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IS THE DECOMPOSITION OF THE PRIMARY OZONIDE A CONCERTED OR STEPWISE PROCESS?

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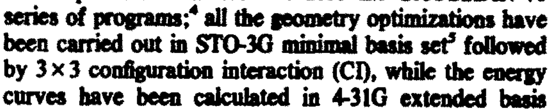
Abstract—An *ab initio* SCF-MO calculation shows that both concerted and stepwise processes are equally probable for the cleavage of the primary ozonide, leading to the Criegee intermediate. The value of the corresponding activation energy is discussed, and the results are found in agreement with the stereochemistry of the reaction. A very facile ring opening is also predicted.

INTRODUCTION

The ozonolysis of olefins is known to occur *via* an instable primary adduct.[1] In a previous paper,[2] we had calculated the relative stabilities of various structures of this primary adduct, and found the 5-membered ring 1,2,3-trioxolane as the most stable. The concerted cleavage of this primary ozonide was studied, and we concluded that the pathway suggested by Kuczkowski *et al.*,[3] involving an envelope-like transition state, was a low-energy process, likely to be responsible for the stereochemical features of the reaction. Nevertheless, this did not rule out a possible non stereoselective competitive mechanism (Section 1), where a single OO bond is first broken, to give diradical 1, which splits further into a carbonyl and a carbonyl oxide.



Scheme 1.

Reported here are the results of an *ab initio* study of this stepwise mechanism. We used the GAUSSIAN 70 series of programs;[4] all the geometry optimizations have been carried out in STO-3G minimal basis set[5] followed by 3 × 3 configuration interaction (CI), while the energy curves have been calculated in 4-31G extended basis set,[6] plus 3 × 3 CI. Both closed shell and restricted open shell[7] procedures have been used, and for each calculation the lowest energy has been retained.

Conformational analysis of diradical 1

The rotations about the C_2C_3 and C_3O_4 bonds (Fig. 1) are characterized, respectively, by the angles θ and φ which both have the value 0° in the planar trioxolane ring. From our study it follows that the energy of diradical 1 is grossly independent of θ and φ, as long as the radical centers are neatly separated. The best values are $\varphi = 180°$ and $\theta = 60°$–$80°$, and the following parameters have been optimized: $O_1C_2 = 1.473$ Å, $O_4C_3 = 1.466$ Å, $O_5O_4 = 1.325$ Å, $< O_5O_4C_3 = 112.0°$. The remaining parameters are standard: $C_2C_3 = 1.54$ Å, $CH = 1.09$ Å and all the bond angles around the carbons are tetrahedral. In our reaction scheme, we chose the values $\theta = 60°$ and $\varphi = 90°$ for diradical 1. Indeed, this value of φ is well adapted to the C–C cleavage, since it allows one of the nascent unpaired electrons to be delocalized into the π system of the $H_2\dot{C}O\dot{O}$ fragment. Furthermore, this structure is destabilized by less than 1 kcal/mol with respect to the most stable one.

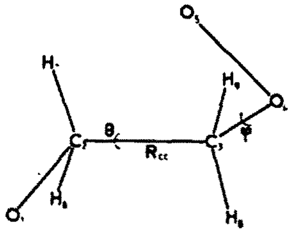


Fig. 1. Coordinate system for the ring opening and the C–C cleavage.

First step

Ring opening. For this step the reaction coordinate is composed of θ and φ, coupled so that θ goes from 0° to 60° while φ goes from 0° to 90°. For the sake of simplicity the initial 1,2,3-trioxolane is taken planar but of course the activation energy of this step is calculated relative to the more stable O-envelope trioxolane. In a first gross calculation, all the parameters have been varied linearly from their initial values to their values in the final diradical, along with the reaction coordinate. Then the geometry of the transition state has been optimized, and we obtained the following values: $O_1C_2 = 1.453$ Å, $O_4C_3 = 1.467$ Å, $O_5O_4 = 1.355$ Å, $< O_5O_4C_3 = 102.6°$, $< O_1C_2C_3 = < O_4C_3C_2 = 104.7°$. Lastly, the parameters of the intermediate points have been reevaluated so as to vary smoothly from their initial values to their final values via the transition state. The energy profile of this first step, calculated in extended basis set plus 3 × 3 CI (Fig. 2) exhibits a transition state 9.7 kcal/mol higher than the O-envelope trioxolane.

Second step

C–C cleavage. Here the reactant is the diradical 1, with $\theta = 60°$ and $\varphi = 90°$ (Fig. 1); the products are an aldehyde and a carbonyl oxide fragment, described in our previous paper,[2] and the reaction coordinate is the

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C–C bond length. Like for the first step, we carried out a first gross calculation, optimized the transition state, re-evaluated the parameters of the intermediate points and calculated the energy curve in extended basis set. All along the reaction process, all < HCC and < OCC angles have been kept equal, as well as the < HCH and < HCO angles. The pyramidalizations of both carbons are equal and defined as an < HCC angle. The transition state is attained for C–C = 2.14 Å, and its optimized parameters are: O_1C_2 = 1.260 Å, O_4C_3 = 1.393 Å, O_5O_4 = 1.317 Å, carbon pyramidalization: 99.4°. The maximum of the energy profile, (shown in Fig. 2), has an energy of − 301.930 hartrees, extremely close to the value calculated in our previous paper[2] (− 301.929 hartrees), in the same CI and basis conditions, for the transition state of the concerted reaction.

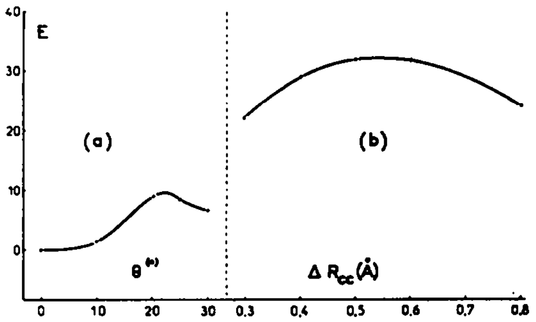

Fig. 2. Energy profile,[8] in kcal/mol, of the ring opening (a) and the C–C cleavage (b) of the 1,2,3-trioxolane.

DISCUSSION

The first prediction of our calculations is a very facile ring opening, since only 9.7 kcal/mol are required for this process, which is close to the thermochemical estimation of Benson[9] (13 ± 2 kcal/mol). For this part of the energy curve (Fig. 2a), one can expect a reasonable reliability of the method we use, since our CI, involving the simple and double excitations from the O–O bonding to the O–O antibonding σ orbitals, is generally considered as well adapted to the diradicals. At any rate, a lack of CI would rather destabilize the transition state with respect to the saturated initial trioxolane.

On the other hand, our calculations suggest that, for the Criegee splitting, both stepwise and concerted mechanisms are equally probable. Indeed, both transition states have been calculated in the same basis set, with the same 3 × 3 CI, which is insufficient for the same reason: lack of CI involving the nascent π orbitals of the aldehyde and the carbonyl oxide. Furthermore, the results of a large CI and a 3 × 3 CI, in 4-31G basis set, have already been compared in a similar case, the concerted and stepwise hydrogen-abstraction from diimide: the difference between both activation energies does not depend, within 2 kcal/mol, on the type of CI.[10] Nevertheless, if our calculated relative stabilities of both transition states are reasonably reliable, the same does not hold true for the absolute activation energy. Because of a lack of π electron correlation, our calculated activation energy (33 kcal/mol) is overestimated. In our previous paper,[2] we grossly estimated this correlation energy by performing an adequate CI in minimal basis set, and assuming that the resulting stabilization was kept, at least in a 2:3 ratio, in extended basis set. This gave an activation energy of 11–17 kcal/mol, which is not in good agreement with the thermochemical estimations of O'Neal and Blumstein.[11] They evaluated the activation energy of the Criegee splitting between 30 ± 2 kcal/mol considering the carbonyl oxide as a pure diradical, and 26 ± 2 kcal/mol, assuming a 7–9 kcal/mol stabilization of the carbonyl oxide by charge polarization. Two points are noteworthy: (i) this last stabilization seems to be underestimated since Goddard[12] found a 19.4 kcal/mol gap between the lowest singlet and triplet states of the carbonyl oxide, and (ii) by ascribing to the nascent carbonyl oxide half of the resonance energy, O'Neal and Blumstein assumed the transition state to be half-way between reactant and products. This assumption can be checked by following the O_1C_2 bond length along the reaction: it goes from 1.451 Å in the trioxolane, to 1.308 Å in the concerted transition state and 1.260 Å in the stepwise one, and to 1.22 Å in the aldehyde. This suggests that both transition states resemble products rather than reactants, and are consistently stabilized by charge polarization. Lastly, Pitts[13] considered, on the basis of a revised O'Neal and Blumstein mechanism, the Criegee mechanism to occur only 2.5 slower than the α-abstraction from diradical 1, which requires 8 ± 2 kcal/mol.[11] Since this diradical is formed from the trioxolane with a 9.7 kcal/mol barrier (our calculation), and is slightly stabilized relative to this transition state, one sees that the activation energy of the Criegee splitting is presumably lower than 26–30 kcal/mol.

CONCLUSION

Our calculations suggest that both stepwise and concerted Criegee splitting require the same activation energy, although there remains an uncertainty about its absolute value. The concerted mechanism, with an envelope-like transition state, has been shown by Kuczkowski[3] to fit the stereochemical tendencies of the reaction, at least when the olefin bears small substituents. The stepwise mechanism is non stereoselective, since *anti*- and *syn*- carbonyl oxides are indifferently formed by this process, due to the very low energy barrier separating the values $\varphi = 90°$ and $\varphi = -90°$ in diradical 1 (0.6 kcal/mol according to our conformational analysis in STO-3G basis set).

The sum of both mechanisms is thus in accordance with the stereochemistry of the reaction.

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