to the fragment. The authors do not mention what might account for this contamination in the present publication. I think a comment or a direct reference to where it is explained in detail should be added. This contamination could not be of high importance for the present reaction since the statistical calculation showed the H-atom elimination as the main channel and was experimentally verified;***

**Response:**

First, we need to inform the Refereethatthe Discussion section had an unintentionally misleading sentence that made the reader to think that both isomers of 2-butene have been studied experimentally. We only tried *cis*‑2*‑*butene experimentally, but *cis*‑ and *trans*-2*‑*butene theoretically. In the revised version it is stated more clearly and straightforwardly.

Since the highly reactive 1-propynyl radical (CH3CC) has a molecular mass of 39 amu and the products of its recombination (C6H6) 78 amu. Contamination of the background signal at *m/z* = 78 and 79 most likely arises from products of 1-propynyl recombination (C6H6 – 78 amu) with the contribution of 13C-compounds (13CC5H6 – 79 amu). C6H6 isomers, according to the NIST database, show peaks at 78 – 80 *m/z* indicating the presence of up to two 13C atoms. Recombination of 1-propynyl most likely occurs during supersonic expansion in the "expansion region", on the stainless walls of the pulse valve (catalyzed by Fe2O3) or through a precursor decay (CH3CCI) during storage. In addition, mass 80 amu can have a contribution from ionized helium clusters He20, common in molecular beams of He1,2, which was used as a carrier gas for the CH3CCI precursor. The ionization energy used in the experiment (80 eV) is sufficient to ionize He clusters (He ionization potential is 24.6 eV).

We added this discussion of background signal to the SI and added a sentence ‘Probable sources of background signal are discussed in the SI’ to the Results section.

1 H. Buchenau, E. L. Knuth, J. Northby, J. P. Toennies and C. Winkler, Mass spectra and time‐of‐flight distributions of helium cluster beams, *The Journal of Chemical Physics*, 1990, **92**, 6875–6889.

2 L. Lundberg, P. Bartl, C. Leidlmair, P. Scheier and M. Gatchell, Protonated and Cationic Helium Clusters, *Molecules*, 2020, **25**, 1066.

***however, in the 1-propynyl radical and 2-butene reaction where no signal was observed neither for the H nor for the CH3 loss masses, it is of great importance, since the theoretical calculations present the methyl channel as the main one.***

**Response:**

In the case of *cis*-2-butene, in the manuscript we do not claim that the CH3-loss signal wasn’t observed, instead, we state ‘*No signal was detected at m/z = 94 and 93 in potential atomic and molecular hydrogen losses, while detection of the CH3-loss channel was prevented by a high background signal at m/z = 80, 79, and 78*’. We don’t have enough evidence to eliminate or prove CH3-loss channels. This is why we keep results for the 1-propynyl + *cis*-2-butene system only in the Discussion and do not mention them in the Title, Abstract, or Results. Theoretical calculations prove that H-loss in the reaction of 1-propynyl + *cis*-butene is a minor channel with a dominance of methyl elimination processes. This, together with the reasonable sources of background signal, explains our experimental results at the used experimental setup under our conditions.

***Another thing that should be noted is that at the end of the discussion, the authors make a small comparison with other reactions between the 1-propynyl radical and other hydrocarbon molecules. This comparison should be further elaborated in case more similar studies exist in these reactions.  
In conclusion, the work is well written and presented, and the results are good, but it would be necessary to reinforce some ideas a bit more.***

**Response:**

A new sentence has been added to the Results: ‘*The reaction mechanism of 1-propynyl with 2-methylpropene follows the main trends that were found out for the reactions of the 1-propynyl radical with unsaturated hydrocarbons25,45–51: (i) the reaction starts with barrierless addition of the radical center to the unsaturated bond, (ii) the overall process is exoergic, (iii) all transition states involved are located below the energy of the separated reactants, (iv) the methyl group of the 1-propynyl radical reactant is not involved in the reaction mechanism and plays a spectator role*’. A more detailed literature review on the chemistry of the 1-propynyl radical is present in our previous works cited in the Introduction, together with similar works. We would like to especially highlight the two following papers with the most detailed literature review:

1. A. M. Thomas, L. Zhao, C. He, A. M. Mebel and R. I. Kaiser, A Combined Experimental and Computational Study on the Reaction Dynamics of the 1-Propynyl (CH3CC) – Acetylene (HCCH) System and the Formation of Methyldiacetylene (CH3CCCCH), *J. Phys. Chem. A*, 2018, **122**, 6663–6672.
2. I. A. Medvedkov, A. A. Nikolayev, C. He, Z. Yang, A. M. Mebel and R. I. Kaiser, A combined experimental and computational study on the reaction dynamics of the 1-propynyl (CH3CC, X2A1) – propylene (CH3CHCH2, X1A′) system: formation of 1,3-dimethylvinylacetylene (CH3CCCHCHCH3, X1A′) under single collision conditions, *Mol. Phys.*, 2023, e2234509.

**Reviewer 2:**

*It's a great experimental and theory paper by the Mebel/Kaiser team. I think the paper should eventually be published in PCCP. However, at this point, the authors should address the minor comments below:****The reviewer is concerned with the comment on page 4 about the background in the mass spectrum that precludes the authors from looking at the 78, 79, and 80 channels. In particular, the 80 channel is of high importance because, later in the paper, the authors show that this is the energetically favored product channel. Can the authors comment more on the "background"? Do the authors know what causes the background?***

**Response:**

Please, see our response to the first comment of the reviewer #1.

***Can the authors work around this background using isotopically labeled CH3CC or iso-butene?***

**Response:**

Isotopically labeled CH3CCI is not a commercially available compound and, due to its low stability, its preparation will be a challenging and expensive task. Isotopically labeled *iso-*butene (2-methylpropene-d8)is commercially available ($680 for 0.5L) and will shift detection mass for the CD3-loss channel to *m/z* = 85 making it, in principle, detectable. However, since the theoretical calculations predict the methyl radical loss as a relatively minor channel in the reaction of 1-propynyl + *iso-*butene, here we focused our attention at the dominant H-loss channels. Alternatively, for future experiments with 2-butene, the use of the fully deuterated C4D8 could be a viable option.

***Because the authors don't address this issue in any detail, it creates a disconnect between the experiments and the theory.***

**Response:**

With the aforementioned revisions addressing the background issue preventing the detection of the methyl loss channel and with the fact that the experimentally observed H-loss channel dominates (>70%) according to statistical calculations, we believe that there is no disconnection between theory and experiment in the revised manuscript.

Sincerely,

Ralf

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