

A CCSD(T) investigation of carbonyl oxide and dioxirane. Equilibrium geometries, dipole moments, infrared spectra, heats of formation and isomerization energies

Dieter Cremer^a, Jürgen Gauss^b, Elfi Kraka^a

^a Department of Theoretical Chemistry, University of Göteborg, Kemigården 3, S-41296 Göteborg, Sweden

^b Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe, W-7500 Karlsruhe, Germany

John F. Stanton and Rodney J. Bartlett

Quantum Theory Project, Department of Chemistry and Physics, University of Florida, Gainesville, FL 32611, USA

Received 5 May 1993; in final form 19 May 1993

A CCSD and CCSD(T) investigation of carbonyl oxide (**1**) and its cyclic isomer dioxirane (**2**) has been carried out employing DZ+P and TZ+2P basis sets. Calculated geometries, charge distributions, and dipole moments suggest that **1** possesses more zwitterionic character (CCSD(T) dipole moment 4 D) than has been predicted. **1** can be distinguished from **2** by its infrared spectrum as indicated by CCSD(T) frequencies, intensities, and isotopic shifts. The heats of formation $\Delta H_f^\circ(298)$ for **1** and **2** are 30.2 and 6.0 kcal/mol, respectively; the CCSD(T) barrier to isomerization from **1** to **2** is 19.2 kcal/mol. Decomposition of **1** and **2** can lead to CO, CO₂, H₂O, H₂ but not to free CH₂, O₂ or O. Both isomers should be powerful epoxidation agents in the presence of alkenes, but they should differ in their ability to form cyclopropanes with alkenes.

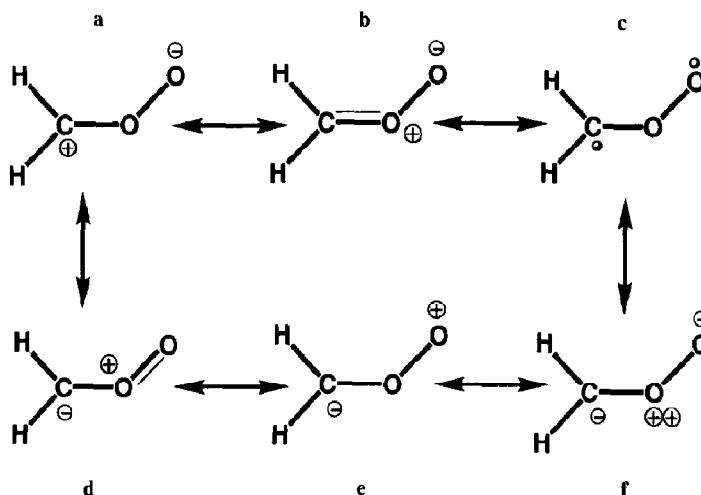
1. Introduction

Carbonyl oxide, CH₂OO (**1**), and its cyclic isomer dioxirane (**2**) are key compounds in many oxidation processes that can take place in organic syntheses, [1,2], the polluted atmosphere [3], or in biogenic media [4]. The importance of **1** and **2** is well reflected by the six review articles that have been written on carbonyl oxides and dioxiranes during the last five years [5–10]. Both substituted carbonyl oxides and substituted dioxiranes have been isolated and characterized by sophisticated spectroscopic methods^{#1}. Also, the parent compound **2** has been found in the gas phase ozonolysis of ethylene and investigated by microwave spectroscopy [11]. However, all experimental attempts to detect **1** either in the gas phase or in solution phases have been unsuccessful. Therefore, **1** is probably one of the most discussed compounds that is still awaiting detection.

Synthetic chemists prefer to view **1** as 1,3 dipolar

compound or zwitterion as shown in scheme 1 (forms **1a** and **1b**) [1,2]. Theoreticians, however, tend to describe **1** as a biradical, that attains zwitterionic character only by substitution and/or environmental effects [12–21]. Both descriptions are really speculative since experimental evidence on the nature of **1** is completely based on carbonyl oxides with conjugated π systems [5,6] and high accuracy calculations for **1** have not been done so far. We report here for the first time an extensive coupled cluster (CC) investigation of **1** and **2** that reveals that the electronic nature of **1** possesses more zwitterionic character than expected on the basis of previous calculations. In addition, we provide data such as energies, geometries, dipole moments, harmonic frequencies, infrared (IR) intensities, and isotopic shifts that should facilitate the detection of **1** and **2** in reaction mixtures. Finally, we discuss the energetics of chemical processes involving either **1** or **2** concentrating in particular on the rearrangement **1**→**2** via transition state (TS) **3** and possible decomposition modes of the two isomers.

^{#1} See references cited in refs. [5–9].



Scheme 1. Resonance formulas of carbonyl oxide (1).

2. Computational methods

Both many-body perturbation theory (MBPT) and coupled-cluster theory (CC) have been employed to investigate **1**, **2**, and **3**. Since MBPT calculations up to fourth order (MBPT(4)) have been carried out before [15,19] with rather inconclusive results (see below), we have used second-order MBPT (MBPT(2)) just to get reasonable starting geometries for CCSD (CC with all single and double excitations) [22] and CCSD(T) (CCSD with a perturbative treatment of triple excitations) [23] calculations. 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 proven to lead to reasonable results in cases with some multireference character [24] such as ozone, O_3 , and compound **1**.

All calculations at the CC level of theory have been carried out with Dunning's [25] (9s5p1d/4s1p) [4s2p1d/2s1p] (DZ+P) and (11s6p3d/5s3p) [5s3p2d/3s2p] (TZ+2P) basis set augmented with polarization functions optimized at the correlated level for some prototype molecules^{#2}. Geometries and frequencies have been determined using analytical energy gradients at the CCSD and CCSD(T)

level of theory^{#3}. Calculations have been performed with the ACES II program [29], which has been especially designed for large scale correlated energy and energy gradient calculations using CC/MBPT methods. For **1**, we have also carried out some lower-level calculations using Hartree-Fock (HF), MBPT(n) ($n=2, 3, 4$), quadratic CISD (QCISD) and QCISD(T)^{#4} methods in combination with Pople's 6-31G(d, p) [33] basis set. Results of these calculations have been used for reasons of comparison.

3. Results and discussion

Calculated energies, geometries, and dipole moments are listed in table 1. In fig. 1, final geometries obtained at the CCSD(T)/TZ+2P level are shown together with some notations used in this work. Tables 2 and 3 summarize calculated harmonic frequencies, IR intensities, and isotopic shifts for **1** and **2**. Finally, in table 4 and fig. 2 relevant data for the energetics of reactions involving **1** or **2** are shown.

^{#3} For CCSD, see ref. [27], for CCSD(T), see ref. [28].

^{#4} For QCISD and QCISD(T), see ref. [30]. For analytical gradients for QCISD, see ref. [31]. For analytical gradients for QCISD(T), see ref. [32].

^{#2} For the polarization exponents, see ref. [26].

Table 1

Calculated energies, geometries, and dipole moments of carbonyl oxide (1), the transition state 3 and dioxirane (2)^{a)}

Method	Energy	R(OO)	R(CO)	R(CH _c)	R(CH _t)	COO	H _c CO	H _t CO	μ		
carbonyl oxide, CH ₂ OO (1)											
HF/6-31G(d, p)	-188.56252	1.482	1.201	1.079	1.080	114.5	119.7	118.5	5.46		
MBPT(2)/6-31G(d, p)	-189.06865	1.293	1.297	1.078	1.074	120.4	118.3	114.1	3.34		
MBPT(3)/6-31G(d, p)	-189.06918	1.338	1.252	1.078	1.076	118.7	118.8	115.8	4.44		
SDQ-MBPT(4)/6-31G(d, p)	-189.08658	1.329	1.274	1.086	1.083	119.2	118.6	115.3	4.04		
SDTQ-MBPT(4)/6-31G(d, p)	-189.10975	1.306	1.314	1.081	1.077	119.8	118.3	114.3	3.25		
CCD/6-31G(d, p)	-189.07370	1.344	1.254	1.080	1.078	118.6	118.8	115.9	4.47		
QCISD/6-31G(d, p)	-189.09689	1.369	1.281	1.078	1.078	116.4	118.7	115.4	3.97		
QCISD(T)/6-31G(d, p)	-189.11148	1.363	1.286	1.080	1.078	117.8	118.8	115.1	3.76		
MBPT(2)/DZ+P	-189.14822	1.285	1.300	1.087	1.083	120.8	118.5	113.8	3.36		
MBPT(2)/TZ+2P	-189.27393	1.297	1.282	1.077	1.074	119.8	118.2	114.1	3.70		
CCSD/DZ+P	-189.17138	1.358	1.263	1.090	1.088	118.2	119.2	115.5	4.42		
CCSD/TZ+2P	-189.28927	1.368	1.248	1.079	1.078	117.2	118.9	115.7	4.60		
CCSD(T)/DZ+P	-189.19414	1.348	1.289	1.091	1.088	118.2	119.2	114.9	3.82		
CCSD(T)/TZ+2P	-189.32045	1.355	1.276	1.080	1.078	117.0	118.7	115.0	3.97		
Method	ΔE	R(OO)	R(CO)	R(CH _c)	R(CH _t)	COO	H _c CO	H _t CO	H _c COO	H _t COO	μ
transition state (3)											
MBPT(2)/DZ+P	25.2	1.452	1.273	1.089	1.098	91.4	120.2	117.6	46.1	-139.7	4.18
MBPT(2)/TZ+2P	23.3	1.451	1.267	1.077	1.086	91.3	119.8	117.3	46.3	-139.4	4.19
CCSD/DZ+P	20.8	1.491	1.273	1.090	1.098	91.1	120.5	118.1	49.1	-136.0	3.99
CCSD/TZ+2P	19.9	1.495	1.262	1.079	1.087	90.6	120.2	118.0	49.3	-135.8	4.04
CCSD(T)/DZ+P	20.3	1.462	1.305	1.090	1.096	92.3	119.5	118.0	50.0	-135.5	3.31
CCSD(T)/TZ+2P	19.2	1.473	1.290	1.079	1.086	91.8	119.3	117.7	48.9	-135.0	3.51
Method	ΔE	R(OO)	R(CO)	R(CH)	HCH	μ					
dioxirane (2)											
MBPT(2)/DZ+P	-33.6	1.526	1.393	1.094	116.1	2.66					
MBPT(2)/TZ+2P	-32.7	1.523	1.393	1.082	117.0	2.62					
CCSD/DZ+P	-29.5	1.511	1.387	1.095	115.9	2.69					
CCSD/TZ+2P	-28.3	1.505	1.385	1.083	116.6	2.65					
CCSD(T)/DZ+P	-24.2	1.535	1.393	1.097	116.1	2.65					
CCSD(T)/TZ+2P	-25.6	1.532	1.393	1.085	116.6	2.60					
exp. (ref. [11])		1.529	1.388	1.090	117.3	2.49					

^{a)} For the definition of H_c and H_t see fig. 1. Absolute energies in hartree, relative energies ΔE in kcal/mol, bond lengths in Å, angles in deg, dipole moments in D.

3.1. Ab initio geometries and electronic structure

HF and MBPT(2) give two contradicting descriptions of the geometry of 1. The HF geometry corresponds to an aldehyde oxide that is best described by resonance formulas 1a and 1b shown in scheme 1: the CO double bond of formaldehyde is largely maintained ($r(\text{C}=\text{O}) = 1.20 \text{ \AA}$)⁵ and the OO bond

resembles a slightly elongated peroxide single bond ($r(\text{O}-\text{O}) = 1.45 \text{ \AA}$) (see footnote 5). The MBPT(2) geometry, on the other hand, corresponds better to the biradical structure 1c with two single π electrons being formally localized at C and the terminal oxygen atom O_t while a π-electron pair is positioned at the central oxygen atom O_c. In this way, both the CO and OO bond formally get about 50% π-bond character. Since typical values for CO and OO single and double bonds are (see footnote 5): $r(\text{CO}) = 1.43, 1.20 \text{ \AA}$, $r(\text{OO}) = 1.45, 1.21 \text{ \AA}$, one can expect bond

⁵ CO in CH₃OH: 1.427 Å [34]; CO in H₂C=O: 1.203 Å [35]; OO in HOOH: 1.451 Å [36]; OO in ³O₂: 1.207 Å [37].

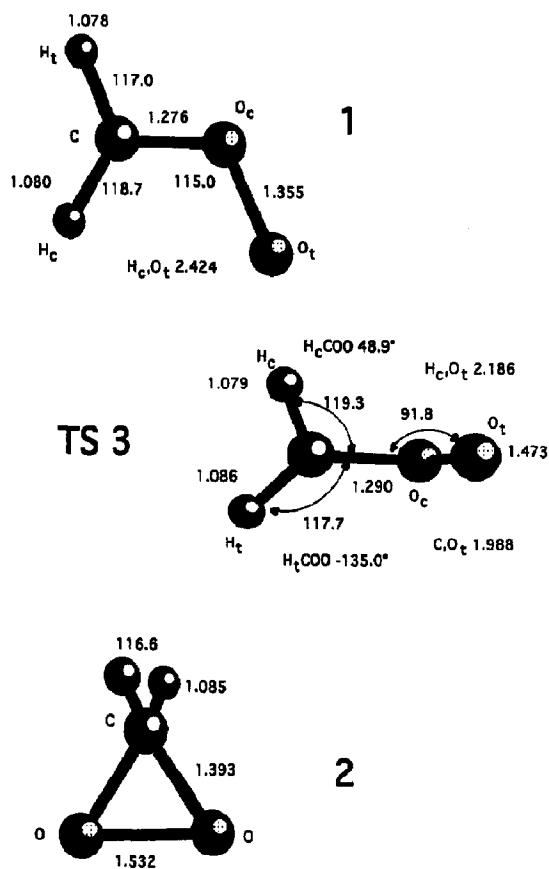


Fig. 1. CCSD(T)/TZ+2P geometries of carbonyl oxide (1), dioxirane (2), and the transition state (TS) of the carbonyl oxide-dioxirané isomerization (3). Bond lengths are given in Å, angles in deg. Central and terminal oxygen (O_c and O_t) as well as cis and trans hydrogen (H_c and H_t) are indicated. For 3, HCOO dihedral angles and two nonbonded distances are also given.

lengths of about 1.3 Å for both CO and OO in the case of **1c**. Exactly, this prediction is confirmed by the calculated MBPT(2) geometry of **1** (see table 1) [15].

Since the MBPT(2) description of **1** was the best description available for some time, there was a tendency to attribute biradical rather than zwitterionic character to **1**. However, both the HF and the MBPT(2) description are incorrect because HF overestimates the importance of polar and ionic structures while MBPT(2) does the same with regard to biradical structures. The latter results from the fact that at this level of theory only the interaction of double (D) excitations with the ground

state is considered. MBPT(2) is partially corrected at the MBPT(3) level by a coupling between D excitations. This slightly shifts the geometry in the direction of the HF values as shown in table 1. But this trend is reversed at the MBPT(4) level with the inclusion of higher correlation effects described by S, T, and quadruple (Q) excitations (table 1). Since one cannot foresee at what MBPT(*n*) level oscillations damp out, MBPT(2), MBPT(3), and MBPT(4) are not sufficient to predict to which geometry the perturbation theory calculations will converge.

A more reliable prediction of equilibrium geometry and electronic nature of **1** is obtained by CC theory. At all levels of CC theory employed the electronic structure of **1** is shifted from the biradical-type description at the MBPT(4) level in the direction of a more zwitterionic description. This is clearly reflected by the calculated dipole moments (table 1), which are 0.4–1.2 D larger depending on the CC method employed. At the same time, the CO bond length becomes shorter adopting values between 1.25 and 1.29 Å while the OO bond length increases to 1.34–1.37 Å. The strongest alternation of the CO and OO bond lengths is found for CCSD while CCSD(T) leads to values intermediate between those obtained at the CCD and at the CCSD level of theory. This, of course, suggests that there is still some dependency of the electronic structure on the CC level employed, though variations are not as strong as at the MBPT level (see table 1). QCISD and QCISD(T) values are rather close to CCSD(T) results which may have to do with a fortunate cancellation of terms at the QCI level [38].

Table 1 displays the basis set dependence of the results. However, changes in calculated molecular parameters are sufficiently small in going from the DZ+P to the TZ+2P basis set that further changes with larger basis sets are not expected to be significant. Hence, results obtained at the CCSD(T)/TZ+2P level (fig. 1) provide a rather reliable description of **1**. They suggest CO and OO bond lengths of 1.276 and 1.355 Å, a dipole moment of 4 D, and a charge distribution which can be described by formula **1a** but with charges of +0.4 and -0.4 electron rather than ±1 at CH₂ and the terminal O atom.

Table 2
Harmonic vibrational frequencies of carbonyl oxide (1) and dioxirane (2) ^{a)}

Mode	Sym.	Assignment	MBPT(2)	CCSD	CCSD(T)
carbonyl oxide					
ω_1	A'	CH str., asym.	3293(0.8)	3340(0.1)	3333(0.2)
ω_2		CH str., sym.	3209(15.2)	3187(3.1)	3174(5.5)
ω_3		CH ₂ scissor	1487(0.7)	1566(37.4)	1493(25.4)
ω_4		CO str., CH ₂ rock	1303(42.8)	1407(26.7)	1281(113.3)
ω_5		CH ₂ rock, CO str.	1171(196.4)	1247(13.0)	1228(9.9)
ω_6		OO str.	1077(849.2)	867(127.4)	948(85.1)
ω_7		OOC deform.	559(10.5)	528(0.3)	531(0.8)
ω_8	A''	CH ₂ wag.	643(57.4)	928(37.8)	783(38.1)
ω_9		CH ₂ twist	762(10.5)	665(3.1)	297(12.3)
dioxirane					
ω_1	A ₁	CH str., sym.	3140(44.0)	3127(45.4)	3102(48.6)
ω_2		CH ₂ scissor	1585(5.7)	1593(8.8)	1579(7.9)
ω_3		CO str., sym.	1305(35.8)	1338(42.3)	1303(39.7)
ω_4		OCO deform., OO str.	763(1.0)	768(0.7)	701(0.5)
ω_5	A ₂	CH ₂ twist	1028(0.0)	1041(0.0)	1027(0.0)
ω_6	B ₁	CH str., asym.	3247(34.1)	3221(38.5)	3196(42.2)
ω_7		CH ₂ rock	1195(8.8)	1200(10.3)	1189(9.7)
ω_8	B ₂	CH ₂ wag.	1286(0.1)	1289(1.0)	1275(1.4)
ω_9		CO str., asym.	962(30.4)	954(23.1)	932(19.6)

^{a)} DZ+P calculations. Wavenumbers in cm⁻¹, intensities in km/mol.

Table 3
Calculated ¹⁸O isotopic shifts for the vibrational frequencies of carbonyl oxide (1) and dioxirane (2) ^{a)}

Mode	Carbonyl oxide			Dioxirane	
	H ₂ ¹² C ¹⁸ O ¹⁶ O	H ₂ ¹² C ¹⁶ O ¹⁸ O	H ₂ ¹² C ¹⁸ O ¹⁸ O	H ₂ ¹² C ¹⁶ O ¹⁸ O	H ₂ ¹² C ¹⁸ O ¹⁸ O
ω_1	0	0	0	0	0
ω_2	0	0	0	0.3	0.8
ω_3	1.6	0.4	2.0	14.9	31.1
ω_4	33.1	0.1	33.1	17.4	35.3
ω_5	14.7	1.7	16.0	2.5	4.9
ω_6	16.6	28.9	45.7	0	0
ω_7	8.1	9.2	17.2	1.3	2.7
ω_8	1.6	0.9	2.9	0.4	0.8
ω_9	2.6	0.4	2.6	16.8	32.5

^{a)} CCSD(T)/DZ+P calculations. Isotopic shifts in cm⁻¹.

3.2. Isomerization of 1 to 2

The arrangement of 1 to its cyclic isomer 2 involves rotation at the CO bond without any pyramidalization at the C atom. Any change in the electronic structure, which influences CO bonding, will also influence the barrier to isomerization. This pre-

diction is confirmed by MBPT(2) and CC description of TS 3 (table 1). MBPT(2) calculations suggest a relatively high TS energy of 25 kcal/mol in line with the results of previous investigations carried out at different levels of MBPT theory [15,16,19]. CCSD leads to a decrease of the TS energy to 20 kcal/mol and CCSD(T) causes a further decrease to 19.2 kcal/

Table 4
Thermochemical data ^{a)}

Molecule	ZPE	$\Delta H_f^0(0)$	$\Delta H_f^0(298)$
CH ₂ O ₂ , 1	18.7	31.7	30.2
CH ₂ O ₂ , 2	20.5	7.9	6.0
H, ² S		51.6	52.1
O, ³ P		59.0	59.5
O, ¹ D		104.4	104.9
H ₂	5.9	0	0
O ₂ , ³ Σ _g ⁻	2.2	0	0
O ₂ , ¹ Δ _g			22.5
O ₂ , ¹ Σ _g ⁺			37.5
CO	3.1	-27.2	-26.4
H ₂ O	12.9	-57.1	-57.8
CH ₂ , ³ B	10.4	92.2	92.3
CH ₂ , ³ B			99.7
H ₂ C=O, ¹ A ₁	16.1	-26.8	-27.7
H ₂ C=O, ³ A''			44.3
H ₂ C=O, ¹ A''			52.9
CO ₂	7.2	-94.0	-94.1
HCOOH			-90.6
H ₂ C=CH ₂	30.9	14.6	12.5
cyclopropane	49.6	16.8	12.7
oxirane			-12.6

^{a)} From ref. [39] with the exception of **1** and **2**. All values in kcal/mol.

mol (table 1). These changes may not be so dramatic for the parent carbonyl oxide **1**, but they are important for substituted **1** where, e.g. in the case of F-substituted **1** a barrier of 7 kcal/mol has been predicted at the MBPT(2) and SDQ-MBPT(4) level of theory [19]. Further reduction of this barrier would imply that F-substituted **1** immediately isomerizes to the more stable F-substituted dioxirane.

The CCSD(T)/TZ+2P geometry of TS **3** suggests that the saddle point lies roughly halfway along the reaction coordinate linking structures **1** and **2** (table 1). For example, the rotation of the CH₂ group at the CO bond has proceeded by more than 50% and the decrease of the COO angle is carried out by 45%. The OO bond length, 1.473 Å, has a typical value for a peroxide single bond [17], corresponding to an increase by 66% compared to the total increase reached in **2**. All these data suggest a late or at least far advanced TS, but the dipole moment (3.5 D, table 1) and charge distribution are typical of an early TS being electronically related more to **1** than to **2**. This is also suggested by the C, O₁ distance, which with 1.988 Å is closer to that in **1** than that in **2**.

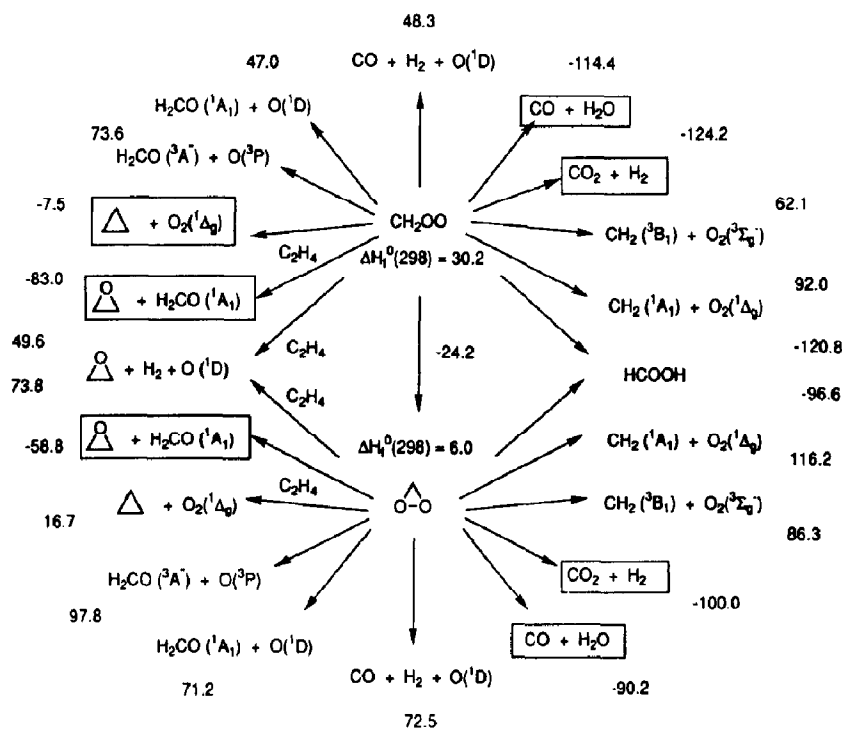


Fig. 2. Reaction enthalpies (kcal/mol) for various dissociation and rearrangement reactions of carbonyl oxide (**1**) and dioxirane (**2**) as calculated from the data in table 4.

According to the data in table 1, the isomerization reaction is strongly exothermic (-33.6 to -25.6 kcal/mol), which is in line with previous results [15,16,21]. Clearly, larger basis sets and methods with higher correlation effects lead to less negative reaction energies ΔE because of an improved description of **1**. According to CCSD(T)/TZ+2P ΔE is -25.6 kcal/mol (table 1). For an exothermic reaction the Hammond postulate predicts an early TS as indicated by the calculated charge distribution but in contradiction with some of the geometrical parameters obtained for **3**. We note that the common procedure to describe the character of a TS (early or late) with the help of calculated geometrical parameters may be misleading and, therefore, has to be verified by properties that are directly related to the electronic structure of the TS.

We have also investigated the cyclic isomer **2** although quite accurate descriptions have already been published earlier [12–21]. The MBPT(2) geometries are close to the experimental r_s geometry and, therefore, improvements at the CCSD(T)/TZ+2P level are rather small (see, e.g. HCH angle in table 1). The CCSD(T)/TZ+2P OO bond length is 0.003 and the CO bond length 0.005 Å longer than the experimental r_s values. These small differences can result either from basis set deficiencies [27,28] or from vibrational effects. All calculated dipole moments of **2** are quite close to the experimental value of 2.48 D [11], but the best agreement is obtained for the CCSD(T)/TZ+2P value (2.60 D, table 1).

3.3. Infrared spectrum

The CCSD(T) description of **1** clearly differs from both the HF and MBPT(n) ($n=2, 4$) descriptions published previously [12–21] and, therefore, it is advisable to reinvestigate the IR spectrum of **1** [18].

When going from MBPT(2) to CCSD strong changes in both frequencies and intensities of vibrational modes are obtained (table 2). From CCSD to CCSD(T) most of these changes are somewhat reduced, but the difference between the MBPT(2) and the CCSD(T) result is still large. Since the importance of T correlation effects for **1** is obvious from the discussion of calculated geometries and charge distributions, we refrain from discussing the CCSD IR spectrum and consider just the CCSD(T) spec-

trum as the most reliable prediction possible at the moment. For discussion of the CCSD(T) spectrum, we refer to the MBPT(2) IR spectrum published earlier [18] since differences in the two spectra motivated this work.

The largest differences between MBPT(2) and CCSD(T) spectrum pertain to calculated intensities, which differ with regard to both the absolute magnitude of the strongest IR band and the relative intensity of the individual bands. At the MBPT(2) level the OO stretching mode ω_6 (table 2) attains an intensity of 850 km/mol but drops down to 85 km/mol to become the second strongest IR band at the CCSD(T) level. The strongest IR band at the CCSD(T) level is the CO stretching mode ω_4 (113 km/mol, table 2), which strongly couples with the CH₂ rocking motion. The CH₂ rocking motion ω_5 itself drops down from the second largest band (196 km/mol) at the MBPT(2) level to a very low-intensity band at the CCSD(T) level of theory. A similar intensity loss is calculated at the CCSD(T) level for the OOC deformation mode ω_4 but this band is also relatively weak at the MBPT(2) level of theory.

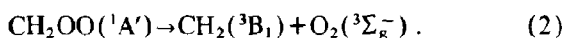
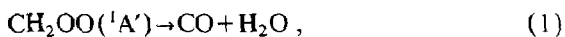
Compared to the changes in intensities, changes in the frequencies are moderate. The largest occurs for the CH₂ twisting mode ω_9 , which is shifted by 465 cm⁻¹ to lower frequencies (762, MBPT(2); 297 cm⁻¹, CCSD(T), table 2). But for an experimental detection of **1** this is not so important since ω_9 possesses a relatively low intensity and accurate measurements at low frequencies are difficult. In addition, one has to consider that fundamental modes involving the CH₂ group will most probably overlap with CH_{*n*} modes of other compounds present in an IR probe. Because of this, an identification of **1** most probably has to be based on the CO and OO stretching modes ω_4 and ω_6 which should appear near 1200 and 880 cm⁻¹, respectively, if one applies an empirical scaling factor of 0.9 to the harmonic frequencies to account for vibrational anharmonicity.

The CCSD(T) IR spectrum of **2** is fully in line with results published previously [18]. As can be seen from table 2, CCSD(T) intensities agree with MBPT(2) values and the corresponding frequencies are shifted ≈ 20 cm⁻¹ on the average to lower frequencies reflecting small changes in the geometry. CO and OO stretching modes of **2** appear in the same region of the IR spectrum as the corresponding modes

of **1**, but intensities in the former case are lower by a factor 2 to 4, which should facilitate a distinction of **1** and **2**. Also helpful for the differentiation or identification of **1** and **2** are ^{18}O isotopic shifts, which can be as large as 45 cm^{-1} according to CCSD(T) results shown in table 3.

3.4. Heats of formation and stability

Since there are no experimental thermochemical data on either **1** or **2**, an investigation of the energetics of formation and decomposition of the two molecules depends on accurate ab initio calculations. Here, we report for the first time CCSD(T) based $\Delta H_f^0(0)$ and $\Delta H_f^0(298)$ values for both **1** and **2**. As suitable reference equations for the determination of $\Delta H_f^0(0)$ we have taken the following decomposition reactions:



The CCSD(T)/TZ+2P reaction energies calculated for (1) and (2) are -112.9 and 66.1 kcal/mol, respectively. These values have to be corrected for zero-point energies (ZPE) to obtain reaction enthalpies at 0 K, $\Delta\Delta H_f^0(0)$. If one used the CCSD(T) vibrational frequencies of table 2 to determine ZPE(**1**) and experimental frequencies for the ZPE values of the decomposition products [39] of reactions (1) and (2) (see table 4), one obtains -116.8 and 60.1 kcal/mol, respectively. With the help of appropriate vibrational, rotational, and translational corrections [40] one gets reaction enthalpies at 298 K, $\Delta\Delta H_f^0(298)$, which are -114.1 and 61.8 kcal/mol. Since all the $\Delta H_f^0(298)$ values of the reactants are known [39] $\Delta H_f^0(298)$ of **1** is calculated to be 29.8 (from reaction (1)) and 30.6 kcal/mol (from reaction (2)) yielding as an average $\Delta H_f^0(298) = 30.2$ kcal/mol.

Previous theoretical determinations of $\Delta H_f^0(298)$ for **1** range from $16-48$ kcal/mol [10,12,13,16,21] where the semiempirical methods lead to the lower and the ab initio methods to the higher values. Critical evaluation of these data reveals that highly parameterized semiempirical methods such as MNDO, AM1 or PM3 suggest a value close to 30 kcal/mol even though their equilibrium geometry is close to

the unlikely resonance structure **1d**. Cremer has predicted $\Delta H_f^0(0) = 38$ kcal/mol on the basis of MBPT(2) calculations [16], which in view of the deficiencies of MBPT(2) is about 8 kcal/mol too high. GVB calculations [12] have led to $\Delta H_f^0(0) = 48$ kcal/mol, which was later revised to 29 kcal/mol [13]. We conclude that $\Delta H_f^0(298) = 30$ kcal/mol is a rather reliable prediction of the heat-of-formation of **1**.

With the heat-of-formation for **1**, the CCSD(T) energy difference between **1** and **2**, and the calculated vibrational frequencies for **1** and **2**, determination of the $\Delta H_f^0(2)$ values given in table 4 is straightforward. With the data of table 4, the reaction enthalpies for various decomposition reactions can be predicted. Results are shown in fig. 2 and can be summarized as follows.

Decomposition to aldehyde and oxygen transfer. Calculated reaction enthalpies show that this is not a spontaneous reaction since the formation of aldehyde and oxygen atoms is for all possibilities considered highly endothermic^{#6}. However, in the presence of an oxygen acceptor such as alkene, oxygen transfer from **1** or **2** becomes exothermic. For example, the epoxidation of ethylene is with -83 and -59 kcal/mol strongly exothermic. In this way, oxygen transfer is probably the most important reaction of both **1** and **2**.

Rearrangement to formic acid. It is very unlikely that **1** rearranges directly to formic acid, but cyclization to **2** followed by a H transfer from C to O is possible. In any case, formic acid is much more stable than both **1** or **2** and, therefore, the rearrangement reaction should be highly exothermic.

Decomposition to CO or CO₂. Since both reactions are highly exothermic for **1** and **2**, CO, CO₂, H₂O and H₂ should be observed upon decomposition of **1** or **2**. Mass spectra seem to confirm this prediction [1,5].

Decomposition to carbene and molecular oxygen. Since **1** and **2** are formed by addition of carbene to O₂ [6], it is not astonishing that the addition reaction is highly exothermic. A direct decomposition to carbene can be excluded. However, if the carbene is transferred directly from **1** to ethylene cyclopropane

^{#6} However, if **1** is formed from CH₂ and O₂, the molecule will possess enough energy to decompose spontaneously to aldehyde and atomic oxygen (see fig. 2).

can be formed in an exothermic step (-7.5 kcal/mol). This is in line with the observation of cyclopropanes in ozonolysis reactions [1]. On the other hand, carbene transfer from **2** to ethylene is clearly endothermic (16.7 kcal/mol). Thus, the formation of cyclopropanes seems to be a reaction that would allow a distinction between **1** and **2**.

4. Conclusion

We conclude by stressing the following observations.

(1) The electronic structure of **1** is closer to that of a zwitterion than has been predicted by previous ab initio calculations. This is suggested by the CCSD(T) geometry, charge distribution and dipole moment.

(2) Identification of both **1** and **2** in reaction mixtures is possible with the help of IR spectroscopy. The CO and OO stretching modes of **1** should be very intensive and should appear at 1200 and 880 cm^{-1} . Also helpful for an identification of **1** and **2** are typical ^{18}O isotopic shifts to 30 – 40 cm^{-1} .

(3) The heats of formation $\Delta H_f^0(298)$ for **1** and **2** are 30.2 and 6.0 kcal/mol.

(4) Decomposition of **1** and **2** to CO , CO_2 , H_2O , and H_2 is thermodynamically favorable, while fragmentation to CH_2 , O_2 or O is not.

(5) In the presence of an O acceptor O transfer is possible. Both **1** and **2** have to be considered as powerful epoxidation agents.

(6) **1** differs from **2** in the way that it can lead to cyclopropane formation in the presence of an alkene.

Acknowledgement

This work was supported by the Swedish Natural Science Research Council (NFR) at Göteborg, by the Fonds der Chemischen Industrie at Karlsruhe and US AFOSR Grant No. F49620-92-J0141 at Gainesville. Calculations were done on the CRAY YMP of the Ohio Supercomputer Center (OSC), on the CRAY XMP/48 of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden, and on IBM RS6000/320H and 350 work station computers at Karlsruhe. The authors thank OSC and NSC for a generous allotment of computer time.

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