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Decomposition modes of dioxirane, methyldioxirane and dimethyldioxirane — a CCSD(T), MR-AQCC and DFT investigation

Dieter Cremer [a,*], Elfi Kraka [a], Peter G. Szalay [b]

[a] *Department of Theoretical Chemistry, University of Göteborg, Kemigården 3, S-41296, Göteborg, Sweden*
[b] *Department of Theoretical Chemistry, Eötvös Loránd –University, P.O. Box 32, H-1518, Budapest, Hungary*

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Abstract

Formation and decomposition of dioxirane (**2a**), methyldioxirane (**2b**) and dimethyldioxirane (**2c**) in the gas phase were investigated by carrying out CCSD(T), MR-AQCC and B3LYP calculations with the 6-31G(d, p), 6-311 + G(3df, 3pd) and cc-VTZ2P + f, d basis sets. The inclusion of f functions in the basis set was essential to determine the heat of formation $\Delta H_f^o(298)$ of carbonyl oxide (**1a**) and **2a** to be 27.0 and −0.3 kcal/mol, respectively. With the latter value, we calculate the same ring strain energy for cyclopropane, oxirane and **2a**. Molecule **2a** decomposes at 298 K with an activation enthalpy of 18 kcal/mol to methylenebis(oxy) (**3a**), which is calculated to be 1.2 kcal/mol less stable than **2a**, in contrast to previous investigations. Two methyl substituents increase the ring opening barrier to 23 kcal/mol and, thereby guarantee the kinetic stability of **2c**. The biradicals **3** decompose with barriers smaller than 4 kcal/mol to esters and therefore will be difficult to intercept in dioxirane decomposition reactions.

1. Introduction

Dioxiranes and their acyclic isomers carbonyl oxides play an important role in many oxidation processes [1–4]. The former are ~20 kcal/mol more stable than the latter [5] and, accordingly, it was possible to synthesize and investigate the parent dioxirane [6] and several substituted dioxiranes [1–3,7–9]. Both isomers are probably generated as decomposition products of primary ozonides in the ozonolysis of alkenes [1–5]. Furthermore, they are produced or supposed to be produced in carbene–oxygen reactions, the reactions of singlet oxygen with diazo compounds, alkyl radical–ozone reactions, the matrix photooxidation of oxygen–alkene mixtures and as intermediates in reactions of carbonyl compounds with atomic oxygen [1–4]. Curci et al. [10] postulated dioxiranes as oxidants in the caroate–ketone system and Murray and Jeyaraman [11] based their synthesis of dialkyldioxiranes on this system. Apart from this, dioxiranes may play a role in the chemistry of the polluted atmosphere [12,13] and in enzymatic processes [14].

Due to the importance of dioxiranes in many oxidation processes there is a large literature on these compounds covering different aspects of their

* Corresponding author. Fax: +46-31-7722933.

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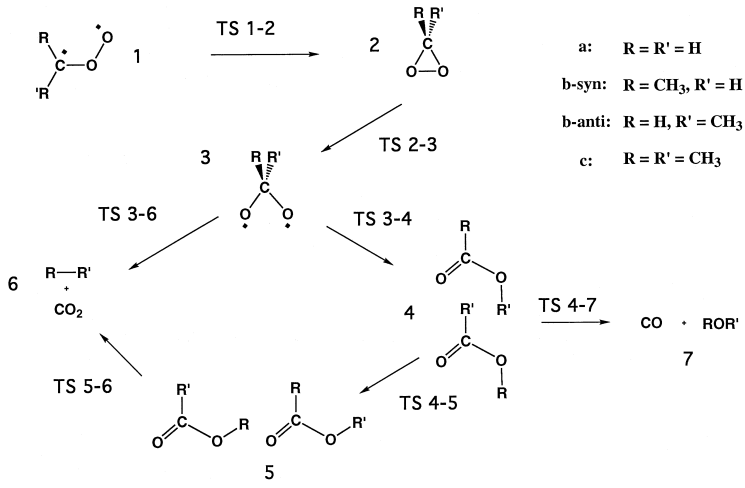


Scheme 1.

chemistry viewed both from the point of experimental and theoretical investigations [1–5]. In particular, quantum chemical investigations added much to the understanding of the properties of dioxiranes and their chemistry [5,9,15,16]. Nevertheless, it is still unclear why certain dioxiranes are stable, but others are not. Murray and Jeyaraman [11] succeeded in synthesizing dimethyldioxirane, which can be kept for several days at room temperature, while dioxirane itself has only been observed as a labile species in the gas-phase ozonolysis of ethene [6]. Mass spectrometry investigations have found that dioxirane decomposes to CO_2, H_2, CO and H_2O [4]. However, in matrix isolation experiments esters as dioxirane rearrangement products were observed rather than the decomposition products [1,7,9].

We will investigate in this Letter the rearrangement and decomposition modes of dioxirane and its methyl substituted derivatives. For this purpose, we investigate the rearrangement of carbonyl oxide (**1a**), syn- and anti-methylcarbonyl oxide (**1b**-syn and **1b**-anti) and dimethyl carbonyl oxide (**1c**) to the corresponding dioxiranes **2a**, **2b** and **2c**, respectively; ring opening of the latter to the methylenebis(oxy) biradicals **3a**, **3b** and **3c**; rearrangement of the biradicals **3** to formic acid or esters (**4a**, **4b** and **4c**); rotation of **4** to the less stable conformation **5**; decomposition of either **4** or **5** to $CO + R_2O$ (**7**; for **7a**, $R_2O = H_2O$) or $R_2 + CO_2$ (**6**; for **6a**, $R_2 = H_2$) where **6** may also be formed by direct decomposition of **3** (Scheme 1). Our investigation will be based on coupled cluster (CC), multi-reference averaged quadratic CC (MR-AQCC) and density functional theory (DFT) calculations. The primary goal of our work will be to explain the increase in stability when substituting dioxiranes by methyl (alkyl) groups and to predict which products can be expected when generating dioxiranes.

2. Computational methods

For the parent systems **1a** to **7a**, CCSD(T) (CCSD with perturbative inclusion of triple (T) excitations) [17] were carried out using Dunning's correlation corrected cc-VTZ2P + f, d basis, which is composed of a (10s 5p 2d)[4s 3p 2d] contraction augmented by a set of spherical f functions for the heavy atoms and a set of spherical d-functions for H atoms (α(C): 1.097, 0.318 (d), 0.761 (f); α(O): 2.314, 0.645 (d), 1.428 (f); α(H): 1.407, 0.388 (p), 1.057 (d)) [18] and has proven to lead to reliable results in the case of dioxiranes [15,16]. The ring opening of **2** to form **3** represents a multi-reference problem involving two configurations of the same symmetry. As a result, MR-AQCC [19] calculations were performed employing a 6-311 + G(3df, 3pd) basis set [20]. MR-AQCC is essentially a modified MR-CI procedure,

which contrary to MR-CI leads to nearly size-extensive results [21]. According to test calculations [22], potential energy surfaces obtained by MR-AQCC are parallel to those of full CI calculations and, therefore, MR-AQCC provides reliable energy differences.

The reference space for the MR-AQCC of **2**, TS**2-3** and **3** was carefully chosen to give a balanced description at all three geometries. The highest occupied MOs and the LUMO of **2** are

$$6a_1\text{–}\sigma(\mathrm{OO});\ 2b_1\text{–}\pi(\text{OO bond});$$

$$1a_2\text{–}\pi(\text{OO antibond, CO nonbond});\ 4b_2\text{–}\sigma*(\mathrm{OO}).$$

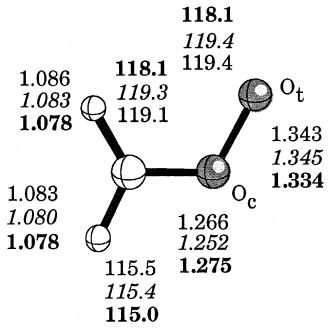
The ground state (GS) of **2** is defined by the electron configuration $\ldots (6a_1)^2 (2b_1)^2 (1a_2)^2$ ($^1A_1, 4\pi$). Ring opening to **3** formally involves a rotation of the two $2p\pi$ electron pairs at the O atoms into the ring plane so that both the $6a_1\text{–}\sigma(\mathrm{OO})$ and the $4b_2\text{–}\sigma*(\mathrm{OO})$ become doubly occupied and, consequently, σ-bonding between the O atoms is no longer possible. At the equilibrium OO distance of **3** (close to 2 Å) the two π MOs $1a_2$ and $2b_1$ are of comparable energy and, therefore, both the $\ldots (6a_1)^2 (1a_2)^2 (4b_2)^2$ and the $\ldots (6a_1)^2 (2b_1)^2 (4b_2)^2$ electron configuration contribute to the $^1A_1, 2\pi$ GS of **3**. The analysis of the ring opening process reveals that the $^1A_1, 2\pi$ of **3** corresponds to a low-lying excited state of dioxirane obtained by $2b_1 \rightarrow 4b_2$ or $1a_2 \rightarrow 4b_2$ double excitation and that the $^1A_1, 4\pi$ and $^1A_1, 2\pi$ state undergo an avoided crossing situation close to TS**2-3**. Hence, a consistent description of **2**, TS**2-3** and **3** requires the inclusion of orbitals $6a_1$, $2b_1$, $1a_2$ and $4b_2$ into the reference space, which in the present work was extended by adding the unoccupied orbitals $7a_1$ and $5b_2$ to have some more flexibility in the MR-AQCC calculations.

All possible excitations of the 6 active electrons among the 6 active orbitals were considered, thus leading to a 6×6 CAS (complete active space). After freezing the three core orbitals, all S and D excitations out of these reference functions were included in the wavefunction. The orbitals were optimized at the multiconfiguration SCF (MCSCF) level using the same 6×6 CAS wavefunction. For the 6-311 + G(3df, 3pd) basis set used, the dimension of the CI became larger than 10 million.

Since the extension of the CCSD(T) and MR-AQCC calculations to the methyl substituted systems **2b** and **2c** was not feasible because of computational limitations, we checked various methods as to whether they can provide a reasonable, but computationally much less expensive description of the reactions of Scheme 1. It turned out that density functional theory (DFT) with Becke's three-parameter functional B3LYP [23] provided the best description. DFT covers significant correlation effects in an unspecified way and has proven to be useful in the description of typical single-determinant problems but also some multi-reference problems, in which one configuration is still dominating the wavefunction. For biradicals such as **3**, unrestricted DFT (UDFT) can provide reasonable descriptions, in particular if the symmetry of the molecule is broken (broken symmetry UDFT) as was shown in the case of metal bonding for transition metal complexes [24]. Broken symmetry UDFT calculations of singlet biradicals lead to a mixing of singlet and triplet (and higher) state(s).

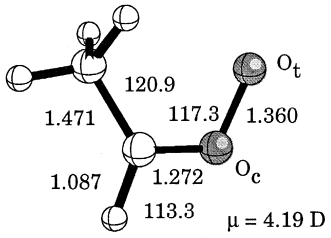
Mixing might be assessed by calculating the expectation value of the operator S^2 for the Kohn–Sham single determinant wavefunction. However, $\langle S^2 \rangle$ is of somewhat dubious value in DFT since the Kohn–Sham wavefunction corresponds to the unphysical situation of non-interacting electrons. Calculation of $\langle S^2 \rangle$ requires knowledge of the pair density, which is not known. Therefore, we refrained from improving the UDFT results by simple summation rules or spin-projection techniques applied for ab initio wavefunctions and instead based the direct use of the UDFT results on the fact that the electron density is less sensitive to spin contamination effects than the wavefunction. This was confirmed by the observation that the properties of **3** calculated at the UB3LYP level are in good agreement with MR-AQCC results.

Explorative B3LYP calculations were carried out with the 6-31G(d, p) basis set [25], while for the more accurate calculations Pople et al.'s 6-311 + G(3df, 3pd) basis [20] was used, which is slightly larger than the cc-VTZ2P + f, d basis of the CC calculations. For all molecules and transition states considered, B3LYP vibrational frequencies at the optimized geometries were determined to characterize the stationary points. Zero-point energy (ZPE)



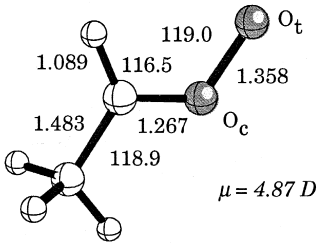
μ = 3.90 D
μ = *4.30 D*
μ = **3.74 D**

1a (C_s)



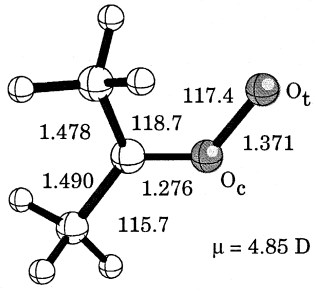
μ = 4.19 D

1b-syn (C_s)



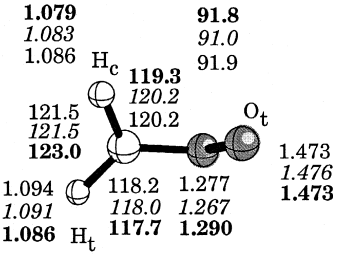
μ = 4.87 D

1b-anti (C_s)



μ = 4.85 D

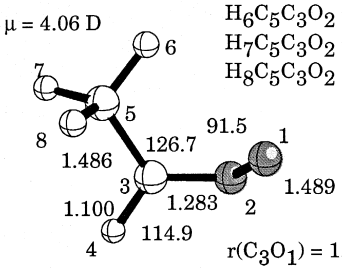
1c (C_s)



$r(CO_t)$= 1.982 *1.963* **1.988**
H_tCOO = -135.9 *-134.9* **-135.0**
H_cCOO = 48.0 *49.9* **48.9**

μ = 3.68 D *μ = 3.93 D* μ = **3.51 D**

TS1a (C_1)

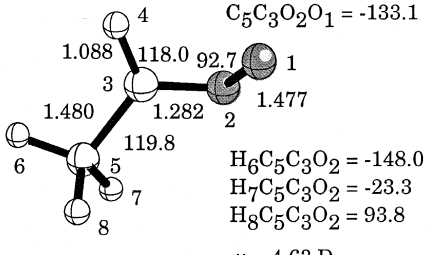


μ = 4.06 D
$H_6C_5C_3O_2$ = 1.9
$H_7C_5C_3O_2$ = 125.4
$H_8C_5C_3O_2$ = -117.8

$r(C_3O_1)$ = 1.991
$H_4C_3O_2O_1$ = -133.3
$C_5C_3O_2O_1$ = 56.5

TS 1-2 b-syn (C_1)

TS 1-2 b-anti (C_1)

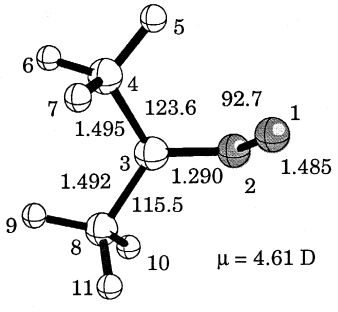


$r(C_3O_1)$ = 2.000
$H_4C_3O_2O_1$ = 47.7
$C_5C_3O_2O_1$ = -133.1

$H_6C_5C_3O_2$ = -148.0
$H_7C_5C_3O_2$ = -23.3
$H_8C_5C_3O_2$ = 93.8

μ = 4.63 D

$r(C_3O_1)$ = 2.012
$C_4C_3O_2O_1$ = 56.6
$C_8C_3O_2O_1$ = -129.3
$H_5C_4C_3O_2$ = 1.5



μ = 4.61 D

$H_6C_4C_3O_2$ = 124.5
$H_7C_4C_3O_2$ = -118.1
$H_9C_8C_3O_2$ = -154.8
$H_{10}C_8C_3O_2$ = -29.8
$H_{11}C_8C_3O_2$ = 85.9

TS 1-2 c (C_1)

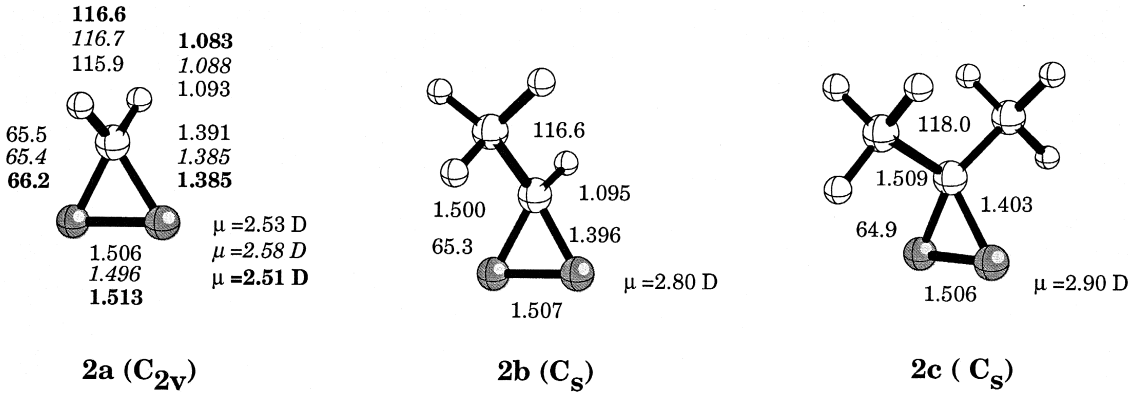


Fig. 1. Geometries of **1**, TS**1-2** and **2** (see Scheme 1). Distances in Å, angles in degree, dipole moments μ in debye. Numbers in normal print refer to B3LYP/6-31G(d, p) results, numbers in italics to B3LYP/6-311 + G(3df, 3dp) results and numbers in bold to CCSD(T)/[4s 3p 2d 1f / 3s 2p 1d] results. Black balls denote the positions of O atoms, large white balls those of C atoms and small white balls those of H atoms.

and thermal corrections were used to obtain reaction and activation enthalpies at 298 K. Utilizing experimental heats of formation $\Delta H_f^o(298)$ for suitable reference compounds [26,27], heats of formation for all molecules shown in Scheme 1 were determined. Calculations were carried out with COLOGNE96 [28], ACES II [29], COLUMBUS [30] and GAUSSIAN94 [31].

3. Results and discussion

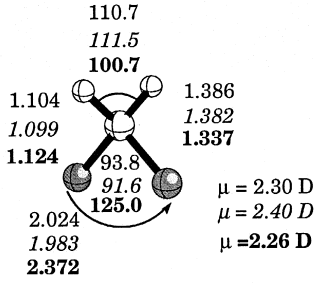
Calculated geometries are shown in Figs. 1–3, while the corresponding energies, ZPE values, reaction (activation) enthalpies $\Delta\Delta H_f^o(298)$ and heats of formation $\Delta H_f^o(298)$ are listed in Table 1 (parent system) and Table 2 (methyl substituted systems). Details of the MR-AQCC calculations are given in Table 3. In Table 4, methyl stabilization effects are compared.

Heats of formation $\Delta H_f^o(298)$ were calculated using the experimental value of **4a** (−90.6 kcal/mol [27]) as a suitable reference and comparing with the experimental values for $CO_2 + H_2$ (−94.1 kcal/mol [27]) and $CO + H_2O$ (−84.2 kcal/mol [27]). Deviations were smallest for the CCSD(T)/MR-AQCC values (0.1 and 1.9 kcal/mol, Table 1) so that the following discussion is based, if not otherwise noted, on differences in enthalpies, $\Delta\Delta H_f^o(298)$ calculated at the CC level of theory. However, B3LYP results differ from the CC results on average just by 2.3 kcal/mol (6-31G(d, p)) and 1.7 kcal/mol (6-311 + G(3df, 2pd), respectively, which is comparable to the magnitude of the vibrational corrections.

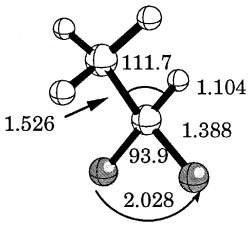
3.1. Formation and decomposition of dioxirane

CCSD(T) calculations predict dioxirane **2a** to be 27.3 kcal/mol more stable than carbonyl oxide **1a** ($\Delta\Delta H_f^o(298)$, Table 1), which is 3 kcal/mol higher than predicted by the best CCSD(T) calculation carried out previously [5]. Recently, it was shown that the geometry of **2a**, in particular the OO bond length, can only be calculated accurately when CCSD(T) calculations are carried out with a TZ2P basis set that includes f-type polarization functions [15,16]. The necessity of f-functions for predicting the correct geometry is confirmed by our calculations (Fig. 1) and, in addition, it turns out to be relevant when determining the stability of **2a**. Therefore, we recalculated the $\Delta H_f^o(298)$ of **1a** and **2a** with the help of the CCSD(T) $\Delta\Delta H_f^o(298)$ between **1** (**2**) and **4** (Table 1). The values thus obtained ($\Delta H_f^o(298)$ = 27.0 and −0.3 kcal/mol, Table 1) are 3 and 6.3 kcal/mol below the best previous values (30.2 and 6.0 kcal/mol [5]), which clearly demonstrates the necessity of using f-type polarization functions.

The revised values describe the dioxirane ring as having the same conventional strain energy (CSE) −26.4 kcal/mol (obtained from the homodesmotic

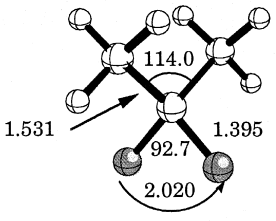


TS 2-3a (C_{2v})



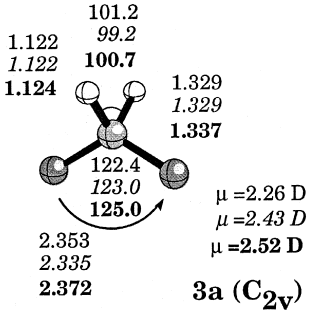
μ = 2.59 D

TS 2-3b (C_s)

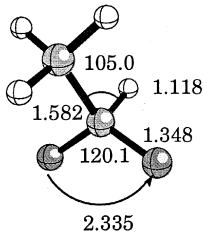


μ = 2.62 D

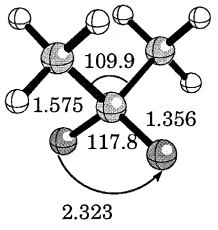
TS 2-3c (C_s)



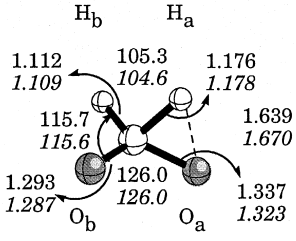
3a (C_{2v})



3b (C_s) μ =2.67 D



3c (C_{2v}) μ =2.76 D

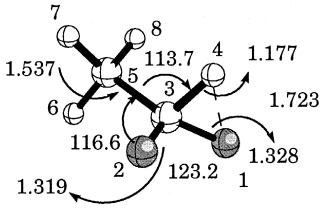


$O_aCO_bH_a$ = 87.9, *98.1*

$O_aCO_bH_b$ = -158.3, *-158.6*

μ = 2.19D

TS 3-4a (C_1)



$O_1C_3O_2H_4$ = 86.2

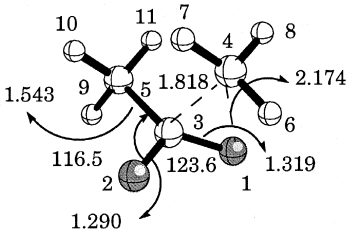
$H_6C_5C_3O_1$= 79.7

μ = 2.51D $H_8C_5C_3O_1$= -38.8

$O_1C_3O_2C_5$ = -157.0

$H_7C_5C_3O_1$= -161.9

TS 3-4b-H (C_1)



$O_1C_3O_2C_4$ = 89.3

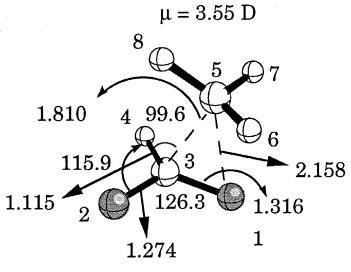
$O_1C_3O_2C_8$ = -156.7

$H_{6,7,8}C_4C_3O_1$ = -66.0; 175.4; 56.4

$H_{9,10,11}C_5C_3O_1$ = 79.9; -162.2; -38.5

μ = 3.34D

TS 3-4c (C_1)



μ = 3.55 D

$O_1C_3O_2C_5$ = 93.7

$O_1C_3O_2H_4$ = -159.2

$H_6C_5C_3O_1$= -60.6

$H_7C_5C_3O_1$= 57.2

$H_8C_5C_3O_1$= 176.6

TS 3-4b-Me (C_1)

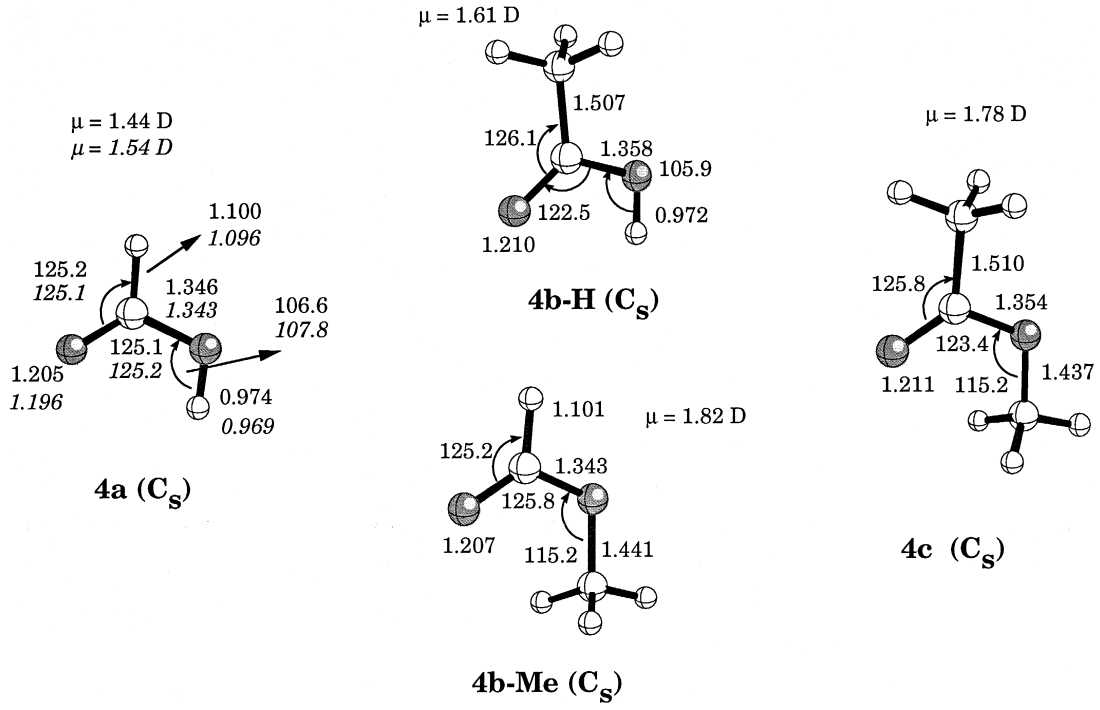


Fig. 2. Geometries of TS**2-3**, **3**, TS**3-4** and **4** (see Scheme 1). See caption of Fig. 1.

reaction: $\mathbf{2} + HOOH + 2CH_3OH \rightarrow HOCH_2OH + 2CH_3OOH$ and $\Delta H_f^o(298)$ values of -0.3, -32.6, -48.0, -93.5 and -30.9 kcal/mol [26,27]) as cyclopropane (-26.5 kcal/mol [32,33]) or oxirane (-27.6 kcal/mol [32,33]). Since cyclotrioxolane possesses a higher CSE (33 kcal/mol [31]), it is reasonable to assume that special electronic effects balance the strain of the three cyclic molecules cyclopropane, oxirane and **2a** and that the CH bonds in the cyclic molecule take over one of these balancing functions. In related work, we found that the adiabatic CH bond stretching frequencies and force constants [35], which provide a reliable measure for the CH bond strength, decrease in the order cyclopropane, oxirane, **2a**, which is parallel to the enhanced possibility of anomeric delocalization of the O lone pair electrons into the σ^*(CH) orbitals and the larger electron withdrawing ability of the C atom in **2a** relative to that of the C atoms in oxirane or cyclopropane.

The CCSD(T) activation enthalpy for isomerization of **1a** is 19 kcal/mol (Table 1) in agreement with earlier results [5]. Once **2a** is formed in the reaction **1a** → **2a**, it possesses 46.3 kcal/mol of excess enthalpy, which is sufficient to break the OO bond (OO bond length in TS**2-3a**: 2 Å, Fig. 2) and to open **2a** to the biradical **3a** since the activation enthalpy for this process is just 18 kcal/mol at the MR-AQCC level of theory. UB3LYP predicts values between 19.6 and 21.7 kcal/mol, which is surprisingly good in view of the fact that the wavefunction for both the TS**2-3** and the biradical **3a** are dominated by two configurations, one corresponding to the $^1A_1, 4\pi$ and one to the (with regard to **2a** doubly (D) excited) $^1A_1, 2\pi$ state as shown in Table 3. UB3LYP includes the D excited configuration at the price of a triplet contamination. It seems that contrary to an orbital-based method a density-based method is less sensitive to the triplet contamination, which indicates that it is not justified to use in this case an orbital-based method such as spin-projection to get a non-contaminated state. B3LYP describes both isomerization to and opening of **2a** with reasonable accuracy, which is sufficient to investigate the

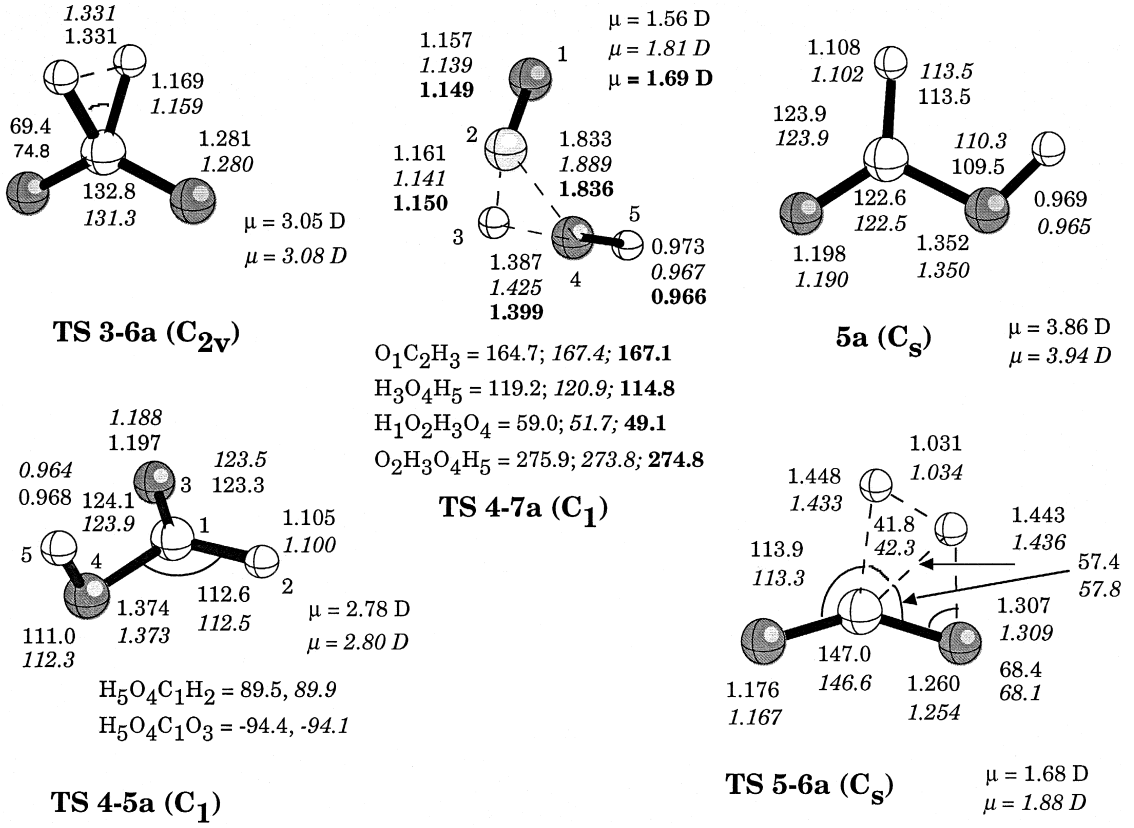


Fig. 3. Geometries of TS**3-6**, TS**4-5**, TS**4-7**, TS**5-6** and **5** (see Scheme 1). See caption of Fig. 1.

corresponding processes of the methyl substituted molecules.

In view of the magnitude of the calculated ring opening barrier, there is little chance to isolate **2a** at room temperature in the gas phase. Even in the solution phase where there is the possibility of energy dissipation, a barrier of 18 kcal/mol is too small to guarantee kinetic stability under normal conditions, which explains why **2a** could only be observed at low temperatures [6].

3.2. Decomposition of methylenebis(oxy)

The biradical **3a** is just 1.2 ($\Delta\Delta H_f^o(298)$, MR-AQCC) to 3.2 (B3LYP) kcal/mol less stable than **2a**. We note that most previous calculations underestimated the stability of **3a**, suggesting relative energies 11–12 kcal/mol [4,36,37]. However in view of the electronic structures of **2a** and **3a**, it is more likely that both molecules possess comparable stabilities ($\Delta H_f^o(298)$ for **3a**: 0.9; for **2a**: −0.3 kcal/mol, Table 1). Ring opening is accompanied by a strengthening of the CO bonds (shortening from 1.385 to 1.329 Å) and the loss of a weak OO bond (lengthening from 1.51 to 2.34 Å, Figs. 1 and 2). The dipole moments of the two molecules are 2.5 D (**2a**) and 2.4 D (**3a**), which means that formation of **3a** should have little dependence on the dielectric constant of the environment.

The reactions of the biradical **3a** should proceed rapidly via TS**3-4** (H-migration) or TS**3-6** (fragmentation into $H_2 + CO_2$), since the CCSD(T) activation enthalpies for these processes are just 1.8 and 2.4 kcal/mol (Table 1), i.e. even at low temperatures there is little chance of ever detecting the singlet biradical **3a** experimentally. Both formic acid **4a** and $CO_2 + H_2$ (**6a**) are more than 90 kcal/mol (Table 1) below **3a** so that the back formation of the biradical

Table 1
Energetics of dioxirane formation and decomposition according to the mechanism of Scheme 1[a]

Quantity	Method/basis set	**1**	TS**1-2**	**2**	TS**2-3**	**3**	TS**3-4**	**4**[c]	TS**4-5**	TS**4-7**	**5**	TS**5-6**	**6**	TS**3-6**	**7**
Energy	with regard to structure ***n***		**1**	**1**	**2**	**2**	**3**	**2**	**4**	**4**	**4**	**5**	**5**	**3**	**4**
Energy	B3LYP/6-31G(d,p)	−189.57992	21.5	−24.1	23.2	6.3	3.9	−90.3	14.1	73.5	5.1	68.6	−3.4	4.6	20.7
	B3LYP/ 6-311+G(3df,3pd)	−189.65736	21.8	−21.9	21.9	5.1	3.1	−93.7	12.9	69.5	4.0	68.8	−3.3	2.2	12.8
	CCSD(T)/ [4s3p2d1f/ 3s2p1d]	−189.35431	20.1	−28.0	20.3[b]	4.6[b]	2.8	−91.1	13.0	73.9	4.5	71.3	−2.3	4.3	11.3
ZPE	B3LYP/6-31G(d,p)	19.6	18.7	20.4	19.0	17.1	16.1	21.3	20.0	16.5	21.1	15.1	13.7	14.9	16.6
	B3LYP/ 6-311+G(3df,3pd)	19.6	18.6	20.4	18.1	16.8	15.8	21.2	19.9	16.3	20.9	15.0	13.7	14.8	16.5
$\Delta\Delta H_f^o(298)$	B3LYP/6-31G(d,p)	0	20.4	−23.4	21.7	3.2	2.8	−89.3	12.8	69.0	4.9	62.7	−9.1	2.3	17.8
	B3LYP/ 6-311+G(3df,3pd)	0	20.7	−21.2	19.6	1.7	2.1	−92.9	11.5	65.2	3.8	62.9	−8.8	0.2	10.0
	CCSD(T)/ [4s3p2d1f/ 3s2p1d]	0	19.0	−27.3	18.0[b]	1.2[b]	1.8	−90.3	11.6	69.6	4.3	5.3	−7.9	2.4	8.5
$\Delta H_f^o(298)$	CCSD(T)/ [4s3p2d1f/ 3s2p1d]	27.0	46.0	−0.3	17.7[b]	0.9[b]	2.7	−90.6 (−90.6∗)	−79.0	−21.0	−86.3	−21.0	−94.2 (−94.1∗)	8.0	−82.1 (−84.2∗)

[a]Absolute energies in hartree, relative energies in kcal/mol. Heats of reaction $\Delta\Delta H_f^o(298)$ (kcal/mol) obtained from reaction energies, zero-point energies (ZPEs unscaled) and temperature corrections. CC geometries were obtained for **1**, TS**1-2**, and **2** while in all other cases B3LYP/6-311+G(3df,3pd) geometries were used. CC enthalpies were obtained with B3LYP/6-311+G(3df,3pd) ZPEs and temperature corrections. For the calculation of $\Delta H_f^o(298)$ values, see text. ∗ Values from experiment [26,27].
[b]MR-AQCC/6-311+G(3df,3pd) results (see also Table 3).
[c]The B3LYP and CCSD(T) energies of **4** are −189.76222 (6-31G(d,p)), −189.84163 (6-311+G(3df,3pd)), and −189.54402 hartree ([4s3p2d1f/3s2p1d]), respectively.

Table 2
Energetics of methyldioxirane (**2b**) and dimethyldioxirane (**2c**) formation and decomposition (Scheme 1)[a]

Quantity	Method/ basis set	Molecule	**1**	TS**1-2**	**2**	TS**2-3**	**3**	TS**3-4**	**4**
Energy	with regard to structure ***n***			**1**	**1**	**2**	**2**	**3**	**2**
Energy	B3LYP/ 6-31G(d, p)	**b:** Me, syn	−228.91609	25.0	−21.0	23.6	11.2	2.7 (H)	−89.0
		b: Me, anti	−228.91120	18.1	−24.1	23.6	11.2	4.3 (Me)	−74.5
		c: Me;Me	−268.24593	22.6	−19.8	25.0	14.7	3.8	−74.8
ZPE	B3LYP/ 6-31G(d, p)	**b:** Me, syn	37.4	36.5	38.1	36.8	35.6	33.8 (H)	38.9
		b: Me, anti	37.3	36.2				35.4 (Me)	39.0
		c: Me;Me	54.9	53.9	55.4	53.4	53.5	53.1 (Me)	56.4
$\Delta\Delta H_f^o(298)$	B3LYP/ 6-31G(d, p)	**b:** Me, syn	0	23.8	−20.5	22.2	9.0	1.0 (H)	−88.0
		b: Me, anti	0	16.9	−23.6			4.0 (Me)	−73.3
		c: Me;Me	0	21.4	−19.5	23.1	13.1	3.2 (Me)	−73.5
$\Delta\Delta H_f^o(298)$	Best	**b:** Me, syn	0	22.4	−24.4	22.2	7.0	1.0	−88.0
		b: Me, anti	0	15.5	−27.4			4.0	−73.3
		c: Me;Me	0	20.0	−23.4	23.1	11.1	3.2	−73.5
$\Delta H_f^o(298)$		**b:** Me, syn	10.6	33.0	−13.8	8.4	6.8	−5.8	−101.8 (−103.3∗)
		b: Me, anti	13.6	29.1				−2.8	−87.1 (−85.0∗)
		c: Me;Me	−1.9	18.1	−25.3	−2.2	−14.2	−11.0	−98.8 (−98.5∗)

[a]Absolute energies in hartree, relative energies in kcal/mol. Heats of reaction $\Delta\Delta H_f^o(298)$ (kcal/mol) obtained from reaction energies, zero-point energies (ZPEs unscaled) and temperature corrections. Best values are obtained by using CC corrections for **1**, TS**1-2**, **2**, and **3** from Table 1. $\Delta H_f^o(298)$ values are obtained as described in the text. Experimental $\Delta H_f^o(298)$ (values with ∗) from Ref. [26,27]. For TS**3-4** the migrating group is indicated in parentheses.

is impossible. On the other hand, the excess energy of **4** in the gas phase is more than sufficient for an internal rotation of **4a** into the H—O—C=O anti form **5a** (activation enthalpy 11.6 kcal/mol, Table 1) and subsequent decomposition into **6a** (activation enthalpy 65.3 kcal/mol, Table 1). Alternatively, **4a** can directly decompose to $CO + H_2O$ (**7a**, Scheme 1) via TS**4-7** since the corresponding activation enthalpy (70 kcal/mol, Table 1) is lower than the value of 76.9 kcal/mol needed for decomposition of **4a** via TS**4-5a** and TS**5-6a** into **6**. Both CO_2, H_2, CO and H_2O were found in the gas-phase ozonolysis of ethene [5], which should proceed via intermediate carbonyl oxide to these products following the mechanism sketched in Scheme 1. On the basis of our calculations we can conclude that biradical **3a** is kinetically highly unstable and even more difficult to detect than its two isomers **2a** and **1a**. On the other hand, it is a fact that **2** is significantly stabilized by methyl groups and therefore, we have to investigate in the following whether this is also true for **3**.

3.3. Methyl substituted carbonyl oxides, dioxiranes and methylenebis(oxy) biradicals

All energy and enthalpy data for the methyl substituted systems are based on B3LYP/6-31G(d, p) calculations (Table 2), which were in some cases improved by CCSD(T) corrections found for the parent system (Table 1). Heats of formation $\Delta H_f^o(298)$ for **1b** and **1c** were derived from formal reactions (1) and (2) (see below) and the $\Delta H_f^o(298)$ value for **1a** (see Table 1). For all other molecules, $\Delta H_f^o(298)$ was derived from the best $\Delta\Delta H_f^o(298)$ values of Table 2 using the $\Delta H_f^o(298)$ of **1** as a reference. Comparison with the experimental $\Delta H_f^o(298)$ of **4** (starred values in Table 2) suggests errors of calculated $\Delta H_f^o(298)$ values lower than 2 kcal/mol.

Methyl group stabilization effects can be measured by the formal reactions

$$H - X - H + CH_3CH_3 \rightarrow CH_3 - X - H + CH_4\,, \quad (1)$$

$$H - X - CH_3 + CH_3CH_3 \rightarrow CH_3 - X - CH_3 + CH_4\,, \quad (2)$$

where X = COO. The largest stabilization is found for **1c** (−22.9 kcal/mol, Table 4) since the effect of a syn-positioned Me group leads to 13 kcal/mol of a second Me group to 10 kcal/mol, where both hyperconjugative and inductive stabilization of the COO group play a role. As a result of additional stabilizing through-space interactions between the CH_3 group and the terminal O atom, syn-**1b** is more stable than anti-**1b** by 3 kcal/mol as was already pointed out in early investigations on carbonyl oxides by Cremer [34,38]. This is also the reason why syn-**1b** has a higher isomerization barrier (22.4 kcal/mol, Table 2) than **1a** while anti-**1b** has a lower one (15.5 kcal/mol) and that of **1c** (20 kcal/mol, Table 2) is comparable to **1a**. From **1** to **4**, the stabilization effect of two methyl groups decreases from 22.9 (**1**) to 3.2 kcal/mol (**4**, Table 4) because the role of the substituents changes. For **2c**, steric repulsion between the Me groups leads to a widening of the external ring angle (HCH (**2a**): 115.9; HCC(**2b**): 116.6; CCC(**2c**): 118.0°, Fig. 1) and, thereby, to a slight decrease of the internal OCO angle and a stiffening of the OO bond. These effects are also found for TS**2-3** and biradicals **3** and are the reason for an increase in the ring-opening barrier (TS**2-3b**: 22.2, TS**2-3c**: 23.1 kcal/mol, Table 2) and a lower stability of the methyl substituted biradicals **3** (**3b**: 7.0, **3c**: 11.1 kcal/mol above **2**, Table 2).

Formation of biradical **3** requires an opening of the OCO angle to keep the pair–pair repulsion between the in-plane electron lone pairs at the O atoms

Table 3
MR-AQCC/6-311 + G(3df, 3pd) results obtained from a 6 × 6 CAS reference[a]

Molecule	MCSCF	MR-AQCC	Main configuration	c_1	Second configuration	c_2
2a	−188.736406	−189.337355	$\ldots (6a_1)^2 (2b_1)^2 (1a_2)^2$	0.908	$\ldots (2b_1)^2 (1a_2)^2 (4b_2)^2$	−0.165
TS**2-3a**	−188.767303	−189.304992	$\ldots (6a_1)^2 (2b_1)^2 (1a_2)^2$	0.843	$\ldots (2b_1)^2 (1a_2)^2 (4b_2)^2$	−0.378
3a	−188.725062	−189.330069	$\ldots (6a_1)^2 (1a_2)^2 (4b_2)^2$	0.790	$\ldots (6a_1)^2 (2b_1)^2 (4b_2)^2$	0.436

[a] Energies in hartree. For the notation of the MOs see text. The coefficients of the MR-AQCC expansion are denoted as c_1 and c_2.

Table 4
Stabilization by methyl groups as determined by reactions (1) and (2)[a]

Structure	Reaction (1)	Reaction (2)	Sum
1	−13.5 (−10.4)	−9.5	−22.9
TS**1-2**	−10.0 (−13.8)	−11.9	−21.9
2	−10.4	−8.3	−18.7
TS**2-3**	−10.0	−7.8	−17.8
3	−5.5	−4.7	−10.2
TS**3-4**	−6.7	−3.7	−10.4
4	−9.1	5.9	−3.2

[a] B3LYP/6-31G(d,p) values in kcal/mol referring to the syn forms if two forms are possible. Values in parentheses: stabilization energy for anti form. Energies for methane and ethane are: −40.52401 and −79.83874 hartree, respectively. B3LYP/6-311 + G(3df, 3pd) values change slightly as, e.g. for **1**: −14.1, −10.2, −24.3 kcal/mol.

small. However, OCO widening implies a reduction of the external angle (HCH(**2a**): 116.7; HCH(**3a**): 111.5°, Figs. 1 and 2), which is hindered if steric repulsion between the substituents becomes larger. Kinetic stability of a compound at room temperature requires that all activation enthalpies for decomposition or rearrangement reactions are higher than 21 kcal/mol, which means that dioxirane **2c** is kinetically stable at room temperature since the two methyl groups lock the OO atoms in a bond. This effect should be more pronounced with the increasing steric bulk of the substituents, as was verified by the fact that bismesityldioxirane forms stable crystals at room temperature [9].

Biradicals **3** decompose via H or Me group migration (ester rearrangement), where the former process is considerably faster as is suggested by the activation enthalpies calculated for H and Me migration in **3b** (1 vs. 4 kcal/mol, Table 2). The decomposition of **3b** or **3c** via TS**3-6** is a high-energy process, which we did not study further since it cannot compete with the ester rearrangement. It is interesting to note that Me group migration leads to an increase of the dipole moment from 2.7 to 3.5 D (Fig. 2), which suggests that the ester rearrangement is slightly favoured in solvents with large dielectric constants.

In conclusion, we state that dialkyl substituted dioxiranes can be synthesized in solution because of their increased kinetic stability (activation enthalpies > 21 kcal/mol) caused by the OO locking effect of the substituents. The parent compound is kinetically unstable at room temperature (activation enthalpy 18 kcal/mol) and opens to biradical **3a**, which rearranges with rather low barriers to formic acid, $CO_2 + H_2$, and $CO + H_2O$. For the alkyl substituted biradicals **3**, ester rearrangement is the preferred decomposition mode, which proceeds with barriers lower than 4 kcal/mol. Accordingly, there is little chance to intercept biradical **3** in the decomposition reaction of **2**. Of the three R_2CO_2 isomers considered in this work, dioxiranes are the only ones which can be both thermodynamically and kinetically stable and, therefore, intercepted experimentally. The improved $\Delta H_f^o(298)$ values for **2** obtained in this work reveal that the dioxirane ring is less strained than previously thought.

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