**Response to Reviewers and Editor’s Comments**

Reviewer: 1

Recommendation: This paper is publishable subject to minor revisions noted.  Further review is not needed.

**Response:** We thank the reviewer for his/her recommendation.

Comments:  
Foremost, I have reviewed the paper as the organic chemist specializing in synthesis and photochemistry.  
According with my background, I could denote the following:

1. What is the major advance reported in the paper?

A keto-enol equilibrium is an interesting phenomenon with high impact on various fields of chemistry. Kaiser and coworkers developed the concept of the role of keto-enol equilibrium in astrochemistry, and have elaborated a method for detection and distinction of these tautomers in extreme conditions. In the present work, they applied this methodology (photoionization + ReTOF-MS) on a well-known energetic material, RDX (hexogen). The major advance of the paper – an experimental evidence of the formation of enol species during RDX decomposition, which confirmed the corresponding prediction from 1992 year.

2. What is the immediate significance of this advance?

The enormous importance of explosive materials in the technology requires a deep insight into combustion and decomposition processes. The presented results will be interested for the corresponding community as well as to all organic chemists, interested in tautomeric reactions.

**Response:** The above-mentioned comments made by the reviewer are correct. The reviewer has understood the subject described in the present manuscript very well. Thank you.

3. Technical suggestions of the reviewer:

I have some comments for further improvement of the manuscript:

1)     Prefix “s” in oxy-s-triazine should be marked by italic throughout the manuscript.

**Response:** The prefix “s” in oxy-*s*-triazine is marked by italic font throughout the manuscript.

2)      Abstract and the text. Maybe, it is better to replace “electronic structure calculations” by “quantum chemical calculations”.

**Response:** “electronic structure calculations” are replaced by “quantum chemical calculations throughout the manuscript.

3)      P. 1. line 21. “[CH2C(OH)COOH]” should be replaced by “[CH2=C(OH)COOH]”.

**Response:** We have replaced “[CH2C(OH)COOH]” with “[CH2=C(OH)COOH]” on page 1.

4)      P. 1. line 48. “Scheme 1” should be revised. It is rather Chart 1 or Figure 1.

**Response:** Following reviewer 2 comments, we have removed scheme 1 from the main manuscript and included it in the supporting information. Scheme 1 is renamed to Figure S1.

***Relevant changes in the manuscript****: Scheme 1 is removed from page 1 of the main article and added to the supporting information as Figure S1.*

5)      P. 4. line 48. “photoionization (PI) reflectron” replace by “photoionization (PI) and reflectron”?

**Response:** On page 4, we have replaced “photoionization (PI) reflectron” with “photoionization (PI) and reflectron”.

***Relevant changes in the manuscript (on page 4)****: “*photoionization (PI) reflectron” is replaced by “photoionization (PI) and reflectron”.

6)      P. 5. line 44. Could you please clarify the origin of the structures from Figure 1? All possible structures with M = 97? Or most possible?

**Response:** To identify the most possible isomeric forms of oxy-s-triazine and 1,3,5-triazine, we used SciFinder’s web-based structure search program. Considering the fact that the product at m/z = 97 is formed at the early stage of RDX decomposition,its structure must retain the -N-C-N-C-N- or -C-N-C-N-N- skeletal framework of RDX. Therefore, we selected only those cyclic and acyclic isomeric species that have aforementioned structural backbone, are neutral and possess similar functional groups as of previously proposed structures of products at m/z = 97 and 81.

***Relevant changes in the manuscript (on page 6):*** *“*The computed structures of possible cyclic and acyclic isomers…” is replaced by “The computed structures of most possible cyclic and acyclic isomers…”

*Following sentences are added on page 5: “Their simplified structures are depicted in Figure S6 of the supporting information.* *To identify these isomeric forms, we used SciFinder’s web-based structure search program. Considering the fact that the products such as at m/z = 97 is formed at the early stage of RDX decomposition,15 their structures must retain the -N-C-N-C-N- or -C-N-C-N-N- skeletal framework of RDX. Therefore, we selected only those cyclic and acyclic isomeric species that have aforementioned structural backbone, are neutral and possess similar functional groups as of previously proposed structures of products at m/z = 97 and 81.”*

7)      P. 6. Figure 1. For organic chemists, it is more understandable to present “simple” structures, rather than optimized geometries.

**Response:** We kept optimized 3D structures in Figure 1 so that the readers can have a 3D perspective of the molecular geometries. However, for easy visualization, we have now provided simple structures of the molecules in Figure S6 of the supporting information.

8)      P. 9. line 7. “…revealing implying…” should be revised.

**Response:** We have removed “revealing”

***Relevant changes in the manuscript (on page 9):***  *“… the complete ion signal revealing implying” that isomers…” is changed to “**….the* *complete ion signal implying that isomers…”*

Additional Questions:

Urgency: High

Significance: High

Novelty: Top 10%

Scholarly Presentation: Top 10%

Is the paper likely to interest a substantial number of physical chemists, not just specialists working in the authors' area of research?: Yes

Reviewer: 2

Recommendation: This paper may be publishable, but major revision is needed; I would like to be invited to review any future revision

Comments:  
This is an interesting paper that probably is publishable (at some point). Currently, some issues need to be resolved before I can recommend publication:

a) Scheme 1 seems unnecessary.

**Response:** We have removed scheme 1 from the main manuscript and included it in the supporting information. Scheme 1 is renamed to Figure S1.

***Relevant changes in the manuscript****: Scheme 1 is removed from page 1 of the main article and added to the supporting information as Figure S1.*

b) The FTIR information seems not to add anything to the subject of this paper. According to the title it's about the identification of elusive keto and enol intermediates. But the FTIR is not adding anything.

**Response:** FTIR spectroscopy provides the signature of small decomposition products such as nitrous acid (HONO) which is a key molecule eliminated during the decomposition of RDX to oxy-*s*-triazine and 1,3,5-triazine. Following the reviewer comments, we have now reduced the discussion of FTIR spectroscopy in the main article and have discussed only the most important result that is useful to support the mechanisms described in Scheme 1 and Figure 4.

***Relevant changes in the manuscript (on page 6-7)***: ***We changed the following paragraph***

*“In contrast, the upbeat ‘absorptions’ imply vibrational features of product species. IR bands of* ***1*** *in the spectral regions of 3100 - 3000 cm-1 and 1600 - 600 cm-1 are in excellent agreement with those reported in the literature and manifest the amorphous structure of RDX(Figure S5). 21,51-52 Features at 2343, 2235, 2138, 2079, 1866, 1749, 1717, 1687, and 1303 cm-1 substantiate the formation of small product molecules: carbon dioxide (CO2;* ***ν3****)21, dinitrogen monoxide (N2O;* ***ν1*** *)53, carbon monoxide (CO;* ***ν1****)53, the formyl radical (HCO;* ***ν1****), nitrogen monoxide (NO;* ***ν1****)21, the nitrogen monoxide dimer ([NO]2;* ***ν4****)54, formaldehyde (H2CO)55, nitrous acid (HONO;* ***ν2****)56, and dinitrogen trioxide (N2O3;* ***ν3****)57 respectively (Table S4). A broad absorption feature covering the spectral range from 3500 - 3100 cm-1 arises from OH stretching modes of water (H2O)58 and nitrous acid (HONO). The FTIR spectroscopy has been advantageous to detect functional groups and small photolysis products of* ***1*** *as documented above. However, an explicit identification of higher molecular weight species such as oxy-s-triazine and 1,3,5-triazine by FTIR would be problematic due to the complex mixture of several oxygen-nitrogen-carrying species formed in the photolysis, which would result in overlapping infrared absorptions from similar frequencies of the functional groups. Therefore, a novel analytical approach is essential.”*

**to**

“*In contrast, the upbeat ‘absorptions’ imply vibrational features of small product species (Table S4);21,49-54 among these, observation of nitrous acid (HONO) absorption at 1689 cm-1 implies that HONO-elimination process that could lead to* ***2a-b*** *and* ***3a*** *(Scheme 1) must have facilitated during the decomposition. However, explicit identification of higher molecular weight species such as* ***2a-b*** *and* ***3a*** *by FTIR would be problematic due to the complex mixture of several oxygen-nitrogen-carrying species formed in the photolysis, which would result in overlapping infrared absorptions from similar frequencies of the functional groups. Therefore, a novel analytical approach is essential.”*

c) The authors claim that m/z=97 to be a prominent peak in the mass spectra. What this reviewer sees is a forest of peaks, while m/z = 97 is only a single tree. Not standing out at all.

**Response:** We agree with the reviewer that the peak at m/z = 97 is not the most intense, however, its intensity is higher compared to 80 % of the total product signals observed in the mass spectrum. When decomposition is triggered, several fragmentation channels initiate that lead to multiple decomposition products.

Following the reviewer comments, we have now removed the word “prominent” from the main article.

***Relevant changes in the manuscript (on page 7):*** *Following sentence “Measurement at 10.49 eV reveals prominent signals at m/z = 97…” is changed to “Measurement at 10.49 eV reveals observable signals at m/z = 97…”*

d) The potential energy surface they calculated is on the ground state. But I assume there's some involvement of excited states with a certain dynamics. So, I'm questioning the usefulness of the PES shown in Fig. 4 to explain chemistry that may occur on excited states.

**Response:** We agree with the reviewer regarding the involvement of the excited states. Excited-state calculations performed by Bernstein and co-workers suggest that after electronic excitation, the excited RDX molecules undergo internal conversion to the ground state (S0) from the excited states (S1/S2) through conical intersection and finally dissociates in the S0 state. In the ground state, a number of fragmentation channels could open, such as the HONO elimination channel described in Figure 4. In other words, RDX molecules may not dissociate in the excited state, rather relax to the ground state via conical intersection and finally dissociates in the ground state.

We have added the abovementioned discussion in the main article on page 10.

Additionally, the excited-state calculations for molecules like RDX are computationally very expensive and challenging. At present, we don’t have such computational power and time. Based on our literature survey, till now there is only one study that addresses the excited state dynamics of RDX. This area of research still needs to be explored in great detail by the computational chemists.

***Relevant changes in the manuscript (on page 10): We have added the following sentences “****At this stage, it is important to discuss the excited state dynamics of* ***1****. Excited-state calculations performed by Bernstein and co-workers55 suggest that after electronic excitation via UV photons, the excited molecules of* ***1*** *undergo internal conversion to the ground state (S0) from the excited states (S1/S2) through conical intersection (CI) and finally dissociates in the S0 state. In the ground state, a number of fragmentation channels could open.”*

Additional Questions:

Urgency: High

Significance: High

Novelty: High

Scholarly Presentation: High

Is the paper likely to interest a substantial number of physical chemists, not just specialists working in the authors' area of research?: Yes

**Editor’s comments**

jz-2021-01610x Format revision

Manuscript  
- Second Page: Abstract and Table of Contents Image

**Response:** We have added a TOC image with the abstract on the second page.

- A 2x2” (5 cm x 5 cm) TOC graphic is required. The graphic should give the readers a  
visual impression of the essence of the paper without providing specific results.  
Sample TOC graphics can be found in the Author Guidelines  
(<http://pubs.acs.org/paragonplus/submission/jpchax/jpclcd_authguide.pdf>).

**Response:** A TOC image of the designated size is inserted on page 2.

- Please reduce your Abstract to 150 words.

**Response:** Abstract is reduced to 150 words.

- Please make sure all parts of all figures are cited at least once in the text in consecutive  
order. Please review figure 3, as it’s not in order and J is not mentioned.

**Response:** We have reviewed and modified Figure 3. Figure 3j is now cited in the text on page 9 of the main article.

- Please don’t use bold to highlight the word ‘figure’ nor when it’s mentioned or in the  
description.

**Response:** We have removed bold fonts.

- The description of the tables and figures should have the same size, line spacing and  
format than the rest of the manuscript.

**Response:** Figures and tables captions now have the same size, line spacing, and format.

- References on main text.

• Several consecutive references must be separated by a dash (ex: 3-6)

• Two consecutive references must be separated by a comma (ex: 3,4)

• Random references must be separated by a comma (ex: 3,9,21)

**Response:** All the cited references follow the same format as mentioned above.

- After finish your text the section order is (all labeled and only these sectionsrequired):  
• Acknowledgments

• Supporting Information

**Response:** Only Acknowledgments and Supporting Information sections are included after the text.

• Include a statement of financial support in the Acknowledgment section. (ACS now  
requires disclosure of funding institution(s) to ensure compliance with funding  
deposition mandates.)

**Response:** A statement of financial support is included in the Acknowledgment section.

References (bibliography):

• References with more than 10 authors should list the first 10 authors, followed by “et  
al.”(use italics for et. al)

Response: We have reformatted the references style according to the above instruction.

• Unnecessarily long lists of references are to be avoided; the references for this kind of  
text have to be between 40 to 50.

Response: We have reduced the number of references to 55. Only the relevant references are cited. We understand that this number is still slightly higher than the recommended no. of references and would like to request you to allow us to keep the additional references because these are important/ relevant to the current research topic.

• Place the numbers in (), such as (1), (2), (3), etc.

Response: Bibliographic numbers are in ().

• All title of the references should be written in one format, you should choose either  
entirely title case or entirely sentence case. Please, check and unify.

Response: In all the references, the article title is written in title case.

• Journal references should contain author names, article title (preferablywritten in title case), abbreviated journal title (italicized), year (bolded),  
volume (italicized), and pages (first-last). An example of a reference in the JPCLetters format is shown below:

✓ Deschler, F.; Price, M.; Pathak, S.; Klintberg, L. E.; Jarausch, D.-D.; Higler,  
R.; Hüttner, S.; Leijtens, T.; Stranks, S. D.; Snaith, H. J.; et al. High  
Photoluminescence Efficiency and Optically Pumped Lasing in SolutionProcessed Mixed Halide Perovskite Semiconductors. J. Phys. Chem. Lett.2014, 5, 1421-1426.

**Response:** We have reformatted the references style wherever needed. All the references follow the format mentioned above.

Supporting Information:

- Follow the same guidelines for the references than for the manuscript.

**Response:** All the references in the supporting information follow the same format as for the main article.

➢ MPORTANT!: When resubmit your file be sure it is all written in black (no colors  
allowed on text) and free of all markup elements, such as track changes, bold text,  
comments, highlights, etc.