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# A Mechanistic Study of Hydroxide Anion Addition to Cyclobutane-1,2-dione by Density Functional Theory Calculations

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## Abstract

The reaction pathways for the addition of  $\text{OH}^-$  ion to cyclobutane-1,2-dione **I** are calculated by density functional theory procedures [B3LYP/6-31+G(d,p)]. Initially, **I** undergoes attack of the nucleophile, in this case  $\text{OH}^-$  ion, at one of the two equivalent carbonyl carbon atoms leading to formation of a tetrahedral intermediate followed by rearrangement reactions. Density functional theory method (B3LYP) with basis set (6-31+G (d,p)) are used to investigate the addition of  $\text{OH}^-$  (hydrated) to the hydrated species of **I**. The most likely pathway consists in a ring contraction of the tetrahedral intermediate, formed from addition of  $\text{OH}^-$  to **I**, leading to 1-cyclopropan-1-carboxylic acid.

## Introduction

Generally, addition of nucleophiles to carbonyl compounds result in initial formation of tetrahedral intermediates. In the case of 1,2-dicarbonyl compounds, these intermediates – at least in principle – can further react in three different ways (Scheme 1) [1]:

- benzyl-benzilic acid type rearrangement to form 2-hydroxycarboxylate **4**
- fission of the  $\text{C}\alpha$  - carbonyl carbon bond resulting in  $\alpha$ -oxo carboxylate **5**
- fission of the carbonyl – carbonyl carbon atoms to yield aldehyde **7** and carboxylate **8**



cyclobutan-1,2-dione. We carried out the calculation of  $\text{OH}^-$  with a solvent cluster of four water molecules, in addition to two water molecules for hydration of **I**.

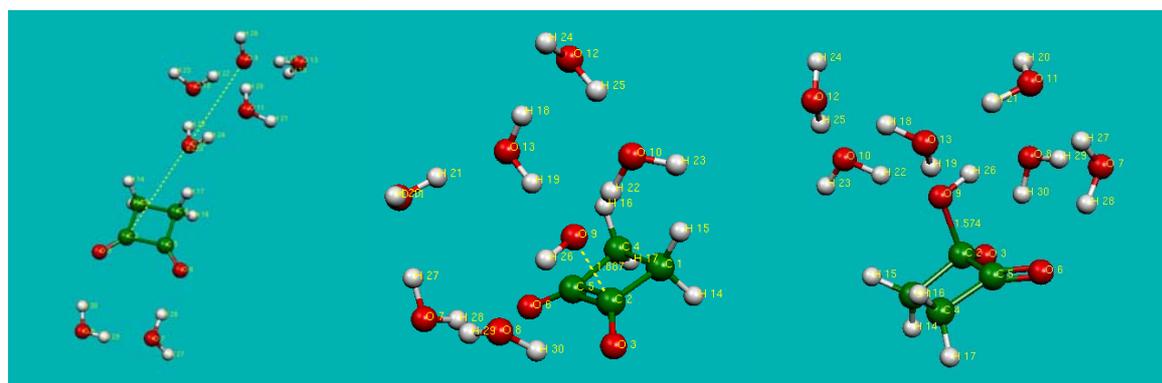
## Computational Details

The calculations were carried out by the Gaussian 03 [3] program package. The geometries were completely optimized at Becke's three-parameter hybrid density functional-HF method with the Lee-Yang-Parr correlation functional (B3LYP) [4] using 6-31+G (d, p) basis set. All transition states characterization has been done by vibrational frequency calculations at the same level of theory and basis set used for geometry optimization. Moreover the transition states were confirmed by intrinsic reaction coordinate (IRC) calculations [5].

## Results and Discussions

Reaction 1,  $\text{I}(\text{H}_2\text{O})_2 + [(\text{OH})(\text{H}_2\text{O})_4]^- \rightarrow \text{TS1} \rightarrow \text{II} \rightarrow \text{TS2} \rightarrow \text{III}$  proceeds via formation of an ion-dipole complex (**Ia** in Fig. 3), addition of the nucleophile to cyclobutan-1,2-dione via transition state **TS1** to the tetrahedral intermediate (**II**). Calculated structures are displayed in Fig. 1.

Figure 1



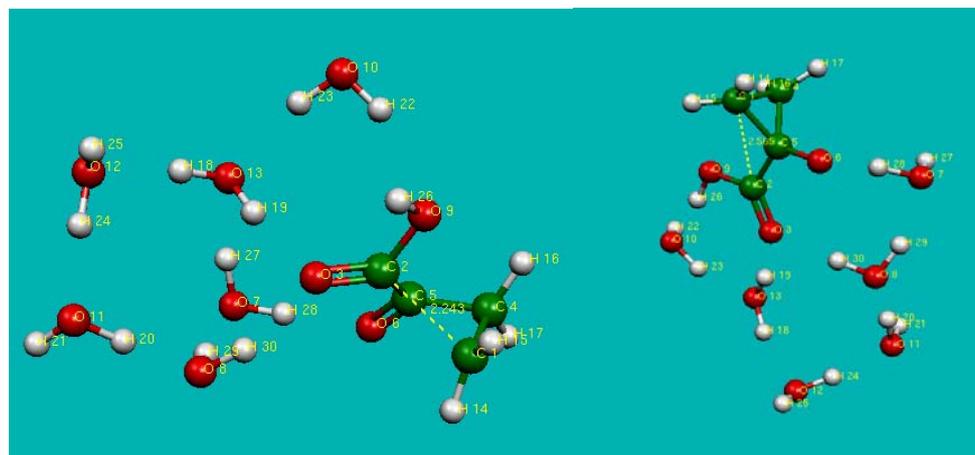
$\text{I}(\text{H}_2\text{O})_2 + [(\text{OH}^-)(\text{H}_2\text{O})_4]$

TS1

II

This intermediate further reacts by rearrangement via **TS2** to the ring-contracted 1-hydroxycyclopropan-1-carboxylate **III** [1, 6], Fig. 2. Formation of **III** was found to occur directly from **II** without any ring-opened intermediate, e.g. **IIIa** (Scheme 2).

**Figure 2**



**TS2**

**III**

Our study shows that case 1, i.e. the benzylic acid type rearrangement leading to the ring-contracted cyclopropane carboxylic acid derivative **III** should be the preferred reaction of **I**. So far, no transition state for breaking the bond between the two oxygen-bearing carbon atoms (case 2 in Scheme 2) could be located.

## References

- [1] K. Bowden, W. M. Fabian, *J. Phys. Org. Chem.* 14, 794 (2001)
- [2] M. Uhlar, and W. M. F. Fabian, *ECCC9*, Poster 18 (2003)
- [3] Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. L. X. Klene, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz,

Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, (2003).

[4] (a) A. D. Becke, *J. Chem. Phys.* 98, 5648 (1993). (b) C. Lee, Y. Yang, R. G. Parr, *Phys. Rev. B* 37, 785 (1998)

[5] (a) C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.* 94, 5523 (1990). (b) C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.* 90, 2154 (1989)

[6] S. Yamabe, N. Tsuchida, S. Yamazaki, *J. Org. Chem.* 71, 1777 (2006)