Henry Rzepa's Blog

Dioxane tetraketone – an ACS molecule of the week with a mystery.

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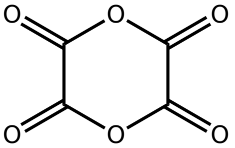
Published June 22, 2022

Citation

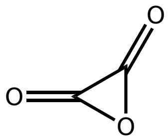
Rzepa, H. (2022, June 22). Dioxane tetraketone – an ACS molecule of the week with a mystery. *Henry Rzepa's Blog*. https://doi.org/10.59350/zp21a-1vg70

Keywords

Reaction Mechanism, Interesting Chemistry

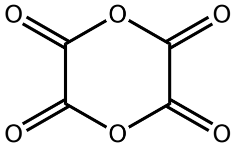


1,4-dioxane-2,3,5,6-tet

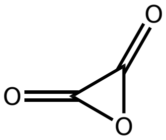


oxirane-2,3-dione

I have long been fascinated by polymers of either carbon dioxide,[†] or carbon monoxide, or combinations of both. One such molecule, referred to as dioxane tetraketone when it was featured on the ACS molecule-of-the-week site and also known as the anhydride of oxalic acid, or more formally 1,4-dioxane-2,3,5,6-tetraone, has been speculated upon for more than a century.[cite]10.1002/cber.19080410335[/cite]



1,4-dioxane-2,3,5,6-tet

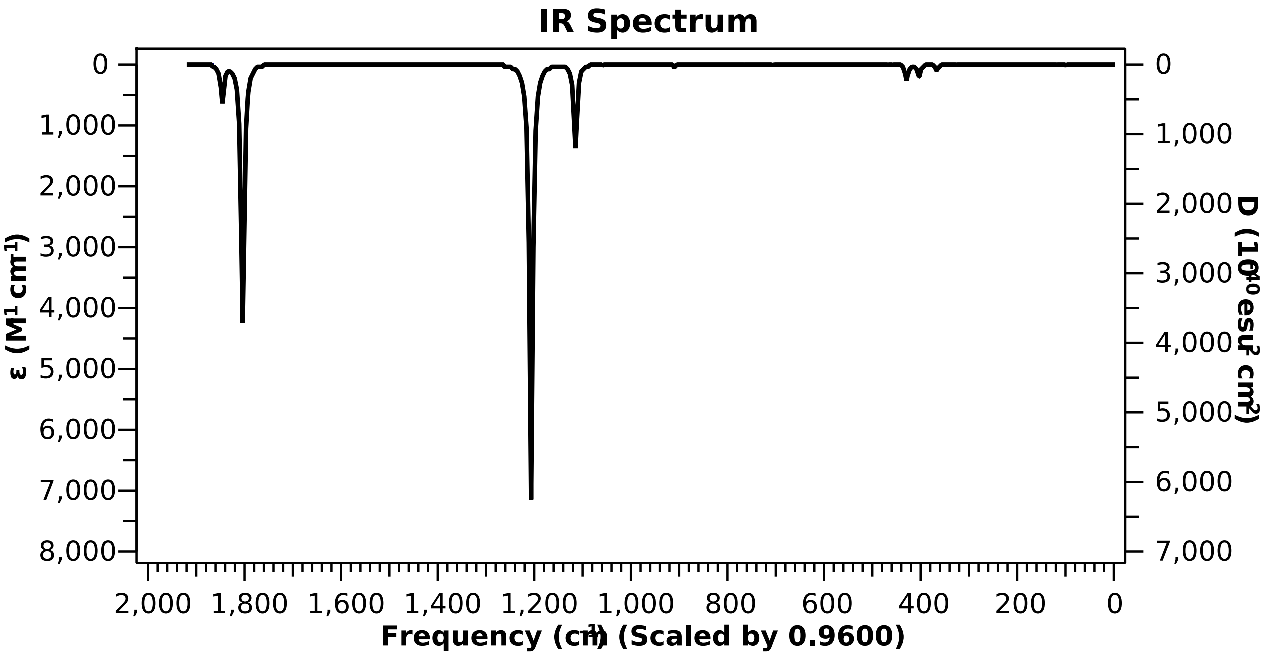


oxirane-2,3-dione

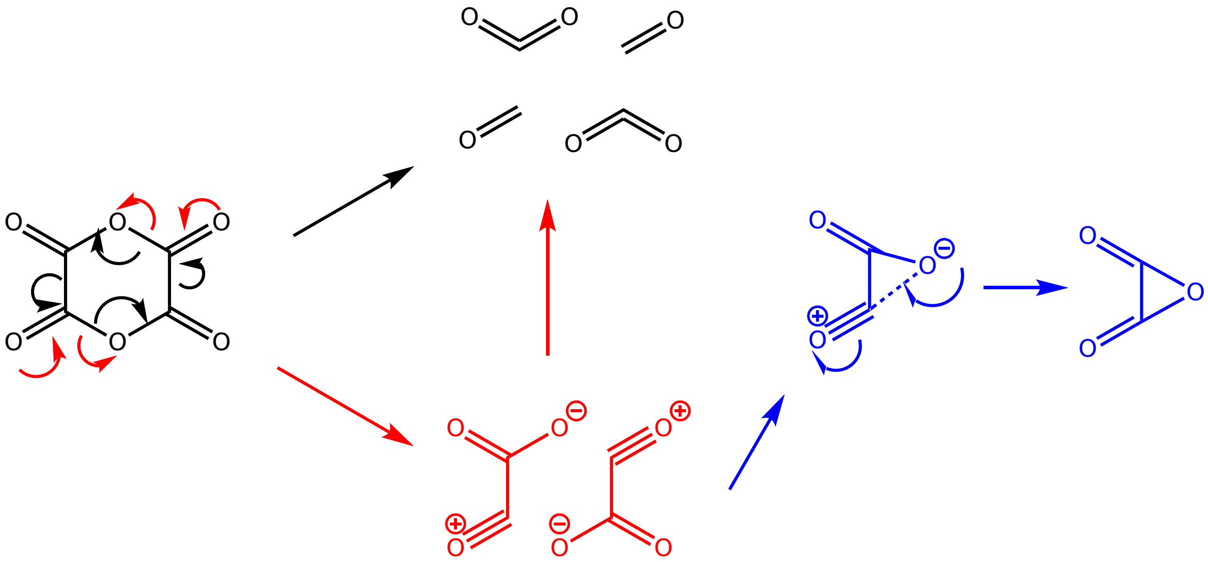
The history of chemistry has many molecules whose existence has been speculated upon, but where attempted syntheses have failed and for which sound theoretical reasons often only emerged many years later.[cite]10.1023/A%3A1009270411806[/cite]

The synthesis of dioxane tetraketone was finally achieved in 1998[cite]10.1039/A803430C[/cite] at low temperatures (243K), although it was noted that in $CDCl_3$/Et_2O solutions at 273K it quickly decomposed to give equal quantities of carbon monoxide and dioxide. The characterisation was by ^{13}C NMR, for which a single signal at 144.9 ppm was observed. The predicted value using the ACD/CNMR Predictor 2.0 Program (a so-called additive rule-based method) was 154 ppm (the value obtained using a similar tool available in Chemdraw is 150.9 ppm). The monomer oxirane-2,3-dione was also eliminated because of its predicted ^{13}C shift using the same method of 167 ppm (155.3 using Chemdraw). Here I thought I would check these chemical shifts using a DFT-based method and also look at the barrier to the decomposition to see if it corresponds to a facile reaction at 273K (FAIR Data DOI: 10.14469/hpc/10619).

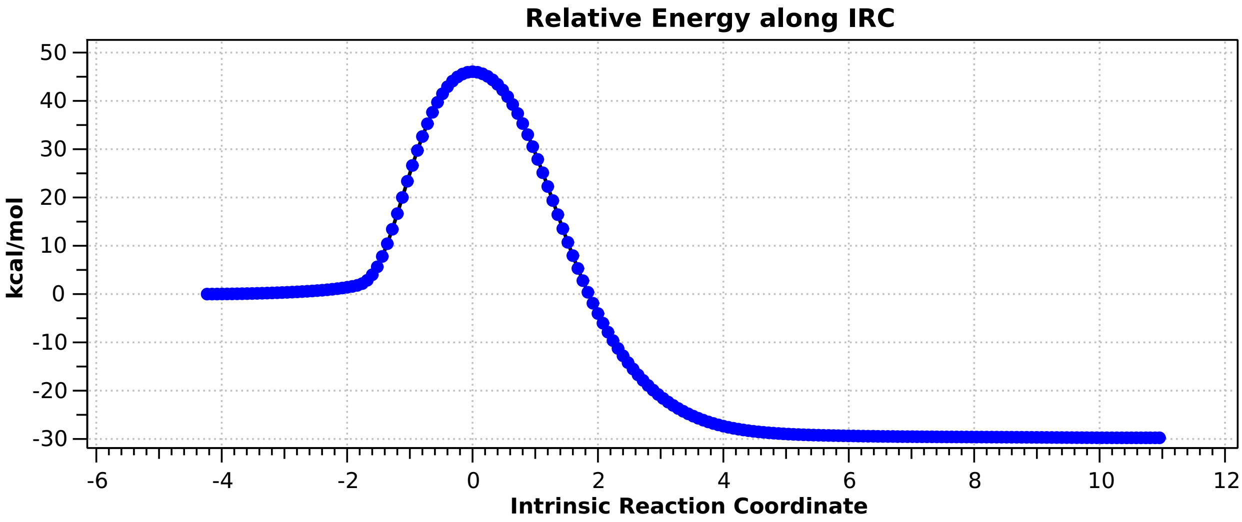
Firstly the NMR, using eg ωB97XD/aug-cc-pvdz/SCRF=chloroform. The calculated value of 148.2 ppm compares well with the observed value of 144.9 ppm. The value calculated for oxirane-2,3-dione was 156.6 ppm, rather lower than the ACD/Predictor method but in agreement with the Chemdraw implementation. The predicted IR spectrum (not reported) is shown below, should it ever be measured for this species.

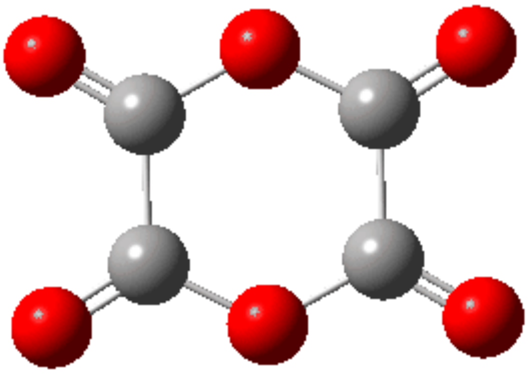


Next, the reaction energy profile, this time calculated using ωB97XD/Def2-TZVPP for the reaction mechanism shown below.



The IRC reveals that the mechanism (black arrows) is followed, in a concerted process that reveals absolutely no sign of any ionic intermediate (red) which could then lead to oxirane-2,3-dione (blue). The barrier ΔG‡ is 36.9 kcal/mol (it is lower than the total energy inferred below because the entropy is very positive, one molecule being converted to four during the reaction) which is far to high to correspond to a reaction that easily occurs at 273K. The value in water as solvent is very similar, again indicating that the ionic route is not enhanced by a polar solvent. The transition state has another feature of interest. It has C_2 chiral symmetry, typical of a pericyclic reaction with **Möbius topology**, as indeed would be appropriate for an eight electron process.





So what about that mystery then? Well, experimentally dioxane tetraketone decomposes at 273K, which would correspond to a free energy barrier of around 14-15 kcal/mol. The calculated value is far higher, too high to be simply an error in the DFT method. So here is a suggestion. $CDCl_3$, unless very carefully purified, contains HCl, which could very easily catalyse the reaction. So if another solvent were to be tried, lets say acetonitrile in which any trace of acid has been removed, would solutions of dioxane tetraketone then persist at room temperatures for far longer? An experiment perhaps to be tried!

[†] Perhaps the most fascinating is the cyclic trimer of carbon dioxide, which arguably has pretensions to be aromatic. It has very recently been synthesized.[cite]10.1021/acs.joc.6b00647[/cite],[cite]10.1021/jp802872p[/cite]