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Reply to "A Thermodynamic assessment of the reported room-temperature chemical synthesis of C_2"

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REPLYING TO H. RZEPA. *Nature Communications* https://doi.org/10.1038/s41467-021-21433-8 (2021)

We are writing in response to Rzepa's theoretical analysis of the generation of C_2, which cites our recent paper describing the first chemical synthesis of C_2 (ref. [1]). Rzepa suggests on the basis of several in silico approaches that the formation of free C_2 from alkynyl-λ^3-iodane and fluoride ion would be prohibitively endo-energetic. He proposes three possible explanations of the apparent discrepancy between these theoretical calculations and our experimental findings, of which one is that some species other than C_2 is actually formed.

As our original paper was primarily experimental, describing room-temperature chemical synthesis of C_2 and the first bottom-up chemical synthesis of nanocarbons from C_2, we should like to respond to the latter point. We believe that the evidence presented in our paper for the generation of C_2 itself is compelling[1]. In particular, the connected-flask, solvent-free experiment clearly supports the generation of free C_2 gas, for the following reasons:

1. When ^{13}*C*-labeled **1b**-$^{13}C_\beta$ was used, a 1:1 mixture of *O*-ethynyl galvinoxyl **15**-$^{13}C_\alpha$ and **15**-$^{13}C_\beta$ was obtained (Fig. 1a).
2. APCI mass spectrum of the contents in Flask B included the peak assignable to acetylene digalvinoxyl ether **16** (Fig. 1b).

It is more difficult to establish conclusively whether free C_2 is generated in solution, but the following experimental facts are relevant:

3. The relative rate of hydrogen abstraction between CH_2Cl_2 and 9,10-dihydroanthracene (**12**) is calculated to be ca. 1:20 (per 1H).
4. Galvinoxyl radical **14** solely produced *O*-ethynyl galvinoxyl **15** (not **16**).
5. The amount of the mixture of **15**-$^{13}C_\alpha$ and **15**-$^{13}C_\beta$ obtained by the reaction of **1b**-$^{13}C_\beta$ with **14** differed in solvents of different viscosities (η).

These results indicated that the radical character of the intermediate is much milder than that of the common unstabilized alkynyl radical, which is consistent with the presence of an interaction between the radicals in C_2, in other words, a singlet biradical (charge-shift bonding) character, as suggested in a recent theoretical study[2].

At present, we cannot explain the discrepancy between Rzepa's theoretical evaluation and our experimental results. However, as discussed in our original paper, we believe that all our experimental observations can only be rationalized in terms of the generation of gaseous C_2. Our findings have attracted great interest, and we anticipate that independent experimental findings will emerge in the near future. We ourselves are

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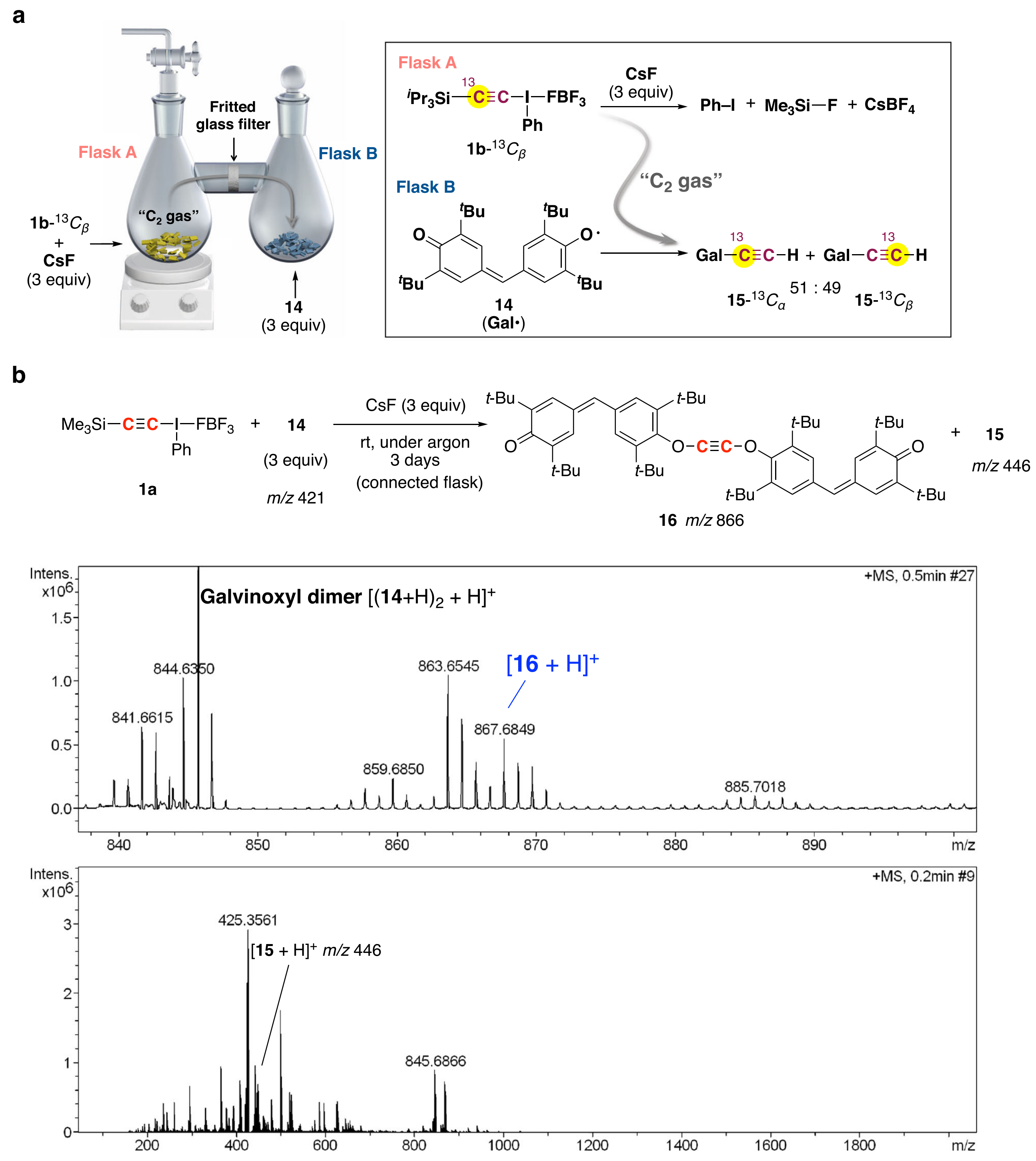

Fig. 1 Connected-flask, solvent-free experiment. a ^{13}C-labeling experiment. **b** APCI mass spectrum (positive ion mode) obtained from the contents in Flask B.

working on the direct observation of chemically generated C_2 by means of Raman spectroscopy, ESR spectroscopy, and other methods, and we hope that this work will provide definitive experimental evidence for the bond length and electronic state of C_2 (ref. [3] and references therein).

Data availability

The data that support the findings of this study are available from the authors on request.

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References

1. Miyamoto, K. et al. Room-temperature chemical synthesis of C_2. *Nat. Commun.* **11**, 2134 (2020).

2. Shaik, S. et al. Charge-shift bonding: a new and unique form of bonding. *Angew. Chem. Int. Ed. Engl.* **59**, 984–1001 (2020).
3. Shaik, S., Danovich, D., Braida, B. & Hiberty, P. C. The quadruple bonding in C_2 reproduces the properties of the molecule. *Chem. Eur. J.* **22**, 4116 (2016).

Author contributions

K.M., M.O., and M.U. conceived and designed the experiments. S.N., Y.M., T.H., T.O., and K.M. conducted the experiments. K.M. and M.U. wrote the manuscript. All authors participated in data analyses and discussions. K.M., M.K., and M.U. directed the project.

Competing interests

The authors declare no competing interests.

Additional information

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