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New insight on the mechanism of 2-oxabicyclobutane fragmentation. A high-level ab initio study

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Abstract—High-level quantum chemical studies have been carried out to explain the unusual chemical reactivity of 2-oxabicyclobutane for the process of its fragmentation to acrolein. The predicted activation energy values for unimolecular and acid-catalysed fragmentation of OBB are high enough to rule out OBB intermediacy in the various thermal, photochemical and chemical reactions. These findings suggest that 2-oxabicyclobutane is so highly stable that there should be another mechanism of above mentioned reactions which leads to the formation of aldehydes and ketones. © 2001 Elsevier Science Ltd. All rights reserved.

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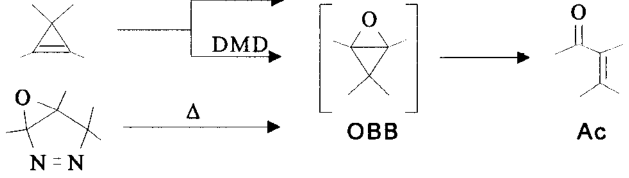
1. Introduction

2-Oxabicyclobutane (OBB) is a parent of a series of highly strained heterocyclic compounds, which have a special role in the chemistry of epoxidic compounds. Its derivatives have been postulated since 1965 as intermediates in various thermal (extrusion of nitrogen from bicyclic azo epoxides),[1] photochemical (irradiation of 2-cyclohexenone[2a] and *cis*-2-cycloheptenone[2b]) and chemical (epoxidation of substituted cyclopropenes by peracids[3a–g] and dimethyldioxirane[3h]) reactions which have as a final product different aldehydes and ketones. However, all attempts to isolate or even spectroscopically detect oxabicyclobutanes were unsuccessful (see Scheme 1).

These experimental observations give rise to the conclusion that the OBB and its derivatives are not stable. At the same time, high-level ab initio calculations[4] for the OBB yield a minimum energy structure characterized by the lowest nonzero vibrational frequency higher than 450 cm^{-1}, suggesting that the titled compound may be thermodynamically stable. Although the above processes have been intensively studied by experimental methods,[1–3] a comprehensive theoretical analysis of the potential energy surface (PES) for any of these reactions is still missing. As far as we know, the only theoretical study concerning the mechanism of the OBB transformation to acroleine (Ac) is that by Friedrich and co-workers performed with the extended Huckel method.[3d] However, since OBB and its derivatives are not detected by experimental methods the only way to shed light whether they are able to exist as the stable intermediate in above mentioned reactions is to investigate the mechanism of 2-oxabicyclobutanes transformation by high-level quantum chemical methods. Here we report the results of such quantum chemical study of the local minima and transition states which characterize the energy hypersurface of the OBB transformation to Ac.

2. Computational methods

Since we assumed the biradical character of fragmentation of Ac, the unrestricted versions of the MP2,[5] QCISD and QCISD(T)[6] approaches have been used to take into account the dynamic correlation effects of the reaction energetics. Structure-dependent (or nondynamical) correlation effects have been included through the calculations at the CASSCF level of theory[7] which comprises 10 electrons distributed on 10 orbitals (CASSCF(10,10)). The standard 6-31G(d) basis set has been used for all geometry optimisations at the UMP2, UQCISD and CASSCF approaches. The single point calculations have been performed at the UQCISD(T)/6-31G(d) and UQCISD(T)/6-311++G(d,p)



Scheme 1.

Keywords: 2-oxabicyclobutane fragmentation; ab initio; mechanism; activation barrier; transition state.

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levels for the UQCISD/6-31G(d) reference geometry. The geometry of the local minima and transition states has been verified by establishing that the matrices of the energy second derivatives (Hessians) at the UMP2/6-31G(d) level have zero and one negative eigenvalues, respectively. The total energies calculated at the UMP2, UQCISD and UQCISD(T) levels have been corrected for the UMP2/6-31G(d) level zero-point energies scaled by a factor of 0.95. Calculations with the UMP2, UQCISD and UQCISD(T) approaches were executed using the GAUSSIAN94 program.[8] CASSCF calculations have been performed by the GAMESS program.[9] The influence of polar solvent has been estimated in the framework of the SCRF model[10] at the CASSCF(10,10)/6-31G(d) level of the theory. The dielectric constant ($\epsilon=8.93$) which formally corresponds to the bulk of dichloromethane has been used.

3. Results and discussion

We have examined first unimolecular fragmentation of OBB. The analysis of the corresponding PES has shown that the fragmentation of the OBB to Ac may occur through two pathways (see Fig. 1). The first one is an asynchronous concerted transformation with a prior breaking of the C_2–O bond of the epoxidic cycle in the transition state TS1. The second mechanism involves stepwise nonconcerted transformation with breaking during the first (rate-determining) stage of the C_1–C_3 bond and the formation of the biradical intermediate BI which transforms to acrolein with a very small barrier through TS3.

Table 1 summarizes the bond lengths, $\langle S^2 \rangle$, occupation numbers of HOMOs and LUMOs, and the contribution of the dominant configuration for stationary points for both considered mechanisms. Total and relative energies of these structures are collected in Table 2.

An analysis of the data presented in Tables 1 and 2 results in the following conclusions.

(1) The geometrical parameters of the OBB molecule predicted at the UMP2 and UQCISD levels of theory are very similar. The CASSCF calculation in comparison to the UQCISD level gives bond lengths shorter by 0.029 Å for the central C_1–C_2 bond and longer C_1–O and C_1–C_3 bonds (by 0.015 and 0.026 Å, respectively). It should be mentioned that, in contrast to other epoxides, the central (epoxidic) C_1–C_2 bond in OBB is shorter than C_1–O bond by 0.072, 0.028 and 0.029 Å at CASSCF, UQCISD and UMP2 levels, respectively. The $\langle S^2 \rangle$ value for OBB amounts to 0.00. It should also be noted that for OBB the contribution of dominant (ground state) configuration is the largest, and the occupation number of the LUMO is the smallest among the considered species.

All of used levels of theory give close geometry of Ac, which are in very good agreement with the geometrical parameters of Ac which are determined experimentally[11] (the same result for the CASSCF(6,5)/6-31G(d) has been obtained in Ref. 12).

(2) Table 1 shows that the concerted transition state TS1 as well as the transition states TS2, TS3, and the intermediate BI have a biradical character. One may see that all these species are characterized by the $\langle S^2 \rangle$ values close to unity. In addition they have a quite significant population of the LUMO and a relatively small weight for the dominant configurations. Thus, the CASSCF data should be more reliable for all of these structures.[13]

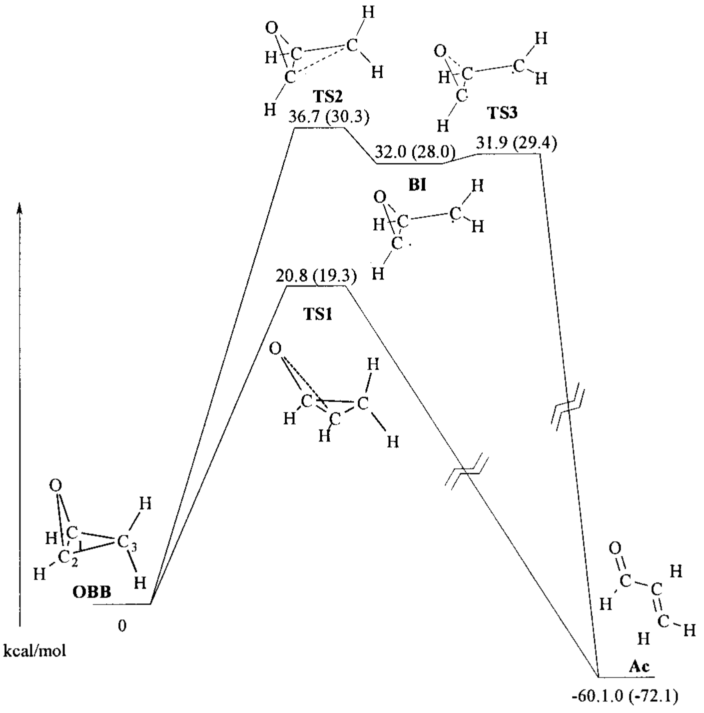


Figure 1. Energy diagram for the various mechanisms of 2-oxabicyclobutane fragmentation reaction, calculated at UQCISD(T)/6-311++G(d,p)//UQCISD/6-31G(d) and CASSCF(10,10)/ 6-31G(d) (in parentheses) levels of theory.

Table 1. Calculated C–C and C–O bond lengths (Å), ⟨S^2⟩, occupation numbers and contribution of dominant configuration for stationary points of the fragmentation of 2-oxabicyclobutane

	OBB	TS1	Ac	TS2	BI	TS3
UMP2/6-31(d)						
C_1–O	1.458	1.307	1.228	1.389	1.370	1.309
C_2–O	1.458	1.963	2.386	1.486	1.509	1.783
C_1–C_2	1.429	1.486	1.473	1.422	1.456	1.483
C_1–C_3	1.499	1.558	2.445	2.127	2.548	2.513
C_2–C_3	1.499	1.444	1.342	1.466	1.458	1.370
OC_1C_2	60.4	89.3	123.9	57.0	64.5	79.1
$C_1C_2C_3$	61.5	64.4	120.6	94.9	121.9	123.5
⟨S^2⟩	0.000	0.772	0.000	0.839	1.029	1.196
UQCISD/6-31(d)						
C_1–O	1.454	1.316	1.221	1.385	1.371	1.344
C_2–O	1.454	2.032	2.387	1.482	1.529	1.695
C_1–C_2	1.426	1.472	1.481	1.427	1.461	1.470
C_1–C_3	1.504	1.547	2.456	2.224	2.533	2.540
C_2–C_3	1.504	1.445	1.341	1.474	1.456	1.416
OC_1C_2	60.7	93.3	123.8	63.6	65.3	73.9
$C_1C_2C_3$	61.7	67.0	120.9	101.1	122.1	123.3
⟨S^2⟩	0.000	0.825	0.000	0.921	1.033	1.168
CASSCF(10,10)/6-31G(d)						
C_1–O	1.469	1.324	1.222 (1.214)[a]	1.397	1.385	1.348
C_2–O	1.469	2.019	2.386 (2.369)	1.488	1.525	1.703
C_1–C_2	1.397	1.454	1.480 (1.466)	1.417	1.442	1.454
C_1–C_3	1.530	1.604	2.465 (2.436)	2.325	2.553	2.550
C_2–C_3	1.530	1.472	1.341 (1.340)	1.481	1.464	1.422
OC_1C_2	61.6	93.1	123.8 (124.0)	57.5	65.2	74.7
$C_1C_2C_3$	62.8	66.5	121.7 (120.4)	106.9	122.9	124.9
Occupation number						
HOMO	1.974	1.840	1.906	1.466	0.908	1.373
LUMO	0.045	0.165	0.099	0.539	1.100	0.640
Contribution of dominant configuration	0.962	0.927	0.947	0.826	0.688	0.705

[a] Experimental data (see Ref. 11).

According to the results of CASSCF calculations, TS1 is characterized by significant elongation of C_2–O bond (by 0.550 Å). The elongation of C_1–C_3 (which amount to 0.074 Å) and shortening of C_2–C_3 bonds of 0.058 Å are rather negligible. In comparison to CASSCF results, at the UMP2 level the position of TS1 at the PES is closer to the reactant (smaller elongation of C_2–O bond by only 0.505 Å), while at UQCISD level TS1 lies closer to the product (bond length of C_2–O in TS1 increases by 0.578 Å compared to OBB).

The transition state of the first (rate-determining) stage of stepwise transformation of OBB (TS2) has more diradical character in comparison to TS1, so it is not surprising that both single-determinantal (UMP2 and UQCISD) methods give larger variations of geometrical parameters than CASSCF method in the case of stepwise mechanism (calculated elongation of C_1–C_3 bond at UMP2, UQCISD and CASSCF levels are 0.628, 0.720 and 0.795 Å, respectively).

(3) The predicted values of activation barriers shed a light on the mechanisms of the studied processes. One may see that the stepwise mechanism has a higher activation barrier at the rate-determining step in comparison to the concerted mechanism (30.3 vs 19.3 kcal mol^{-1} at CASSCF level) so

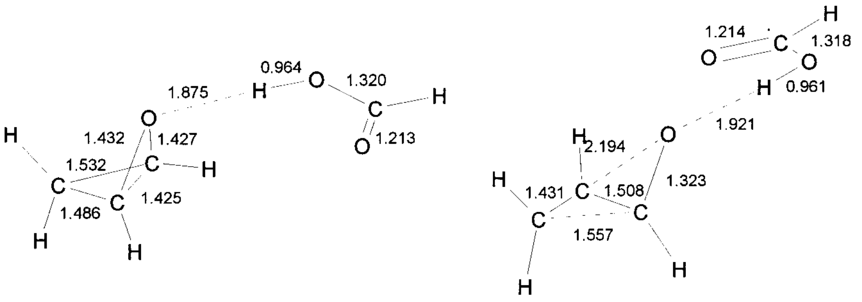
Table 2. Calculated zero-point corrected relative (kcal mol^{-1}) energies (relative to OBB) for stationary points of the fragmentation of 2-oxabicyclobutane

	OBB[a]	TS1[b]	Ac	TS2[b]	BI	TS3[b]
UMP2/6-31G(d)	0.0	42.0	−56.2	47.1	38.4	49.9/11.5[c]
UQCISD/6-31G(d)	0.0	24.2	−59.7	37.2	30.2	31.2/1.0[c]
UQCISD(T)/6-31G(d)// UQCISD/6-31G(d)	0.0	22.4	−59.7	38.2	32.4	32.6/0.2[c]
UQCISD(T)/6-311++G(d,p)//UQCISD/6-31G(d)	0.0	20.8	−60.1	36.7	32.0	31.9/0.1[c]
CASSCF (10,10)/ 6-31G(d)	0.0	19.3	−72.1	30.3	28.0	29.4/1.4[c]

[a] Total energies of OBB at the UMP2/6-31G(d), UQCISD/6-31G(d), UQCISD(T)/6-31G(d)// UQCISD/6-31G(d), UQCISD(T)/6-311++G(d,p)//UQCISD/6-31G(d) and CASSCF(10,10)/6-31G(d) levels are −191.222288; −191.248152; −191.268300; −191.2679972 and −190.741228 Hartrees, respectively.

[b] Transition structures TS1 TS2, TS3 have one imaginary frequency at 654, 606 and 996 cm^{-1} (UMP2/6-31G(d) level), respectively.

[c] Relative to BI.



$\Delta E^{\neq}_{CASSCF(10,10)/6\text{-}31G(d)} =$ 17.8 kcal/mol

Figure 2. Formic acid–2-oxabicyclobutane IC and its transition structure for fragmentation (TS4) optimized at CASSCF(10,10)/6-31G(d) level of theory using SCRF approximation. Distances are in angstrom. The activation barrier is calculated relative to IC.

the former should be less probable. Nevertheless, both of them have the values of activation energy, which could assure the stability of the OBB molecule with respect to the transformation to Ac. The calculated UQCI level values of activation barriers are in reasonable agreement with the corresponding CASSCF barrier heights, especially ones obtained at UQCISD(T)/6-311++G(d,p) level. In contrast, UMP2 calculations dramatically overestimate activation barriers (by 21.7 and 16.8 kcal mol^{-1}) for concerted and stepwise mechanisms, respectively, compared to CASSCF values. We would also like to mention that the calculations performed by us to characterize these species at the UB3LYP/6-31G(d) level yield the closed-shell structures for all stationary points on the PESs. This confirms the conclusion stated in Ref. 13 that DFT and MPn methods cannot be successfully applied to open-shell systems such as singlet diradicals for which wave function must be represented by more than one Slater determinant.

Since interaction of olefins with peroxyacids leads to the formation of acids, which have catalytic effect on transformation of the OBB, the formic acid governing the PES of OBB transformation in dichloromethane has been also investigated. First of all we have found that there is no minimum on the PES, which corresponds to proton transfer with formation of the complex ‘formic anion–protonated OBB’. This is expected, because the difference in the basicity of the formic anion and the OBB is too large.[14] Fig. 2 presents the geometrical structures of the intermolecular complex (IC) between the formic acid and OBB, and the transition state (TS4) for the transformation of OBB, activated by formic acid. The transformation of OBB activated by the formic acid is characterized by virtually the same activation barrier as the gas phase unimolecular process (17.8 vs 19.3 kcal mol^{-1}).

4. Conclusions

The results reported here on unimolecular and acid-catalyzed fragmentation of OBB strongly suggest that this compound is stable enough and should be detectable in case of its intermediacy in chemical reactions. Since this is not the case, there should be another mechanism, which excludes the formation of OBB at the intermediate stage. For example, in case of reaction of cyclopropenes with peroxyacids such process could include an unsymmetrical intermediate which forms just one C–O bond at the initial step of the interaction between cyclopropene derivatives and peroxyacids. One may see that cleavage of C_1–C_3 bond in this intermediate can lead directly to acrolein without the formation of OBB.

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