Comment on “Computational Study on the Vinyl Azide Decomposition”

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In a recently accepted paper by Duarte, Miranda, and Esteves da Silva, the authors report a DFT study of vinyl azide decomposition with calculations of intrinsic reaction coordinates at the B3LYP/6-311++G(d,p) level, essentially concluding that the decomposition of vinyl azide 1 is conformationally dependent. The s-trans conformer 1t reacts in two steps via 2H-azirine 2:

\[ s\text{-}trans\text{-}H_2C\text{=}=\text{CH}\text{-}N_3 \rightarrow \text{cyc-H}_2C\text{=}=\text{CH} \quad (2H\text{-}azirine, 2) + N_2 \]
\[ \rightarrow H_2C\text{-}CN \quad (3) + N_2 \]

without a nitrene intermediate, but via a transition state resembling the closed-shell singlet (CSS) nitrene and lying about 50 kcal/mol above the 2H-azirine (or 69 kcal/mol according to an MP2/6-311++G(d,p) single-point calculation). The s-cis conformer of the azide (1c) leads to the formation of ketenimine in a single-step, again without a nitrene intermediate:

\[ s\text{-}cis\text{-}H_2C\text{=}=\text{CH}\text{-}N_3 \quad (1c) \rightarrow H_2C\text{=}C=\text{NH} \quad (4) + N_2 \]

It is quite possible that ketenimine is formed, as predicted by the authors, in a concerted reaction in the thermolysis of vinyl azide with a barrier of ca. 38 kcal/mol. However, the theoretical treatment is inappropriate as regards the potential vinylnitrene intermediate or transition state, since single-reference methods such as DFT or MP2 cannot provide a correct description. It is now well-known that the lowest singlet state of vinylnitrene is in fact the open-shell singlet (OSS). It cannot be treated adequately by DFT methods, as it requires at least two determinants to be described correctly. Thus, multiconfigurational methods are required. Several such calculations have been reported for the parent vinylnitrene, but references to these publications are missing in the work of Duarte et al.

Indeed, CASPT2 calculations on the relationship between 2H-azirine 2, acetonitrile 3, ketenimine 4, and vinylnitrene 5, have shown that the thermal ring opening of 2 to OSS vinylnitrene 5 has an activation barrier of ca. 33 kcal/mol (Scheme 1). The OSS vinylnitrene 5 undergoes a very facile 1,2-H-shift to acetonitrile with a barrier of ca. 6.5 kcal/mol, whereas the corresponding rearrangement to ketenimine would require ca. 33 kcal/mol.

Although it can be debated whether the OSS vinylnitrene 5 is a transition state for ring closure to 2H-azirine without a barrier, or an intermediate with a small barrier of 5 kcal/mol, the important point is that it lies some 25 kcal/mol below the

CSS nitrene. Thus, the OSS nitrene needs to be considered in thermal and photochemical chemistry of the C_3H_5N ensemble.

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Notes
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■ REFERENCES


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(9) The alternative ring opening of 2 to formonitrile ylide, H2C=\text{N}^\ddagger(\equiv\text{CH})^\ddagger, with a barrier of 48 kcal/mol was also calculated\(^7\) but is less relevant in the present context.