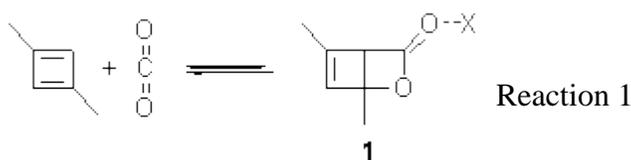


# HAS A CYCLOBUTADIENE SPECIES BEEN ISOLATED? (PART 2)

Henry Rzepa's response<sup>1</sup> to the reported detection and x-ray structure of 1,3-dimethylcyclobutadiene<sup>2</sup> has now been published. He takes a different tack than those take by Alabugin<sup>3</sup> and Scheschkewitz<sup>4</sup> in refuting the analysis of this work. Rzepa discusses computations to evaluate the possible lifetime of 1,3-dimethylcyclobutadiene in the vicinity of CO<sub>2</sub>. In particular, he examines the barrier for the allowed [4+2] cycloaddition to give back the lactone **1** (Reaction 1), which was photolyzed in the experiment to produce the cyclobutadiene and CO<sub>2</sub> species in the first place.



The gas phase free energy barrier at 175 K (the experimental condition) computed at  $\omega$ B97XD/6-311G(d,p) is 16.8 kcal mol<sup>-1</sup>, which is sufficiently high to limit this back reaction. Embedding this into a water continuum lowers the barrier to 12.9 kcal mol<sup>-1</sup>.

But the experiment has these species embedded inside a calixarene host along with guanidinium

cations. The cation could associate with the CO<sub>2</sub> (indicated in Reaction 1 as X), and inclusion of a guanidinium in the gas phase, reduces the barrier to 3.3 kcal mol<sup>-1</sup>. Rerunning this computation now with a water continuum produce an intermediate zwitterion formed by making the C-C bond, and the second step makes the C-O bond.

Finally, modeling the reaction with guanidinium inside a calixarene host leads to a barrier of 8 kcal mol<sup>-1</sup>, 10.5 kcal mol<sup>-1</sup> with water continuum. Rzepa concludes that recombination of 1,3-dimethylcyclobutadiene and CO<sub>2</sub> to give **1** should be too fast on the timescale of the experiment for observation of the cyclobutadiene. This argument, along with the two previous papers, strongly casts doubt on the original claim.

I should point out that Henry has deposited all the structures in a [nice enhanced table](#). You may need a subscription to get to this – I have not checked the access conditions.

Source: <http://comporgchem.com/blog/?p=1394>