

Formation of OH radicals in the gas phase ozonolysis of alkenes: the unexpected role of carbonyl oxides

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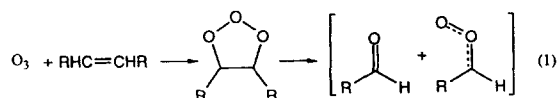
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Abstract

According to CCSD(T)/TZ + 2P calculations, the decomposition of carbonyl oxide, H_2COO , to HCO and OH radicals is unlikely in view of an activation enthalpy $\Delta\Delta H_f^\circ(298)$ of 31 kcal/mol. However, for dimethylcarbonyl oxide there is a low energy rearrangement mode ($\Delta\Delta H_f^\circ(298)$: 14.4 kcal/mol) which involves a H atom of the methyl group and which leads to a hydroperoxy methyl ethene intermediate, which in turn can decompose to OH and CH_2COCH_3 radicals ($\Delta\Delta H_f^\circ(298)$: 23 kcal/mol). In the gas phase ozonolysis of alkyl substituted alkenes the formation of OH radicals is the most likely process. This has important consequences for the chemistry of the atmosphere.

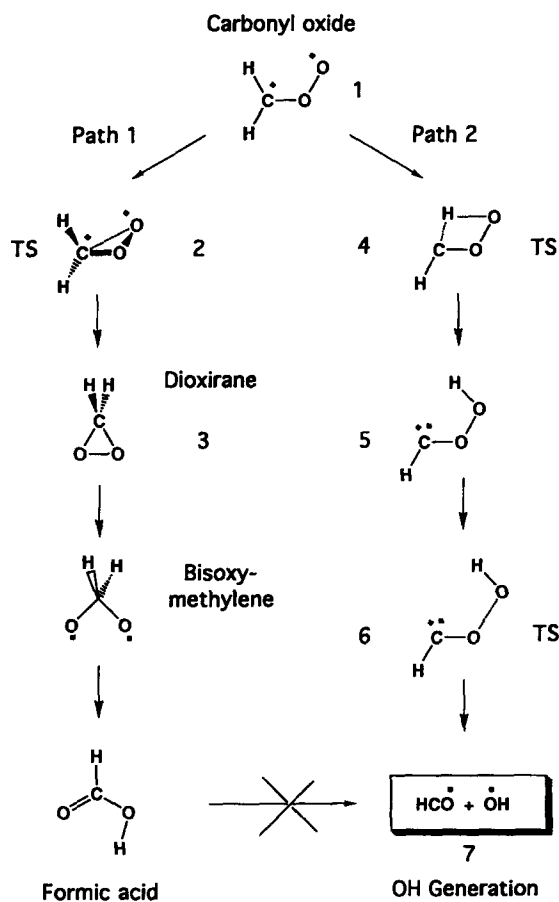
1. Introduction

There exists mounting evidence in recent literature [1–7] that the ozonolysis of alkenes such as biogenic terpenes and isoprene constitutes a night time source of OH radicals. According to Criegee, ozone reacts with alkene by cycloaddition to yield 1,2,3-trioxolane, the so-called primary ozonide. Primary ozonide, in turn decomposes in a highly exothermic cycloreversion step into aldehyde and carbonyl oxide, the so-called Criegee zwitterion [8]:



Herron and Huie [7] were the first to postulate that OH radicals might be formed by a unimolecular decomposition step of the energy-rich carbonyl oxides. Since then, a number of experimental studies have been carried out to confirm this hypothesis. Selective scavengers and a detailed product analysis have been employed to quantify the OH radical yields in various ozonolysis systems [1–6].

There are several suggestions on how carbonyl oxide, H_2COO (1), may decompose to produce OH radicals. Cremer and co-workers [9–11] have shown that in the absence of nucleophilic or electrophilic reaction partners the most likely reaction of 1 is a rearrangement via transition state (TS) 2' to its isomer dioxirane (3, see Scheme 1, path 1). The calculated activation and reaction energy are 19 and –26 kcal/mol, respectively [9].



Scheme 1.

Although **3** is much more stable than **1**, an excess energy of about 75 kcal/mol [12] will lead to rapid ring opening and formation of bisoxymethylene, which in turn rearranges to formic acid (Scheme 1, path 1). It is known that formic acid decomposes to CO_2 , H_2 , CO and H_2O [13]. The decomposition to $\text{OH} + \text{HCO}$ would require 108 kcal/mol [14,15] and, therefore, is not likely under the conditions of the gas phase ozonolysis.

We present in this letter a theoretical study backed up by experiments that explains the generation of OH radicals as a result of a two-step rearrangement–decomposition mechanism. In particular, we will investigate the possible rearrangement of **1** via **TS 4** to an intermediate carbene **5**, which may decompose via **TS 6** to yield CHO (**7a**) and OH (**7b**) radicals.

Clearly, carbenes are labile short-lived species that are probably more unstable than carbonyl oxides. Therefore, it is unlikely that **1** prefers to follow reaction path 2 rather than path 1 shown in Scheme 1. However, we will show that despite the unfavourable energetics of path 1 carbonyl oxides are an important source for OH radicals and, therefore, ozonolysis must be considered as one of the major OH generating reactions in the atmosphere.

2. Computational methods

Since the investigation of carbonyl oxides requires highly correlated ab initio methods, we have used many-body perturbation theory (MBPT) and coupled-cluster (CC) theory to describe the molecules discussed in this work. In particular, we used second-order Møller–Plesset perturbation theory (MP2) [16] to get reasonable starting geometries, which could be used for geometry optimizations at the more accurate QCISD [17–19] (quadratic configuration interaction with all single and double excitations) and CCSD(T) [20] (CCSD calculations with a perturbative treatment of all triple (T) excitations) levels of theory. CC methods contain infinite order effects and are (like MBPT but in contrast to truncated CI methods) size-extensive. Furthermore, advanced CC methods such as CCSD(T) have been proven to lead to reasonable results in cases with multireference character such as carbonyl oxides [9,21].

We used a series of basis sets increasing from $\text{DZ} + \text{P}$ to $\text{TZ} + 2\text{P} + \text{f}$ quality to handle basis set truncation errors within the Gaussian-2 (G2) theory of Curtiss, Raghavachari, Trucks and Pople [22]. For the MP and QCI calculations, we used Pople's 6-31G(d, p), 6-311G(d, p), 6-311 + G(d, p), 6-311G(2df, p) and 6-311 + G(3df, 2p) basis sets [23,24] while for the CCSD(T) calculations we employed a $\text{TZ} + 2\text{P}$ basis, which was derived from Dunning's [25,26] (11s6p3d/5s3p) [5s3p2d/3s2p] basis augmented with cartesian polarization functions and optimized at the correlated level for some prototype molecules [27]. It has been shown in previous work that high accuracy calculations of **1**, **2**, and **3** are possible at the CCSD(T)/ $\text{TZ} + 2\text{P}$ level pro-

vided all geometries are optimized at this level of theory [9].

To compare (thermochemical) G2 results and CCSD(T) results, harmonic vibrational frequencies were calculated at the MP2/6-31G(d, p) and QCISD/6-31G(d, p) levels of theory and scaled with a scaling factor of 0.930 to obtain appropriate zero-point energy (ZPE) and temperature corrections for $T = 298$ K.

Apart from this, we systematically tested lower levels of theory (Hartree–Fock (HF), MP2, MP3, MP4, QCISD) to find a method that provides a

reasonable compromise between accuracy and economy to investigate larger carbonyl oxides with alkyl and aryl substituents. This search was unsuccessful since none of the methods checked turned out to be accurate enough to describe the present problem. Instead, we found that density functional theory (DFT) based on Becke's three parameter functional B3LYP [28–30].

$$(1 - A) E_x(\text{Slater}) + A E_x(\text{HF}) + B E_x(\text{Becke}) \\ + C E_c(\text{LYP}) + (1 - C) E_c(\text{VWN})$$

Table 1
Energetics of carbonyl oxide rearrangements according to path 1 or path 2^a

Method/basis set	Geometry	1	2, TS	3	4, TS	5	6, TS	7
<i>Absolute energies</i>								
MP2/6-31G(d, p)	A	-189.06865	25.0	-34.6	33.7	10.0	31.2	-8.7
PMP2/6-31G(d, p)							8.3	-11.1
MP2/6-311 + G(3df, 2p)	A	-189.26494	31.7	-34.7	31.7	8.3	32.3	-8.2
PMP2/6-311 + G(3df, 2p)							4.3	-11.2
MP4/6-311G(2df, p)	A	-189.28897	31.0	-31.5	31.0	7.3	26.1	-6.7
PMP4/6-311G(2df, p)							4.6	-8.2
QCISD(T)/6-311G(d, p)	B	-189.19048	20.8	-26.0	34.7	7.8	10.2	-9.6
DFT/6-31G(d, p)	C	-189.57989	21.5	-24.1	34.9	10.8	12.1	-0.2
DFT/6-311 + G(3df, 2p)	D	-189.65662	21.7	-21.8	35.9	9.9	10.1	-4.7
CCSD(T)/[5s3p2d/3s2p]	E	-189.32044	19.2	-25.6	34.0	-	-	-7.8
<i>Zero point energies (ZPE)</i>								
MP2/6-31G(d, p)	A	18.4	17.8	19.5	15.8	17.7	16.9	13.0
QCISD/6-31G(d, p)	B	18.3	16.8	19.4	15.3	17.6	13.4	13.0
DFT/6-31G(d, p)	C	18.9	17.9	19.7	15.7	17.7	16.4	13.0
$\Delta \Delta H_f^0(298)$								
MP2/6-31G(d, p)	A	0	24.3	-33.7	31.0	9.5	7.8	-14.5
MP2/6-311 + G(3df, 2p)	A	0	31.0	-33.8	29.0	7.8	3.8	-14.6
MP4/6-311G(2df, p)	A	0	30.3	-30.6	28.3	6.8	4.1	-11.6
QCISD(T)/6-311G(d, p)	B	0	19.3	-25.1	31.5	7.3	5.6	-13.0
G2	B	0	19.3	-23.2	33.7	nv	nv	-7.6; -10.6 ^b
DFT/6-31G(d, p)	C	0	20.4	-23.5	31.6	9.9	<9.9	-3.6; -6.6 ^b
DFT/6-311 + G(3df, 2p)	D	0	20.6	-21.2	32.6	9.0	7.9	-8.1; -11.1 ^b
CCSD(T)/[5s3p2d/3s2p]	E	0	17.7	-24.7	30.8	-	-	-11.2
Best	E	0	17.7	-24.2 ^c	30.8	-	-	-12.0 ^d
$\Delta H_f^0(298)$	E	30.2	47.9	6.0	61.0	-	-	18.2

^a Absolute energies in hartree, relative energies in kcal/mol. Heats of reaction $\Delta \Delta H_f^0(298)$ [kcal/mol] obtained from reaction energies, ZPEs and temperature corrections. Geometry A: MP2/6-31G(d, p); B: QCISD/6-31G(d, p); C: DFT/6-31G(d, p); D: DFT/6-311 + G(3df, 2p); E: CCSD(T)/[5s3p2d/3s2p]. ZPE scaling factors are 0.930 (A, B); 0.963 (C). $\Delta H_f^0(298)$ value of 1 from Ref. [15], $\Delta H_f^0(298)$ of 7 from Ref. [12]. In case of spin contamination, G2 values are not available (nv).

^b Estimated values assuming a correction of -3 kcal/mol because of spin contamination.

^c From Ref. [9].

^d From experimental $\Delta H_f^0(298)$ values of Refs. [14] and [15].

(E_x (Slater): Slater exchange, E_x (HF): HF exchange, E_x (Becke): gradient part of the exchange functional of Becke, E_c (LYP): correlation functional of Lee, Yang, and Parr (LYP), E_c (VWN): correlation functional of Vosko, Wilk, and Nusair; A , B , C : coefficients determined by Becke using the three parameter fit to experimental heats of formation [28]) leads to reliable results, which can be improved by increasing the basis set from 6-31G(d, p) (geometry optimization C , harmonic frequencies, scaling factor 0.963) to 6-311 + G(3df, 2p) quality [30] (geometry optimization D) and including ZPE and temperature corrections to get energy differences directly comparable with CCSD(T) and G2 results.

Calculations have been performed with ACES II [31], COLOGNE94 [32] and GAUSSIAN 92/DFT [33].

3. Results and discussion

Calculated energies, ZPE corrections and heats of formation at 298 K, $\Delta H_f^0(298)$, and reaction enthalpies $\Delta\Delta H_f^0(298)$ are listed in Table 1 for systems 1–7 that correspond to the stationary points of paths 1 and 2 shown in Scheme 1. In Fig. 1, the geometries for 1 and TS 4 obtained at the CCSD(T)/TZ + 2P level are given together with geometries calculated at lower levels of theory. Fig. 2 gives the calculated enthalpy diagram for the two possible rearrangement modes of 1.

Fig. 1 reveals that the CCSD(T)/TZ + 2P and DFT/6-31G(d, p) geometries agree surprisingly well, which also holds to some extent in the case of the QCISD/6-31G(d, p) and MP2/6-31G(d, p) geometries. However, the latter fail with regard to important details such as the CO/OO bond ratio in 1 or the distance between C and terminal O in 2. The largest discrepancy between CCSD(T)/TZ + 2P and the other methods is found for carbene 5 and TS 6. These stationary points do not exist on the CCSD(T) potential energy surface (PES) while all other methods lead to 5 and 6.

The CCSD(T) barrier for isomerization to dioxirane is 19.2 kcal/mol while the reaction energy for the isomerization step $1 \rightarrow 3$ is -25.6 kcal/mol. This corresponds to $\Delta\Delta H_f^0(298)$ values of 17.7

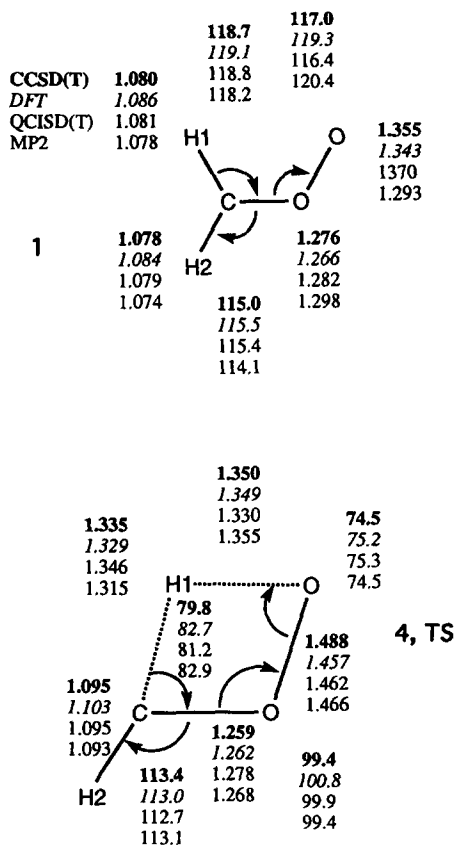


Fig. 1. Calculated geometries for 1 and TS 4. Parameters are given in the order (top to bottom): CCSD(T)/TZ + 2P in bold face, DFT/6-31G(d, p) in italics, QCISD/6-31G(d, p) in normal print, MP2/6-31G(d, p) in normal print. Bond lengths in Å and angles in deg.

(activation enthalpy, Table 1) and -24.7 kcal/mol (reaction enthalpy) in good agreement with previous results [9]. The CCSD(T) barrier for the rearrangement to 5 is 34.0 kcal/mol corresponding to a $\Delta\Delta H_f^0(298)$ value of 30.8 kcal/mol. As already mentioned, CCSD(T)/TZ + 2P theory predicts a single step reaction leading to OH and CHO radical according to



Although all the other methods used suggest the existence of 5 and a TS 6 (Table 1), closer inspection of the results reveals that this is due to a theoretical artefact. Both MP n and QCI fail to describe path 2 correctly because of high spin contamination ($\langle S^2 \rangle$

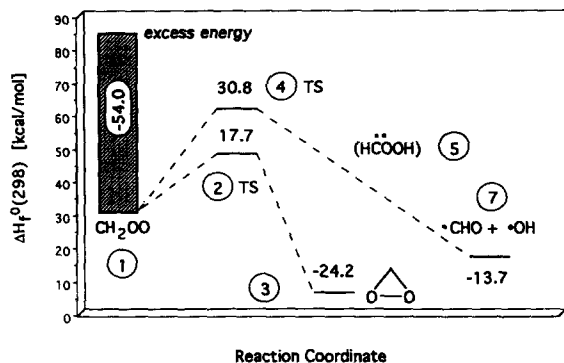


Fig. 2. Heats of formation $\Delta H_f^0(298)$ and reaction enthalpies $\Delta\Delta H_f^0(298)$ for reaction paths 1 and 2 in the case of carbonyl oxide (1).

values of 0.5 to 0.7 instead of 0) of the unrestricted HF (UHF) singlet wavefunction used to describe TS 6. This artificially raises the relative energy of TS 6 and carbene 5 is found in a potential well. As soon as all higher spin states are projected out of the singlet wavefunction of TS 6, relative energies below that of 5 (Table 1) are obtained.

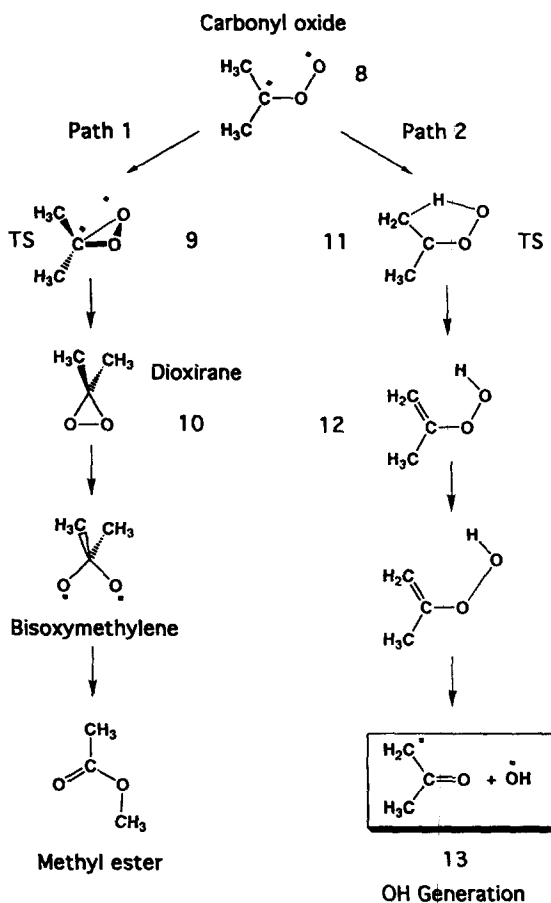
The more correlation effects covered by a given method, the less sensitive it is to spin contamination. This is true in the case of CCSD(T) and DFT, which for geometries similar to TS 6 lead to $\langle S^2 \rangle$ values smaller than 0.2. With the unprojected DFT energy, there remains a shoulder at the PES position of possible 5, however this vanishes as soon as ZPE and temperature corrections are considered (Table 1). We note that the G2 method is unreliable in the present case since it depends on the compatibility of RMP and UMP methods and fails as soon as heavily projected MP (PMP) has to be applied because of large spin contamination.

MP2 and MP4 also fail to correctly predict the relative energies of TSs 2 and 4 and they exaggerate the exothermicity of the formation of 3. We conclude that apart from CCSD(T) (also QCISD(T) if used for the geometry optimization) and DFT, none of the other methods is able to correctly describe the rearrangement modes of 1.

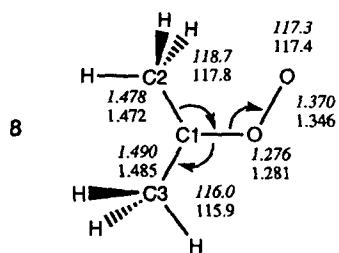
The energy of reaction (2) is -12 kcal/mol (Table 1) as can be derived from the calculated (1, $\Delta H_f^0 = 30.2$ kcal/mol [9]) and experimental heats of formation at 298 K (CHO, $\Delta H_f^0 = 8.9$ kcal/mol;

OH, $\Delta H_f^0 = 9.3$ kcal/mol [14,15]). The CCSD(T) value of $\Delta\Delta H_f^0(298)$ is -11.2 kcal/mol where the small deviation from the experimental value is probably due to some spin contamination for the OH and CHO doublet radicals that could not be eliminated.

Both CCSD(T) and DFT clearly indicate that the mechanism of path 2 (Scheme 1) is in so far wrong as it assumes the intermediate carbene 5, which does not exist. If an H shift from C to the terminal O occurs, decomposition of 1 to CHO and OH will be the immediate consequence. The enthalpy diagram of Fig. 2 clearly shows that formation of 3 (activation enthalpy: 17.7 kcal/mol) is clearly preferred over the decomposition reaction (2) (activation enthalpy: 30.8 kcal/mol), even if one considers the excess energy (54 kcal/mol, Fig. 2) of 1 in the ozonolysis

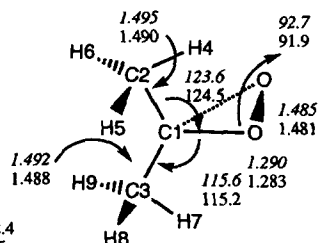


Scheme 2.

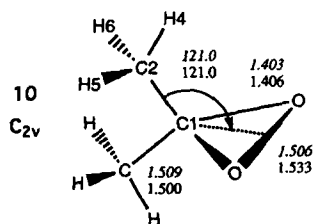


C2C1OO: 56.6; 53.6
 H4C2C1O: 2.2; 4.2
 H5C2C1O: -117.4; -115.0
 H6C2C1O: -234.7; -232.6

C3C1OO: -129.2; -132.4
 H7C3C1O: -29.8; -27.5
 H8C3C1O: 85.9; 88.5
 H9C3C1O: -154.8; -152.5



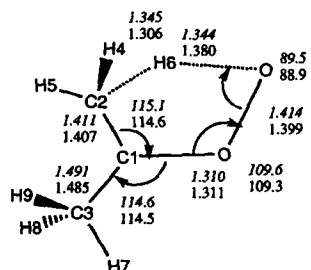
9, TS



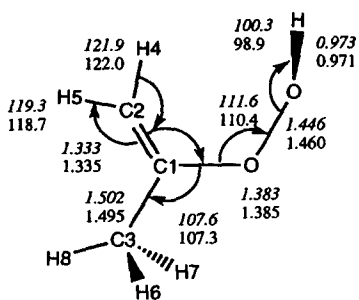
H4C2C1O: 0; 0
 H5C2C1O: -120.4; -120.3
 H6C2C1O: 120.4; 120.3

C2C1OO: -0.2; 1.0
 H4C2C1O: -64.4; 64.4
 H5C2C1O: -159.0; -158.4
 H6C2C1O: 19.1; 20.7

C3C1OO: -170.6; 171.5
 H7C3C1O: -5.6; -5.1
 H8C3C1O: -126.3; -125.4
 H9C3C1O: 115.8; 116.3

TS, 11
C₁

125.8
 126.0 HOOC1: 98.8; 102.9

12
C₁

H6C3C1O: 60.6; 60.7
 H7C3C1O: -58.5; -58.8
 H8C3C1O: 179.1; 179.2

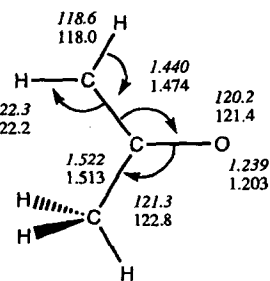
13
C_s

Table 2
 Energetics of the dimethyl carbonyl oxide (**8**) rearrangements according to path 1 or path 2 ^a

Method/basis set	Geometry	8	9 , TS	10	11 ,TS	12	13
<i>Absolute and relative energies</i>							
MP2/6-31G(d, p)	A	-267.47185	24.7	-33.3	15.7	-20.4	10.0
PMP2/6-31G(d, p)							3.3
DFT/6-31G(d, p)	C	-268.24586	22.5	-19.8	17.0	-13.6	9.5
<i>ZPE</i>							
MP2/6-31G(d, p)	A	52.5	51.9	53.1	50.5	52.4	47.8
DFT/6-31G(d, p)	C	52.8	52.0	53.4	50.6	53.1	47.7
$\Delta\Delta H_f^0(298)$							
MP2/6-31G(d, p)	A	0	23.8	-32.9	13.2	-20.3	0.3
DFT/6-31G(d, p)	C	0	21.4	-19.4	14.4	-13.1	6.4
Best		0	18.7 ^b	-20.6 ^b	13.6 ^b	-13.1	10.1 ^c
$\Delta H_f^0(298)$	C	-6.5	12.2	-27.1	7.1	-19.6	3.6 ^c

^a Absolute energies in hartree, relative energies in kcal/mol. A: MP2/6-31G(d, p) optimized; C: DFT/6-31G(d, p); ZPE scaling factors are 0.930 (A, B); 0.963 (C). $\Delta H_f^0(298)$ of **10** has been calculated with the DFT energy for the formal reaction: **10** + CH₄ → CH₃CH₂CH₃ + **1**, and the $\Delta H_f^0(298)$ from Refs. [9], [14], and [15].

^b Corrected according to DFT-CCSD(T) energy differences found for the corresponding reactions of **1** (Table 1).

^c According to known $\Delta H_f^0(298)$ values for **7b** and **13** (see Refs. [14] and [15]).

reaction. We estimate that $\leq 5\%$ of **1** will decompose to yield OH radicals. This is in line with experimental observations we have made previously for the gas phase ozonolysis of ethene [6].

3.1. Decomposition of dimethylcarbonyl oxide

Although **1** can be excluded as a source for a larger amount of OH radicals, we also investigated whether alkyl substituents can facilitate carbene formation and its subsequent decomposition into OH radicals. Cremer [11] showed by ab initio calculations that methyl groups in cis position to the terminal O atom stabilize **1** by attractive interactions between the methyl H atoms and the terminal O atom. These interactions could facilitate an H shift directly from the alkyl group, which both electronically and sterically should be preferred compared to the H shift for **1**. This is indicated in Scheme 2

where the isomerization of dimethylcarbonyl oxide **8** (formed in the ozonolysis of tetramethylethene, TME) via TS **9** to dioxirane **10** (path 1) is compared with a rearrangement (path 2) leading via TS **11** to intermediate **12**. The latter system is a closed shell molecule rather than a carbene or biradical because a formal biradical **12** can immediately stabilize in form of the 1-hydroperoxy-1-methyl ethene shown in Scheme 2. Decomposition of **12** leads to radical **13** and OH similar to the case of **5**.

In view of the usefulness of DFT in the case of **1**, we investigated **8** using DFT/6-31G(d, p) based on the B3LYP functional. In addition, MP2/6-31G(d, p) calculations were carried out to test whether conventional correlation theory predicts at least qualitatively the same changes in energy due to methyl substitution. The calculated geometries are summarised in Fig. 3 while the energetics of paths 1 and 2 (Scheme 2) are given in Fig. 4 and Table 2.

Fig. 3. Calculated geometries for **8**–**13**. Parameters are given in the order (top to bottom): DFT/6-31G(d, p) in italics, MP2/6-31G(d, p) in normal print. Bond lengths in Å and angles in deg.

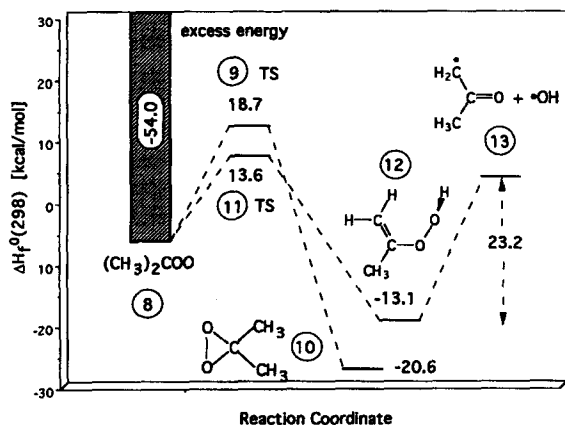


Fig. 4. Heats of formation $\Delta H_f^0(298)$ and reaction enthalpies $\Delta\Delta H_f^0(298)$ for reaction paths 1 and 2 in the case of dimethylcarbonyl oxide 8.

Isomerization of 8 to 10 is exothermic by -19.8 kcal/mol ($\Delta\Delta H_f^0 = -19.4$ kcal/mol, Table 2) involving an energy barrier of 22.5 kcal/mol ($\Delta\Delta H_f^0 = 21.4$ kcal/mol), which reflects the increased stability of 8. However, methyl substitution decreases the relative energy of TS 11 to 17.0 kcal/mol ($\Delta\Delta H_f^0 = 14.4$ kcal/mol), i.e. the barrier of path 2 is 30% lower than the barrier of path 1. The geometry of TS 11 (Fig. 3) reveals that its relatively low energy is a direct consequence of the formation of an aromatic 6-electron system [11] and the lower degree of distortion of the COO unit as compared to the situation in TS 4. Most of 8 should follow path 2 and form the hydroperoxy compound 12, which is about 13 kcal/mol more stable than 8 and about 6 kcal/mol less stable than dioxirane 10 (Table 2). The weakest bond in 12 is the OO bond and, in view of an excess energy of more than 50 kcal/mol, thermal decomposition will lead to radicals 13. The decomposition reaction is endothermic by about 19 kcal/mol ($\Delta\Delta H_f^0(298)$, Table 2).

Experiments carried out parallel to the ab initio investigation are in line with the ab initio results. Ozonolysis of TME leads to almost 50% OH generation measured with regard to the ozone concentration used in the reaction.

In conclusion, we note that the ozonolysis of alkyl-substituted alkenes leads to OH radicals as the decomposition products of carbonyl oxides. For ex-

ample, the ozonolysis of TME yields 50% of OH radicals, which is in line with the calculated energetics of decomposition path 2 shown in Scheme 2. These findings are of large importance for the chemistry of the atmosphere.

Acknowledgements

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