November 28, 2023

Dear Executive Editors

Dr. Nathalie Weickgenannt,

Dr. Frank Maaß

Article No. 202315147

Enclosed please find our **revised** research article No. 202315147 entitled ‘One Collision – Two Substituents: Gas-Phase Preparation of Xylenes under Single-Collision Conditions’ for the journal of the German Chemical Society – *Angewandte Chemie International Edition*. 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:

**Editor:**

*Furthermore, the editorial office requires that you make the following checks/changes before uploading your revision:*

* *Manuscripts generally benefit from careful re-reading before submitting the revised version.*

**Response:**

The manuscript was carefully re-read before submitting the revised version.

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**Response:**

No copyright permission is required.

* *Correct the format of your references. Authors should be listed in the form A. B. Smith, P. Jones, followed by the journal name in italics, the year (in bold), volume (if applicable, in italics), then page or article number. If present, please remove the article titles (but not from books!) and DOI Numbers from the reference citations for journals. (For example: [1]a)P. Gao, W. Pan, N. Li, B. Tang, Chem. Sci.* ***2019****, 10, 6035-6071.); b) J. Liu, Z. Cui, Bioconjugate Chem.* ***2020****, 31, 1587-1595.)*

**Response:**

Format of the references is corrected in the revised version.

* *Check your references carefully. Some are missing information (for example, year, volume, page numbers, or article numbers). Page numbers given as 1-5 or 1-12 are probably not the correct citation and should be replaced by an article number. (For example see Ref. 5)*

**Response:**

Ref. 5 – doesn’t have article number and actually have pages 1-12 in the volume, while other found missing pages are corrected.

**Reviewer 1:**

*In this contribution, the authors have demonstrated that xylenes can be formed in a barrier-less exothermic reaction between isoprene and the methylpropynyl radical. The data, along with comparisons to the reaction of the radical with isomeric 1,3-pentadiene are conclusive and consistent with the known thermochemistry of the reactions. The mechanisms for the two sets of reactions have been explored computationally yielding the anticipated complex minimum energy reaction pathways full of H shift reactions and other rearrangements.*

*I can suggest only minor changes:  
  
1. Abstract line 33: "barrierless addition of the radical to the..."*  
**Response:**

Fixed in the revised version.

*2. Scheme 2 is not really necessary for a chemistry audience.*  
**Response:**

Scheme 2 has been removed from the main manuscript.

*3. R&D: I would like to see at least one raw mass spectrum with m/z 106 in it. Perhaps put it in SI.*  
**Response:**

TOFs spectra for *m*/*z* 106 added as Figure S2 in the SI.

*4. Page 3, line 16: "Here, there was no signal observable at m/z = 106.."*

**Response:**

Fixed in the revised version.

**Reviewer 2:**

*This work discusses a single-collision reactive pathway to xylenes from 1-propynyl and butadiene. The proposed pathway would not only fill a gap in low-temperature chemistry, but would also explain the high meta- and para-xylene abundance with respect to that of the ortho isomer. While the paper is certainly well-written and may be highly relevant, there are a few more questions and comments the authors should address before I can recommend it for publication.  
  
1. Figure S1 and figures S2-15 are missing in the SI. The PES would be needed to assess whether the authors have considered methyl loss channel yielding toluene in the 1-propynyl + isoprene reaction. It is not observed experimentally, and it is unclear whether it is also predicted to be unfavorable computationally.*

**Response:**

The full PES (Figures S3-S16) have been included in the SI. Pathways to toluene were studied and can be seen in Figs. S7, S8, S11, and S16. However, RRKM calculations have shown that these channels are not competitive in the title reaction and the branching ratio of the toluene + CH3 products (p42) is zero in the reaction with isoprene and up to 0.8% in the reaction with 1,3-pentadiene.

*2. In Fig. 1, the TOF distributions are in b and d and the angular distributions in a and c. The question of EI fragmentation could be settled unequivocally if the neutral co-fragment had also been detected. It would also give more information on the kinetic energies, as most is going to go to the lighter fragment. Can the authors follow the H and CH3 reaction products, as well?*

**Response:**

Caption for the Fig. 1 is fixed. Current detection scheme (‘Universal detector’) cannot record the neutral fragments without prior ionization. Signals for H and CH3 coming from the reactive scattering (recorded as H+ and CH3+) overlap with the H+ and CH3+ signals coming from the fragmentation of the reactants and products.

*3. The 1-propynyl radical is certainly widely discussed as a high-energy reactant and has been included in astrochemical models. It is nonetheless difficult to judge the relevance of its reaction with isoprene without the inclusion of this reaction in an astrochemical model. Is the lifetime of 1-propynyl long enough to realistically react with an isoprene molecule? Direct H-addition/elimination driven stabilization of 1-propynyl may keep its concentration exceedingly low unless it has a high enough entrance barrier.*

**Response:**

The 1‐propynyl radical is not expected to be formed in high concentrations, but it is conceivable that when formed it would react quickly, primarily by addition to double or triple bonds in other hydrocarbons to form larger molecules. Since all studied reactions of the 1-propynyl radical with hydrocarbons have no entrance barrier, are exoergic, and can form highly stable products like xylene, 1-propynyl even at low concentration can influence the chemical evolution and the chemical composition of the ISM and Titan atmosphere. On Titan, 1-propynyl is expected to be formed by the photolysis of propyne within the detached haze layer (down to ~400 km above Titan's surface).

*4. The experimental evidence for xylene formation is primarily the high maximum of the kinetic energy, which necessitates a stable product, and only they fit the bill. How about ethylbenzene, though? Can the authors rule out its formation? Maybe the dominant path is still missing from Fig. 3?*

**Response:**

Indeed, according to NIST, the enthalpy of formation of ethylbenzene (29.8 kJ mol–1) is close to that of xylenes (18-19 kJ mol–1). However, an exhaustive PES exploration did not show any plausible pathway to ethynyl benzene because it requires a significant number of unfavorable H migrations, which generally are less competitive than H or CH3 losses.

*5. What do the computed rate constants suggest about the lifetime of the activated complex? The potential energy surface to the branched-chain products is by and large similar on the isoprene as on the pentadiene surface. Thus, without a low-energy intermediate lengthening the lifetime of the activated complex, these, less stable products could be expected to exhibit angular anisotropy, also. While this speaks for the authors' assignment of the butadiene products as xylenes, it also emphasizes the question why the potential energy surface is incapable of capturing the product branching ratios.*

**Response:**

The RRKM-calculated lifetimes appeared to be similar for both isoprene and 1,3-pentadiene reactions. Calculated lifetimes for the initial complexes are included in the SI (Table S12). We cannot agree that the calculated PES “is incapable of capturing the product branching ratios”. In particular, the results from RRKM calculations for the isoprene reaction show up to 15% yield of xylenes, which agrees with the experimentally observed maximal translational energy release, whereas thermodynamically unfavorable products **p3–p9** are likely to be masked in the lower energy section of the CM translational energy distribution. For the 1,3-pentadiene reaction, experimental results can be accounted for by dynamical preference of the initial addition channel toward short-lived **i22**, which has lifetime 32 and 13 times shorter than the evaluated lifetimes respectively of **i3** and **i11** – the main decomposingcomplexes in the isoprene reaction. Since all entrance reaction channels are barrierless, the PES (characterized only in terms of local minima and transition states positioning) is simply insufficient to explain the branching of the reaction flux in the entrance channels. Extremely expensive trajectory (molecular dynamics) calculations are needed in order to quantify this branching.

**Reviewer 3:**

*The submission describes crossed molecular beam experiments on the reactions of the 1-propynyl radical (CH3CC) with 2-methyl-1,3-butadiene (CH2C(CH3)CHCH2 ; isoprene) via an addition reaction to form a long lived complex, yielding, following rearrangement and subsequent H-loss, xylene isomers. The observed reaction dynamics (forward-backward symmetry) are consistent with this mechanism, providing an interesting one step synthesis of an important class of aromatic molecules. As a comparison, the reaction of CH3CC with 1,3-pentadiene (CH3CHCHCHCH2) shows evidence of a short-lived intermediate yielding an acyclic product via CH3 loss. The results are backed up and complemented by high quality ab-initio quantum chemical calculations coupled with RRKM simulations which show that both reactions can occur over submerged barriers, and are therefore of interest not only for high temperature gas-phase environments, but also for very low temperature ones such as dense molecular clouds and planetary atmospheres.  
The article is very nicely written, providing the right level of detail to enable the reader to follow the arguments, and it presents results of high significance for astrochemistry as well as combustion and other applications, and will be of interest to a wide range of readers. In my opinion it is suitable to be published in Angewandte.*  
  
*1. I have only one suggestion for improvement - on page 3 at the top of column 2 the authors state: "Energy conservation dictates that for those molecules born without internal excitation, Emax is the sum of the collision energy (EC) plus the reaction energy (deltarG)." It seems to me that mixing Gibbs Free Energy(Enthalpy) and translational energy is a bit confusing, and should be avoided, the authors should reword and stick to reaction energy (delta U, or delta H which is the same for a bimolecular reaction), without the entropic part.*

**Response:**

Authors agree with Reviewer.

*2. There is also a typo in the abstract, page 1 col 1 line 39 enveloped -> envelope*

**Response:**

The typo has been corrected in the revised version.

Frohe Weihnachten!

Ralf

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