

First evidence for the production of OH radicals by carbonyl oxides in solution phase – A DFT investigation

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Abstract

Dimesitylketone O-oxide (**1**) rearranges in solution to yield the alcohol 2-methylhydroxy-pentamethylbenzophenone (**5**) and dimesitylketone (**6**). DFT-B3LYP/cc-pVTZ calculations reveal that H migration from an *o*-methyl group to the terminal O atom of the COO unit of **1** rather than the isomerization of **1** is energetically the most favorable process. Calculated activation enthalpies (gas phase: 12.8 kcal/mol; CH₃CN solution: 12.4 kcal/mol) are in excellent agreement with measured activation enthalpies (CFCl₃ solution: 13.2 ± 0.2 kcal/mol; CH₃CN solution: 12.5 ± 0.3 kcal/mol). The hydroperoxide formed by H migration decomposes to a OH and a benzyl radical. Recombination in the solvent cage leads to alcohol **5** while diffusion of OH out of the solvent cage yields **6**. © 2001 Elsevier Science B.V. All rights reserved.

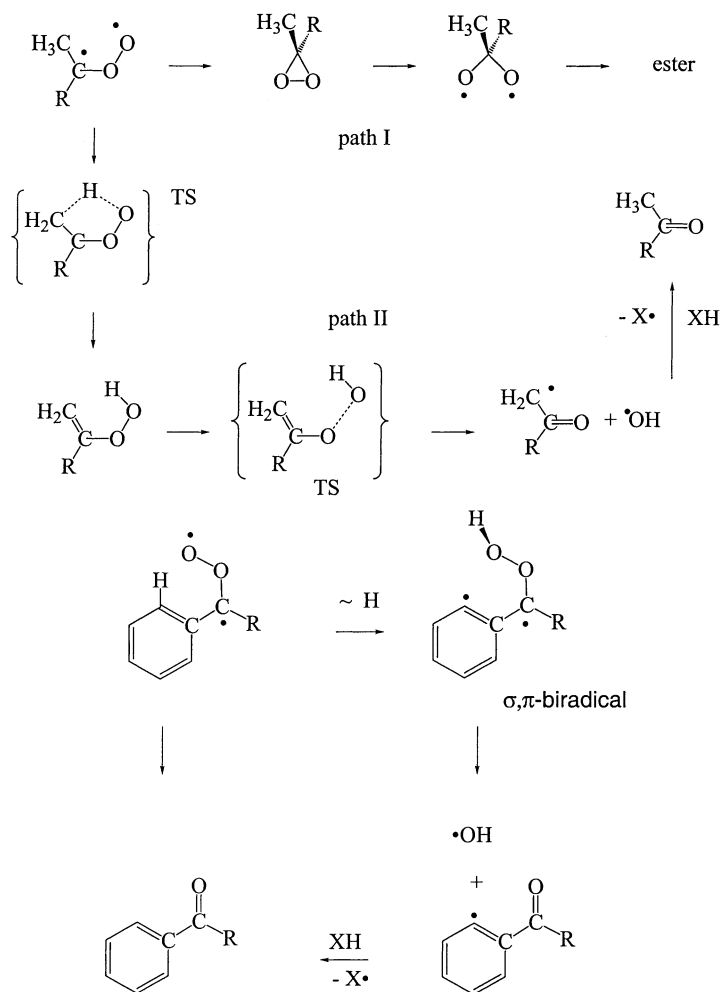
1. Introduction

In recent work, Cremer and co-workers [1–3] demonstrated that carbonyl oxides represent an unexpected source for OH radical production in the polluted atmosphere. This will take place if the carbonyl oxide in question possesses an α -CH_{*n*} group (*n* = 1, 2, 3) in syn-position so that a H atom can migrate to the terminal O atom of the COO unit and form the hydroperoxy derivative of an alkene (Scheme 1, path II). Cleavage of the OO bond and OH radical formation, although an endothermic process, is possible in the gas phase (slow energy dissipation) [1–3]. The mechanism shown in Scheme 1 (upper part) was confirmed for

methyl substituted carbonyl oxides in a three-step procedure. First, the various decomposition and rearrangement paths of methyl carbonyl oxides were calculated using various quantum chemical methods [1]. Then, in collaboration with Schindler and co-workers [2] appropriate kinetic experiments were carried out to quantitatively measure the amount of OH radicals produced in the ozonolyses of small alkenes leading to carbonyl oxides and their decomposition products. In the third step, RRKM calculations were used to verify the measured amount of OH radicals [3]. In this way, it was shown that carbonyl oxides without a syn-positioned alkyl group do not produce any significant amount of OH radicals. For syn-alkyl carbonyl oxide, the barrier for H migration is significantly lower than that for isomerization to dioxirane (Scheme 1, path I). In the case of dimethyl carbonyl oxide (formed in the ozonolysis of

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Scheme 1.

tetramethylethene) a yield of 60–80% OH radicals (relative to consumed ozone) can be produced [3].

It is a common understanding that radical reactions verified for the gas phase may take a different route in solution phase because of the presence of radical scavengers or the influence of the solvent leading to heteropolar rather than homopolar bond cleavage. Thus, it is not surprising that OH production in solution phase ozonolysis was never reported [5,6]¹. Apart from this, OH production is not expected to occur in the case

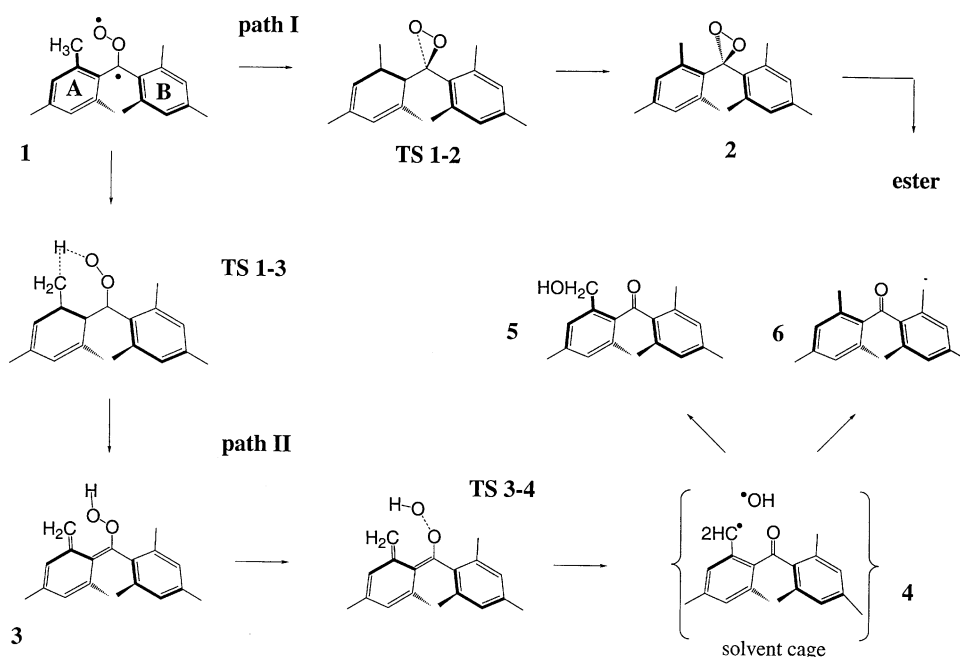
of aryl substituents because this will lead to an intermediate σ, π -biradical with limited stabilization possibilities (Scheme 1, bottom) and a relatively high energy compared to the hydroperoxyalkene formed in the case of a syn-alkylcarbonyl oxide (Scheme 1, path II). However, recent experimental results by Sander and co-workers [7,8] suggest that there is also the possibility of OH production by carbonyl oxide decomposition in solution. These authors managed to synthesize dimesitylketone O-oxide (**1**) in CFCl₃ solution at 203 K and by warming up the solution of **1** to room temperature they were able to detect besides dimesitylketone also 2-methylhydroxy-pentamethyl-

¹ For a review, see [4].

benzophenone, but not dimesityldioxirane (**2**), which, in analogy to other carbonyl oxides, should be considered as the most likely reaction product of **1**. It was possible to measure the Arrhenius energy ($E_a = 13.8 \pm 0.2$ kcal/mol [8]) for the rearrangement of **1** to 2-methylhydroxy-pentamethylbenzophenone and to study the solvent-dependence of this rearrangement, however experimental evidence explaining the formation of an alcohol as rearrangement product of a carbonyl oxide could not be obtained [8].

In line with our previous results for the gas phase decomposition of alkylcarbonyl oxides [1–3] we will show in this work that OH radical formation from carbonyl oxides is also possible in solution and that Sander's experimental work represents the first clear evidence for this mechanism. This is important because the possibility of OH radical formation was never considered in the solution phase ozonolysis or in solution phase reactions of carbonyl oxides and, therefore, would mean an important extension of the well established spectrum of carbonyl oxide reactions.

Our line of argument will exclusively be based on quantum chemical calculations carried out with density functional theory (DFT) (see, e.g. [9]) for the two most likely rearrangement and decomposition modes of **1** as shown in Scheme 2. Path I comprises isomerization via transition state **1–2** (TS **1–2**) to dioxirane **2** and follow-up rearrangements to ester, which would be considered the normal rearrangement mode of a carbonyl oxide and which was found by Sander and co-workers under photochemical reaction conditions [7,8]. As an alternative, we suggest path II leading via H-migration and TS **1–3** to hydroperoxide **3**, which, contrary to a phenyl-substituted carbonyl oxide (Scheme 1, bottom), can stabilize itself by adopting an *o*-quinodimethane structure (Scheme 2). Decomposition of **3** via TS **3–4** leads to OH and a benzyl radical (**4**) in solution probably embedded in a solvent cage. Recombination in the solvent cage yields alcohol **5**. Escape of OH from the solvent cage will lead to ketone **6** because radical **4** can only stabilize itself by H-abstraction from a suitable H donor (solvent or other molecule). We



Scheme 2.

will show that path II is energetically favored in solution and that OH production should be expected in many solution reactions of properly substituted carbonyl oxides.

2. Computational methods

In view of the size of dimesityl compounds **1–6**, quantum chemical calculations were limited by the fact that even with a VDZ+P basis set more than 400 basis functions are needed, which excludes CCSD(T) and other high level ab initio methods because of cost considerations. Therefore, restricted and unrestricted Kohn–Sham theory [10] was applied in connection with Becke's B3LYP hybrid functional [11], which has proven to lead to reliable geometries and energies close to CCSD(T) results when describing carbonyl oxides and their reactions [1–3]. Exploratory calculations were carried out with Pople's 6-31G(d) basis set [12]. For all molecules and transition states considered, vibrational frequencies at B3LYP/6-31G(d) geometries were determined to characterize stationary points and to determine the thermochemistry of the reactions investigated. This was particularly important for finding the minimum conformations with regard to methyl group rotations, which made geometry optimizations difficult and required reoptimizations after appropriate tests with calculated vibrational frequencies. Zero point energies (ZPE) and thermal corrections calculated at B3LYP/6-31G(d) were used to obtain reaction and

activation enthalpies $\Delta_R H$ and $\Delta^\ddagger H$ at 298 K. The determination of entropies S led to Gibbs free energies ΔG at 298 K.

In a second set of calculations, B3LYP/6-31G(d) geometries and energies were improved by using Dunning's cc-pVTZ basis set, [13] which corresponds to a (11s 6p 3d 2f/6s 3p 2d) [5s 4p 3d 1f/4s 3p 2d] contraction and leads to calculations with 938 basis functions in the case of **1** and its rearrangement products. The use of f -functions has been found to be of importance to get a reliable description of dioxiranes and analogous peroxides [14,15] and therefore, we will base our discussion predominantly on cc-pVTZ results.

In a third set of calculations, the influence of the solvent was tested by applying Tomasi's solvation model PISA [16], which is based on the embedding of the target molecule in a polarizable continuum characterized by the dielectric constant ϵ of the solvent considered. PISA-B3LYP/6-31G(d) calculations were carried out for the case of acetonitrile as solvent ($\epsilon = 36.64$ [17]).

The conformation of the two mesityl groups with benzene rings A and B was characterized with the help of the angle ϕ , which describes the relative orientation of A and B with respect to each other. The angle ϕ was calculated by determining first the geometrical center and mean plane [18] of each ring, then the normal to each mean plane and, finally, the angle enclosed by the two normal vectors. The degree of π -delocalization in A and B was assessed by calculating the average CC bond length in each ring as well as the standard deviation σ from

Table 1
Energies and other molecular properties of compounds **1–6** calculated with B3LYP^a

Property	Basis set	1	TS 1-2	2	TS 1-3	3	TS 3-4	4 + OH(² Π)	5	6 + O(¹ D)
ΔE	cc-pVTZ	0	19.0	-7.6	15.8	9.9	13.6	0.2	-83.6	58.4
ZPE	6-31G(d, p)	226.7	226.1	227.1	223.9	226.4	224.7	221.5	228.6	224.8
$\Delta H(298)$	cc-pVTZ	0	18.6	-6.9	12.8	9.9	12.2	-3.1	-81.4	57.9
S	6-31G(d, p)	151.9	154.3	154.0	149.6	152.8	156.2	195.3	156.6	188.1
$\Delta G(298) \epsilon = 1$	cc-pVTZ	0	17.8	-7.5	13.5	9.6	10.9	-16.0	-82.8	47.1
$\Delta G(298) \epsilon = 36.64$	cc-pVTZ	0	18.1	-5.1	15.7	12.2	11.9	-16.7	-81.8	
μ	cc-pVTZ	5.10	5.18	2.71	3.96	2.34	4.51	3.05 ^b	4.88	2.71 ^c
μ_{sol}	6-31G(d, p)	6.75	6.98	3.64	5.07	3.05	5.76	3.99 ^b	6.07	3.54 ^c

^a The absolute energy of **1** is -887.91413 hartree at B3LYP/cc-pVTZ. Relative energies ΔE , relative enthalpies $\Delta H(298)$, relative free enthalpies $\Delta G(298)$, and zero point energies (ZPE) in kcal/mol, entropies S in cal/(mol K), and dipole moments μ in Debye.

^b Dipole moment of **4**.

^c Dipole moment of **6**.

this bond length, which is a measure for bond alternation (bond equilibration). All calculations were carried out with the program packages COLLOGNE 2000 [19] and GAUSSIAN 98 [20].

3. Results and discussion

Calculated energies, enthalpies, entropies and dipole moments are listed in Table 1 while B3LYP/cc-pVTZ geometries for some selected molecules

and TSs shown in Scheme 2 are given in Figs. 1–3. In Table 2, geometrical parameters of the mesityl groups are summarized that facilitate the discussion of conformational features and π -conjugation in rings A and B.

The minimum conformation of **1** is characterized by a 57° rotation of ring A and a 41° rotation of ring B in opposite directions out of the COO reference plane ($\phi = 91.4^\circ$, Fig. 1, top). Molecule **1** exists in two enantiomeric forms, one of which is shown in Fig. 1 while the second is obtained by

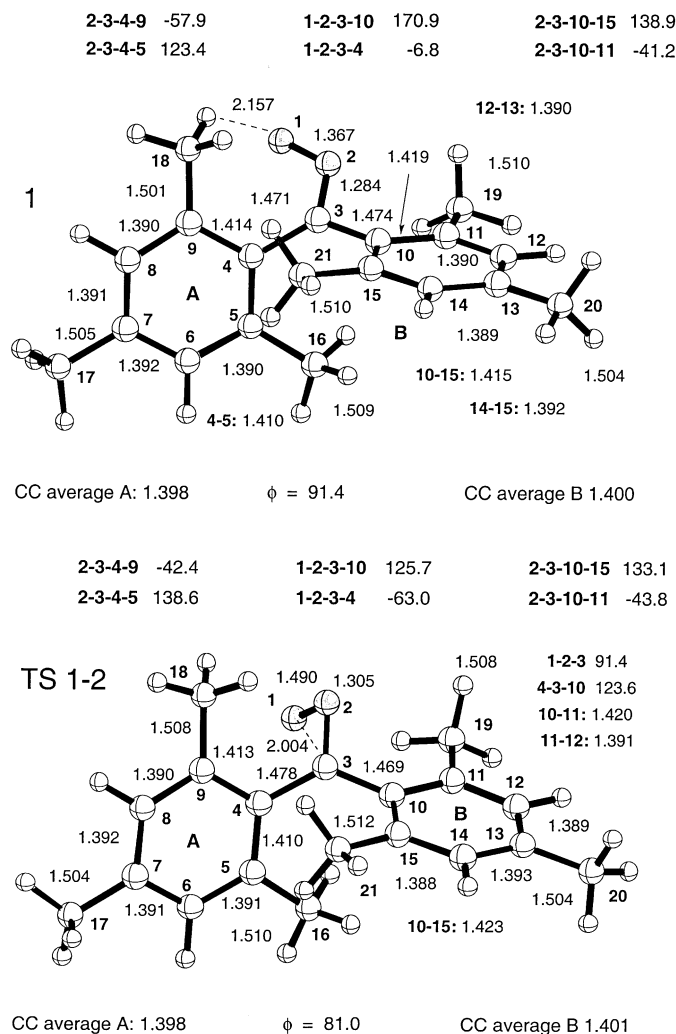


Fig. 1. B3LYP/cc-pVTZ geometries of carbonyl oxide **1** (upper part) and TS **1-2** (lower part). Angle ϕ is the rotational angle between rings A and B (for its definition, see text). Distances in Å, angles in degrees.

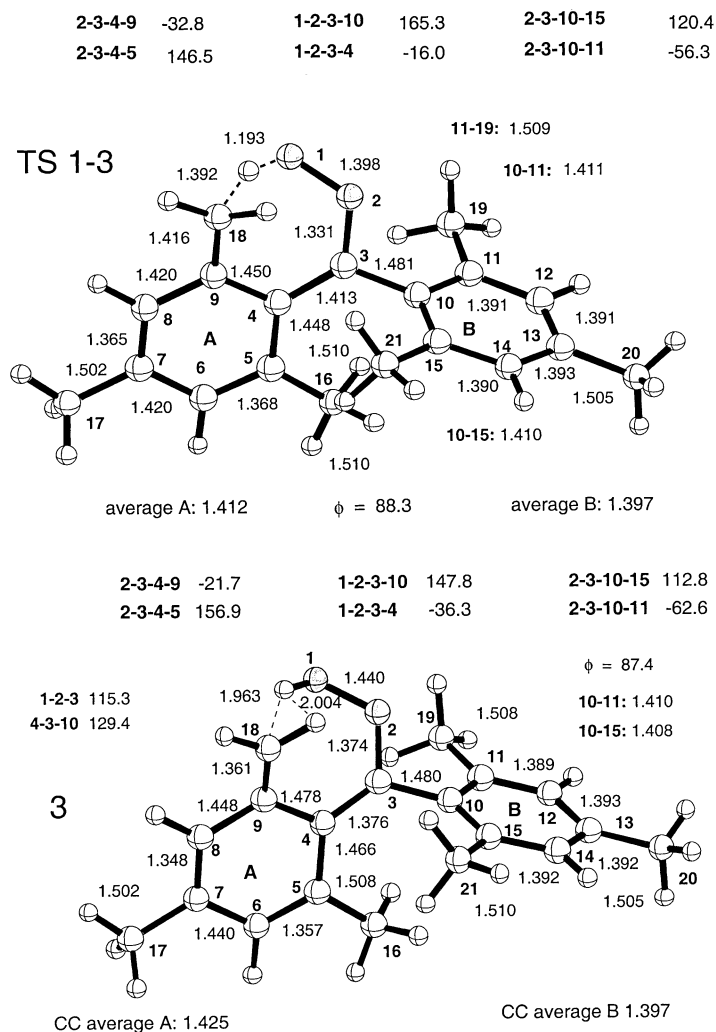


Fig. 2. B3LYP/cc-pVTZ geometries of transition state **TS 1-3** (upper part) and hydroperoxide **3** (lower part). Angle ϕ is the rotational angle between rings A and B (for its definition, see text). Distances in Å, angles in degrees.

reverting the signs of the dihedral angles given in the heading of Fig. 1 (upper part). Ring B can undergo a libration driving ring A in a geared process (keeping A at a ϕ value close to 90°) from one enantiomeric form to the other. The **TS** of the libration is occupied by a conformation, in which both COO unit and ring B are in a common plane. The calculated barrier to libration is 3.3 kcal/mol ($\Delta^\ddagger H = 3.0$; $\Delta^\ddagger G = 2.6$ kcal/mol), which means that at the temperature of measurement ($T = 250$ K [8]) both enantiomeric forms are equally populated. However, a libration of ring A through the

COO plane requires 11.5 kcal/mol ($\Delta^\ddagger H = 15.1$; $\Delta^\ddagger G = 14.0$ kcal/mol) and, therefore, is much slower although it can also occur at 250 K.

Isomerization to dioxirane **2** proceeds via **TS 1-2** (Fig. 1) and an energy barrier of 19.0 kcal/mol (activation enthalpy $\Delta^\ddagger H(298) = 18.6$ kcal/mol, Table 1), which is comparable to the barriers found for other carbonyl oxides (CH_2OO : 19 [21]; Me_2COO : 20 kcal/mol [21]). However, contrary to alkylcarbonyl oxides, which rearrange in a strongly exothermic reaction (CH_2OO : -27.3 [21]; Me_2COO : -23.4 kcal/mol [21]), the formation of **2**

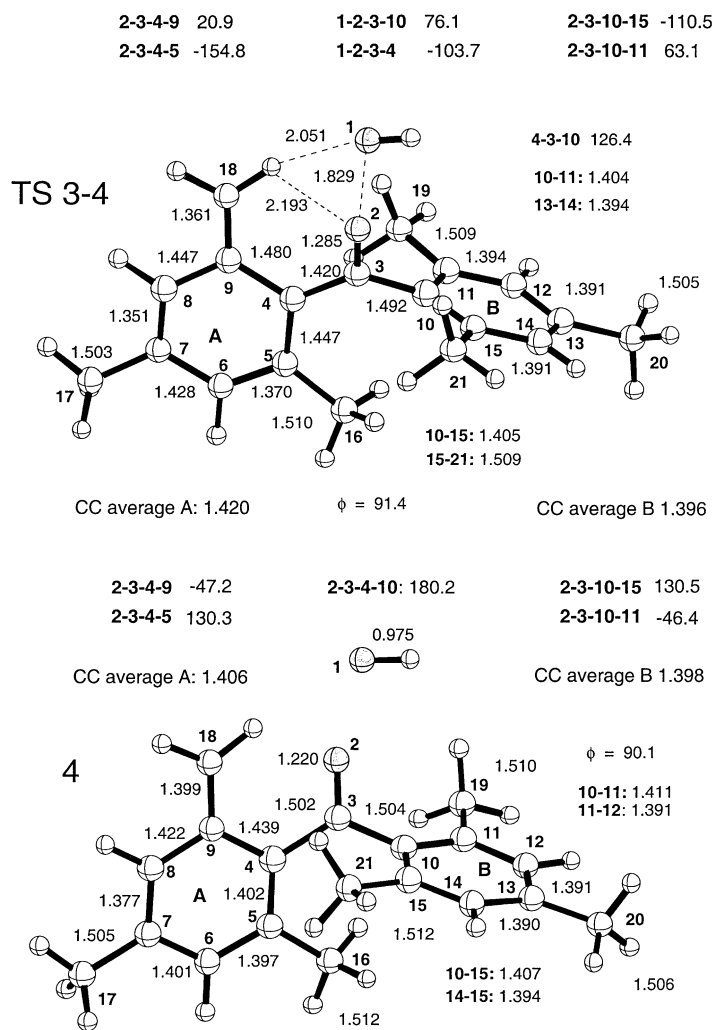


Fig. 3. B3LYP/cc-pVTZ geometries of transition state **TS 3-4** (upper part) and benzyl radical **4** (lower part). Angle ϕ is the rotational angle between rings A and B (for its definition, see text). Distances in Å, angles in degrees.

is moderately exothermic: $\Delta_R E = -7.6$; $\Delta_R H(298) = -6.9$ kcal/mol (Table 1). Dioxirane **2** suffers from steric repulsion between the mesityl groups reflected by a widening of the angle C4C3C10 from 116.7° (parent dioxirane [21]) to 120.6° in the case of **2** [22].

In the gas phase, H migration via **TS 1-3** (Fig. 2) requires 15.8 kcal/mol ($\Delta^\ddagger H(298) = 12.8$ kcal/mol, Table 1) and, by this, is energetically more favorable than dioxirane formation. The activation enthalpy is even lower than that found for

dimethyl carbonyl oxide (13.6 kcal/mol [1]), which is a consequence of two important structural factors. (a) In **1**, one of the *o*-methyl hydrogens is already close to the terminal O atoms (Fig. 1: 2.157 Å), which makes this H prone to migration to the terminal O atom. (b) In **TS 1-3**, only a part of the resonance energy of ring A seems to be lost as indicated by the calculated geometry (Fig. 2): Bond C4C9 is elongated to 1.450 Å (1.414 Å in **1**) while bonds C9C18 and C3C4 are shortened (1.416 and 1.413 Å; **1**: 1.501 and 1.471 Å). Also

noteworthy is that H approaches the terminal O atom much closer in TS 1–3 (CH = 1.392 Å; HO = 1.193 Å) than in the H-migration TS of an alkylcarbonyl oxide (dimethylcarbonyl oxide: CH = 1.345 Å; HO = 1.344 Å [1,2]).

The intermediate hydroperoxide **3** formed by H-migration is 9.9 kcal/mol less stable than carbonyl oxide **1**, which clearly indicates that the resonance energy of ring A is not totally lost. The average CC bond length of ring A is elongated to 1.425 Å (**1**: 1.398 Å, Table 2) and the alternation of bonds as measured by the standard deviation σ (Table 2) is increased to 0.059 Å (**1**: 0.010 Å). Because of the *o*-quinodimethane structure, ring A has to adjust more to the plane defined by C2C3C4 (back-rotation by 34.7°, Fig. 2), a process which is (partially) followed by ring B (rotation by 23.7°) so that the angle between the ring planes reduces from 91.4 (1) to 87.4° (Table 2). The destabilization of ring A is partially compensated by strong H-bond type interactions between C18 and the HOO group (C18–H distance: 1.963 Å, Fig. 2).

Cleavage of the OO bond requires just 3.7 ($\Delta^{\ddagger}H(298) = 2.3$) kcal/mol (Table 1). In TS 3–4, the OO bond is lengthened to 1.829 Å. Both O atoms have stabilizing interactions with one of the H atoms at C11 (Fig. 3). While OO bond dissociation normally proceeds without a barrier and is best described by a Morse potential, decomposition of 3–4 (Scheme 2) is accompanied by significant electronic structure changes in ring A and its exocyclic bonds C3C4 and C9C18. The average CC bond in ring A decreases from 1.425 Å (**3**) to

1.420 Å (TS 3–4) and 1.406 Å (**4**, Table 2) because the *o*-quinodimethane structure of **3** is changed to that of a benzyl radical with an α -keto group (**4**).

Ketone **4** and radical OH are the products of the H-migration, which are of similar stability to carbonyl oxide **1** ($\Delta_R E = 0.2$; $\Delta_R H(298) = -3.1$ kcal/mol). Radical **4** (Fig. 3) is stabilized by (a) the formation of the CO double bond of the keto group and (b) benzyl conjugation (average CC bond for A: 1.406 Å, Table 2) both being not possible in hydroperoxide **3**. In the gas phase, the two radicals should immediately separate and stabilize themselves by H abstraction thus leading to water and ketone **6**. We searched for a TS that leads to a direct OH transfer to C18 in a concerted fashion, but all attempts were unsuccessful. Hence, there is little chance that alcohol **5** is formed in the gas phase. Although OH production is confirmed for **1** as the energetically most favorable reaction mode in the gas phase, it should lead to ketone **6** rather than alcohol **5** found in the experiment [7,8]. This suggests that OH production proceeds in a different way in solution.

Solution phase mechanism. Carbonyl oxide **1** will be strongly solvated in solution phase as is indicated by its large dipole moment $\mu = 5.1$ Debye (B3LYP/6-31G(d): 5.0 Debye). In a polar solvent such as CH₃CN, solvation of **1** leads to a substantial increase of its dipole moment (6.7 Debye, Table 1) and a decrease of its free energy *G* (electrostatic part) by 5.2 kcal/mol according to PISA-B3LYP/6-31G(d) calculations. Hence, it is reasonable to assume that both isomerization and

Table 2

Characterization of the mesityl rings for compounds 1–6 calculated at the B3LYP/cc-pVTZ level of theory^a

Compound	ϕ	A	B	A–B	σ_A	σ_B
1	91.4	1.398	1.400	–0.002	0.010	0.014
TS 1–2	81.0	1.398	1.401	–0.003	0.011	0.017
2	83.1	1.398	1.398	0.000	0.011	0.011
TS 1–3	88.3	1.412	1.397	0.015	0.037	0.010
3	87.4	1.425	1.397	0.028	0.059	0.009
TS 3–4	91.4	1.420	1.396	0.024	0.050	0.006
4	90.1	1.406	1.398	0.008	0.021	0.009
5	83.1	1.398	1.398	0.000	0.010	0.010
6	89.1	1.398	1.398	0.000	0.010	0.010

^a Angle ϕ denotes the angle [deg] enclosed by the normal vectors of rings A and B; averaged CC bond lengths [Å] in rings A and B are listed under headings A and B, difference A–B [Å] compares averaged CC bond lengths in rings A and B, σ [Å] gives the standard deviation of CC ring bond lengths from average CC values for rings A and B.

H-migration followed by radical formation will take place in the solvent cage and that **4** and OH are captured for some time in the solvent cage.

Changes in dipole moment μ indicate how the energetics of the reaction is affected by solvation (provided specific solvation does not play a role). According to the calculated μ values of Table 1, there should be only a slight change in the activation enthalpy for isomerization, but the relative stability of dioxirane **2** should be lowered (more positive $\Delta_R G(298)$ value, Table 1) because of the considerably lower μ value of 2.7 (CH₃CN solvent: 3.6) Debye. The latter situation applies also to TS **1–3** (Table 1) and the free activation energy $\Delta^\ddagger G(298)$ increases from 13.5 to 15.7 kcal/mol, which could result from either energetic effects due to reduced solvation or an accompanying entropy effect (reduced order in the solvation shell circumventing the target molecule thus decreasing entropy).

Noteworthy is that the free energy G of TS **3–4** is lower than that of hydroperoxide **3** (Table 1) suggesting that decomposition of **1–4** in the solvent cage is a one-step reaction initiated by H migration. TS **3–4** has a dipole moment, which is more than 2 Debye larger than that of **3** (Table 1), and therefore should be more stabilized by solvation than hydroperoxide **3**. This observation indicates that the gas and solution phase mechanisms differ with regard to the occurrence of a hydroperoxide intermediate.

Sander and co-workers [7,8] measured an Arrhenius energy E_a of 13.1 ± 0.3 kcal/mol for the rearrangement of **1** in acetonitrile solution in a temperature range 210–298 K. This corresponds to an activation enthalpy of 12.5 ± 0.3 kcal/mol assuming an unimolecular reaction as suggested by the DFT calculations. The A factor was measured to be close to 7×10^9 according to relationship (1),

$$k = A e^{-E_a/RT} = \frac{k_B T}{h} e^{\Delta^\ddagger S/R} e^{\Delta^\ddagger H/RT}, \quad (1)$$

where E_a is the Arrhenius activation energy, k_B the Boltzmann constant, R the gas constant, and h the Planck constant. Considering an average temperature $T = 250$ K for the kinetic measurements [8], the activation entropy can be estimated to be -13.1 e.u. in acetonitrile solution, which deviates considerably from the gas phase value of -2.3 e.u.

(Table 1) because of the formation of solvation shells surrounding the reaction complex. Hence, the calculated $\Delta^\ddagger G(298)$ value should correspond to activation enthalpies $\Delta^\ddagger H(298)$ of 11.8 kcal/mol and $\Delta^\ddagger H(250)$ of 12.4 kcal/mol in excellent agreement with an experimental $\Delta^\ddagger H(250)$ value of 12.7 ± 0.3 kcal/mol. The agreement between measured and calculated activation enthalpies confirms that H-migration is also the preferred reaction of **1** in solution.

If OH radical and radical **4** are formed in the solvent cage, there is a finite chance that they recombine to form alcohol **5** in a strongly exothermic reaction setting free about 80 kcal/mol (Table 1). Of course, some of the OH radicals will leave the solvent cage by diffusion and the remaining radical can only stabilize itself by H-abstraction and formation of ketone **6**. The ratio of the concentrations of **5** and **6** will strongly depend on the temperature T (at low T more ketone; at a T sufficient to surmount the barrier to H migration more alcohol; at a much higher T destruction of the solvent cage by strong translational, rotational, and vibrational movements of target and solvent molecules thus leading again to an increase of ketone), polarity of the solvent (high polarity and large ϵ : stronger solvent cages increase the chance of alcohol formation), and the H donating ability (H-donors as solvent increase the yield of ketone). These predictions are in line with the observed solvent-dependence of the product ratio [5]:[6] [8].

4. Conclusions

This work has verified that OH radicals are produced by carbonyl oxides both in the gas phase and in solution provided the carbonyl oxide in question possesses an H atom prone to migrate, which is normally the case for syn-substituted alkylcarbonyl oxides with α -H atom(s) and when a 5- or 6-membered cyclic TS can be established. If these requirements are fulfilled, the barrier to H migration and OH production will be 4–5 kcal/mol smaller than the barrier to isomerization thus leading to dioxirane. In the case of phenyl substituents, H-migration is not a likely reaction because the relatively high energy of the biradical

intermediates (Scheme 1) implies a relatively large reaction barrier.

The mesityl group behaves like an alkyl rather than an aryl substituent (because of its *o*-methyl groups). H-migration occurs via a seven-membered TS that is 6 kcal/mol lower in enthalpy at 298 K than the corresponding TS for isomerization, which means that carbonyl oxide **1** exclusively reacts via path II shown in Scheme 2. In polar solvents, the two-step reaction mechanism reduces to a one-step mechanism because of an inversion in stabilities of intermediate hydroperoxide **3** and TS **3–4** caused by solvation of the reaction complex.

The formation of alcohol **5** is a direct consequence of the large dipole moment of **1** and the formation of a solvent cage, in which recombination of OH and radical **4** is possible. Clearly, there is a high probability that OH radicals are also formed by other carbonyl oxides in solution. Therefore, it should be rewarding to check previous experiments for unusual decomposition products of carbonyl oxides, which can be related to the formation of intermediate alkenehydroperoxides and their decomposition yielding OH radicals.

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