

The carbonyl oxide–aldehyde complex: a new intermediate of the ozonolysis reaction

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MP4(SDQ)/6-31G(d, p) calculations suggest that the ozonolysis of alkenes in solution phase does not proceed via carbonyl oxide, but via a dipole complex between aldehyde and carbonyl oxide, which is 9 kcal/mol more stable than the separated molecules. The dipole complex is probably formed in the solvent cage upon decomposition of primary ozonide to aldehyde and carbonyl oxide. Rotation of either aldehyde or carbonyl oxide in the solvent cage leads to an antiparallel alignment of molecular dipole moments and dipole–dipole attraction.

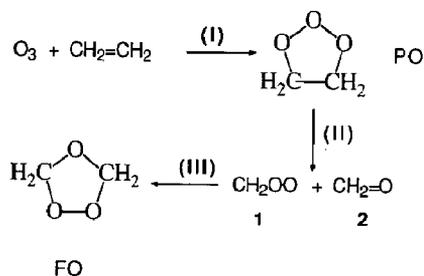
The ozonolysis of alkenes is known to proceed by the Criegee mechanism (scheme 1, reactions (I), (II) and (III)) both in the gas phase and in solution phases [1–3]^{#1}. One of the essentials of the Criegee mechanism of the ozonolysis is the involvement of carbonyl oxide (**1**) as an intermediate of the oxidation process. According to Criegee, carbonyl oxide (**1**) and aldehyde (**2**) are formed by decomposition of primary ozonide (PO) (reaction (II) in scheme 1). Recombination of **1** and **2** leads to final ozonide (FO) (reaction (III) of scheme 1). There is convincing experimental evidence that suggests **1** as an intermediate in the ozonolysis reaction. For example, in the presence of a hydroxylic solvent such as

ROH, alkoxy hydroperoxides are formed through an interception of **1** by the solvent [1,2]. In the gas phase ozonolysis, dioxirane, which is the cyclic isomer of **1**, has been identified and investigated [5,6].

While it is generally accepted that **1** is the key intermediate of the ozonolysis reaction, so far no direct proof of its intermediary existence in the ozonolysis reaction has been given. It is puzzling and also somewhat disturbing that all attempts to directly detect **1** in the ozonolysis have been unsuccessful. This is even more puzzling since derivatives of **1** have been synthesized by oxidation of carbenes, singlet oxygen reactions with diazoalkanes or other reactions. Several recent reviews describe the chemistry of **1** and its derivatives [7–9].

Here, we provide computational evidence which indicates that it is probably impossible to directly detect **1** in the ozonolysis reaction.

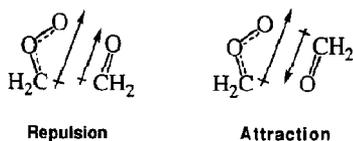
The decomposition of PO (reaction (II), scheme 1) leading to **1** and **2** is endothermic by 12 kcal/mol according to MP4(SDQ)/6-31G(d, p) calculations^{#2}. It is, however, highly unlikely that this reaction takes place in the solution phase ozonolysis.



Scheme 1

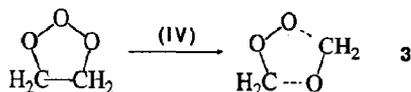
^{#2} Calculated MP4(SDQ)/6-31G(d, p) energies are: –303.31119 (PO), –189.08663 (**1**), –114.20544 (**2**), –303.30620 hartree (**4**).

In solution phases, PO will decompose in a solvent cage [2]. As soon as **1** and **2** are formed, dipole-dipole repulsion ($\mu(1)=4.0$ D; $\mu(2)=2.3$ D at MP4(SDQ)/6-31G(d, p)^{#3})



Scheme 2

between the two decomposition products will lead to destruction of the solvent cage (scheme 2). On the other hand, it is more likely that by rotation of either aldehyde or carbonyl oxide the molecular dipole moments can align in an antiparallel fashion thus leading to dipole-dipole attraction (see scheme 2). We have investigated whether the dipole complex **3** between **1** and **2** is stable.



In fig. 1, the calculated MP4(SDQ)/6-31G(d, p) geometry of **3** is shown, which reveals that the two molecules arrange exactly in a fashion that guarantees both maximum electrostatic attraction and stabilizing overlap between the π orbitals of **1** and **2**. The dipole complex **3** is more stable by 8.9 kcal/mol than the separated molecules according to MP4(SDQ)/6-31G(d, p) calculations. Reaction (IV) is only slightly endothermic by 3.1 kcal/mol.

Since the dipole complex **3** possesses a dipole moment of 2.8 D (MP4(SDQ)/6-31G(d, p)), which is only 0.8 D smaller than that of PO (3.6 D, MP4(SDQ)/6-31G(d, p)), it is likely that decomposition of PO and formation of the dipole complex **3** take place in the solvent cage. If an alcohol or a foreign aldehyde is present, the dipole complex **3** can be destroyed and a new complex can be formed, which leads to a different FO. Otherwise, the cycloaddition reaction between **1** and **2** takes place.

Inspection of fig. 1 reveals that the two molecules are aligned in the dipole complex in the correct orientation to undergo a cycloaddition reaction. Ac-

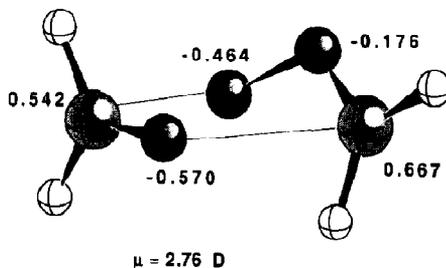
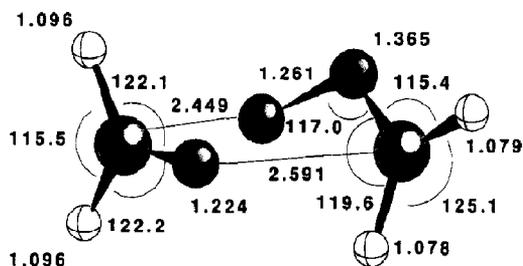
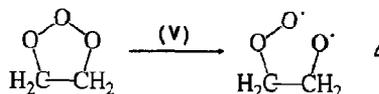


Fig. 1. MP4(SDQ)/6-31G(d, p) geometry of the carbonyl oxide-formaldehyde dipole complex **3**. The bottom figure gives Mulliken population values at MP4(SDQ)/6-31G(d, p). Dark spheres are oxygens, grey spheres are carbons and white spheres are hydrogens.

tually, the geometry of the transition state of the recombination reaction is very similar to that of the dipole complex **3**. As a consequence, the transition state energy is only 3 kcal/mol higher than that of the dipole complex [11].



In the gas phase, PO is formed as a hot molecule (excess energy more than 60 kcal/mol [4]), which can decompose either by reaction (II), (IV) or a bond breaking process (V) leading to the diradical **4**, which then can decompose in various ways [1,12]. If **1** is really formed, then it will be another hot molecule with an excess energy of more than 50 kcal/mol. Therefore, rapid decomposition, rapid rearrangement to dioxirane or rapid cycloaddition will be the consequence.

We conclude that it is highly unlikely to observe free carbonyl oxide in the ozonolysis reaction. In the

^{#3} For previous ab initio calculations on **1**, see ref. [10].

gas phase, its lifetime will be too short and in solution phases, decomposition of PO to the dipole complex **3** will be more likely than formation of free **1**. Accordingly, the Criegee mechanism has to be revised by replacing reaction (II) by reaction (IV). The dipole complex **3** can react in various ways where cycloaddition to yield FO is the most likely way. Reactions with protic substrates or added aldehydes will also start from the dipole complex **3** rather than from free **1**. The lifetime of the dipole complex **3** will be short since the recombination reaction will be fast.

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