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Electrostatic solvent effects on the conversion of substituted carbonyl oxides to dioxiranes

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Abstract The effects of substituents (H, CH₃, CN, OCH₃, di-CH₃, and di-CN) on the conversion of carbonyl oxides to dioxiranes have been examined in the gas phase and in solution, with B3LYP/6–31G(d,p). The solvent has been modeled with the SCIPCM method. Optimizations in solution have shown that the geometry of carbonyl oxides and the reaction barriers for their conversion to dioxiranes depend on the characteristics of the substituents. The *syn* isomers of CH₃ and OCH₃ carbonyl oxides are more stable than their *anti* counterparts, whereas the conversion of *anti* substituted carbonyl oxides into dioxiranes is easier for all the substituents. Disubstitution favors the ring-opening reaction of dioxiranes.

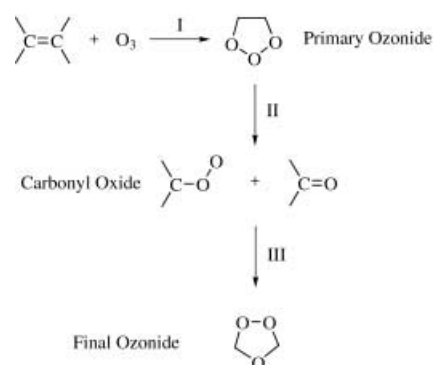
Keywords Carbonyl oxide · Dioxirane · Solvent effect · Ring opening · Reaction barrier

Introduction

The cleavage of olefins by ozone in the gas phase and in solution has been of continuing interest since the beginning of the century [1] and the Criegee mechanism (Scheme 1) has been used to explain the mechanism of this reaction [2]. Carbonyl oxides, the intermediates of the ozonolysis reactions, have been obtained from the reactions between carbenes and O₂, the reactions of diazoalkenes with singlet oxygen, the photooxygenation of C=X systems, furanendoperoxides and other 1,2,4-trioxolanes [3]. Sander et al. [4] have reported the NMR detection of dimesitylene carbonyl oxide. Murray et al. have studied the reactions of carbonyl oxides, confirming that for olefins with aromatic substituents the initially formed 1,2,3-trioxolane cleaves in a manner that favors the carbonyl oxide-bearing substituents stabilizing the positive charge in the carbonyl oxide [5].

It is known that the medium and the substituents affect the electronic behavior of carbonyl oxides [5, 6], whereas different computational methods ascribe the OO and CO bonds different bond lengths [6, 7]. HF methods characterize carbonyl oxides as diradicals [8]; coupled cluster (CC) or quadratic configuration interaction (QCI) calculations characterize them as zwitterions [7, 9]. On the other hand, as the basis set is increased, the electronic character of carbonyl oxide has been found to change from diradical to zwitterion. Karlström et al. [10] have demonstrated the effects of the electronic nature of substituents on carbonyl oxides. Calculations have shown that strong π -donors enhance the zwitterionic character of the carbonyl oxide, whereas weak π -donors or π -acceptors hardly change its biradicaloid character [11]. Kraka et al. [12] have modeled dimesitylene carbonyl oxide and confirmed the spectroscopic results of Sander et al. [4]. The first detailed computational studies on substituted carbonyl oxides were performed using semi-empirical methods [9, 13, 14]. Ab initio calculations have been reported for monofluorocarbonyl oxide [15], difluorocarbonyl oxide [16], methyl carbonyl oxide [17], and cyclopropanone carbonyl oxide [18].

Calculations have also been reported for the chemical behavior of carbonyl oxides in solvated media [19, 20].



Scheme 1 Criegee mechanism for ozonolysis

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Recently, Bernhardsson et al. have used CASPT2 to model carbonyl oxides in solution [21].

The failure to detect carbonyl oxides during ozonolysis reactions has been ascribed to the instability of these compounds and their fast conversion to their cyclic isomers, dioxiranes. After the early experiments conducted by Curci and Edwards [22], dioxiranes were first characterized in the ozonolysis reactions by Murray et al. in the mid eighties [23]. The unusual oxygen-transferring ability of this class of compounds, especially dimethyl dioxirane, has led to their synthesis and use as powerful oxidants. The reviews by Murray [24] and Adam et al. [25] include detailed information about dioxirane chemistry. The structural and electronic properties of dioxiranes have been studied at different levels including CASSCF [26], CCSD(T) [27], MBPT [28], and G2 [29].

The conversion of carbonyl oxides to dioxiranes has been studied computationally [9, 10, 15, 30, 31, 32, 33]. Cremer et al. have conducted a complete analysis of the isomerization of carbonyl oxides to dioxiranes for the unsubstituted and fluoro-substituted species at the MP4(SDQ)/6-31G(d) level [15] and have pointed out that the presence of geminal methyl groups on dioxirane increases the stability of the three-membered ring. Sander and Bucher have shown that electron-donor groups decrease the stability of carbonyl oxides, whereas electron-withdrawing groups increase their stability [34]. Anglada et al. have studied unimolecular isomerizations and oxygen atom loss in carbonyl oxide and methyl carbonyl oxide and investigated the lowest singlet and triplet potential energy surfaces of these two species [32]. Their results showed that for methyl carbonyl oxide there is competition between cyclization to dioxirane and tautomerization to hydroperoxide. Olzmann et al. have studied the reactions of ozone with ethene and 2,3-dimethyl-2-butene and have determined the energetics, kinetics, and product distributions of all reaction intermediates, including the carbonyl oxides and dioxiranes [32]. Cremer et al. studied the modes of decomposition of dioxirane, methyl dioxirane, and dimethyl dioxirane [33] and calculated the geometries and thermodynamic properties by using various *ab initio* and DFT methods.

The purpose of this research was to discover whether carbonyl oxides – 1,3-dipoles with an intriguing electronic structure – undergo cyclization to dioxiranes, which are nowadays used as powerful and convenient oxidants. It was also interesting to determine how the isomerization is influenced by the substituents and the medium. Groups with different characteristics were selected for this purpose – OCH₃ (electron-donating), CN (electron-withdrawing), and CH₃. The interconversion mechanism has been studied for mono- and di-substituted compounds – except di-OCH₃ – in the gas phase and in solution ($\epsilon=78.5$).

Methodology

The calculations were performed with the Gaussian 94 package (Revision C.3) [35]. The geometries were fully

optimized both in the gas phase and in solution, where the media are represented by their dielectric constants ($\epsilon=1$ for vacuum and $\epsilon=78.5$ for water).

Density functional theory (DFT) was used because of its more favorable scaling behavior with system size than for Hartree-Fock (HF) methods [36]. However, unlike HF, the DFT method includes electron–electron correlation energy. This reduces the computational time required by expensive post-SCF calculations to recover the correlation energy. The calculations with Becke's 3-parameter [37] Lee, Yang and Parr [38, 39] (B3LYP) level were performed with the standard 6-31G(d,p) basis set.

Calculations on carbonyl oxide with B3LYP/6-31G(d,p) have been shown to be in good agreement with higher level QCI [7] or CC [9] calculations, and we used this level of theory in this study. All the stationary points are characterized by positive vibrational frequencies calculated analytically for the gas phase and numerically for the solvated media. Transition states have been characterized by one and only one imaginary frequency in both media.

Our previous study [40] on the conversion of hydroxy carbonyl oxide to hydroxy dioxirane showed that single-point calculations with B3LYP/6-311+G(3df,2p) on B3LYP/6-31G(d,p) geometries did not change the values for the activation barriers and reaction energies in both phases. Thus, we rely on the basis set used throughout this work.

The heats of formation (ΔH_f) were calculated using the experimental heats of formation of carbon, nitrogen, oxygen, and hydrogen as described by Clark [41].

For the calculations in solution, the SCIPCM (self-consistent isodensity polarizable continuum model) method developed by Frisch et al. [35], implemented in the Gaussian 94 series, was used. The default value 0.0004 au was chosen for the isodensity. The SCIPCM method follows the methodology developed by Tomasi [42] on a polarized continuum, but uses a cavity that is defined by a self-consistently optimized surface of constant electron density. We considered the case of a highly polar medium ($\epsilon=78.5$) to evaluate the upper limit of the electrostatic solvent effect. Obviously, the electrostatic effect of a less polar solvent might be expected to go in the same direction and to be less intense. Note that experimental data in water are available [43, 44], although in such a solvent other effects expected to be present would require the explicit consideration of water molecules. A theoretical study of the reaction of carbonyl oxide with a water molecule has been reported elsewhere [45].

Results and discussion

The conversion of six different carbonyl oxides to dioxiranes has been analyzed both in the gas phase and in solution (Fig. 1 Fig. 2 Fig. 3 Fig. 4 Fig. 5 Fig. 6). The following nomenclature has been used to denote the compounds: carbonyl oxide (**1**), methyl carbonyl oxide

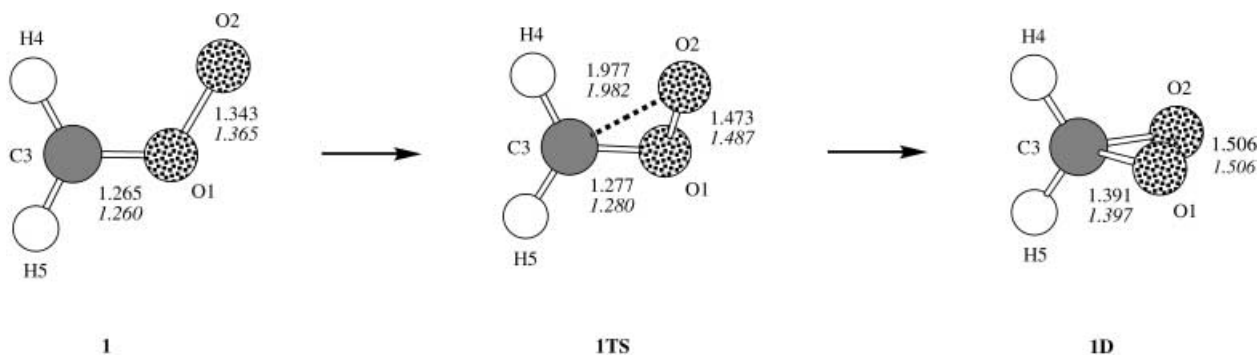


Fig. 1 Optimized structures and some selected atomic distances for the conversion of carbonyl oxide to dioxirane with B3LYP/6-31G(d,p). The parameters in solution are shown in *italics*. Gas-phase geometries are taken from [33]

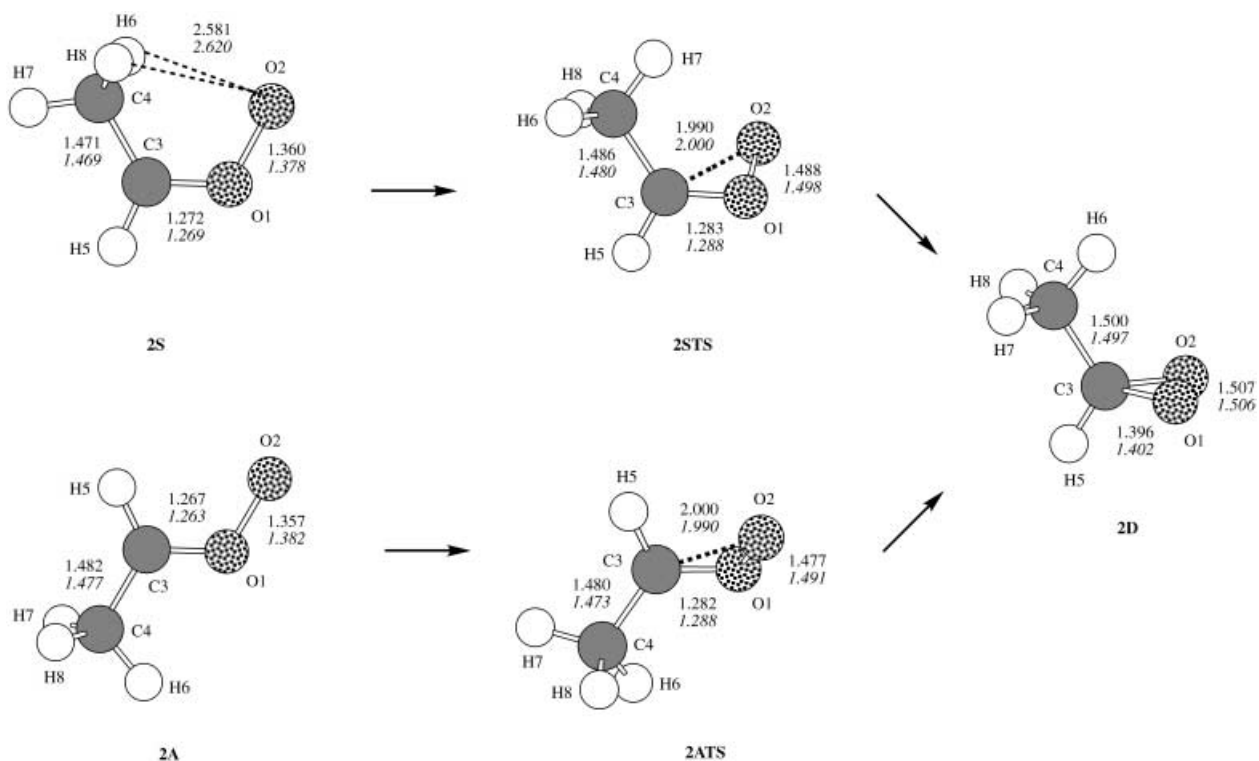


Fig. 2 Optimized structures and some selected atomic distances for the conversion of methyl carbonyl oxide to methyl dioxirane with B3LYP/6-31G(d,p). The parameters in solution are shown in *italics*. Gas-phase geometries are taken from [30] and [33]

(2), cyano carbonyl oxide (3), methoxy carbonyl oxide (4), dimethyl carbonyl oxide (5) and dicyano carbonyl oxide (6). The corresponding dioxiranes have been shown with the same numbers followed by the letter **D**; i.e. **1D**, **2D**, etc. Transition states between carbonyl oxides and dioxiranes have been denoted by **nTS** where **n** stands for the compound of interest, e.g. **1TS** is the transition state between compounds **1** and **1D**. Furthermore, the letters **A** and **S** have been used to represent the *anti* (**A**) and *syn* (**S**) conformers whenever present. The subscripts **i** (in) and **o** (out) denote the position of the methoxy group.

Total electronic energies (E_{ELEC}) and zero point energies (ZPE) are given in Table 1. Relative energies (E_{REL}), dipole moments (μ) and heats of formation (ΔH_f) for the compounds of interest are gathered in Table 2. The calculated reaction energies (ΔE_{RXN}) and the energetics of each reaction step are given in Table 3. ΔE_{I} represents the barrier between the carbonyl oxides and the transition states whereas ΔE_{II} is the energy difference between the transition states and the dioxiranes. The following discussion is based on energies including ZPE corrections, unless otherwise stated.

Carbonyl oxide \rightarrow dioxirane

The conversion of carbonyl oxide (**1**) to dioxirane (**1D**) has been studied by Cremer et al. first at the

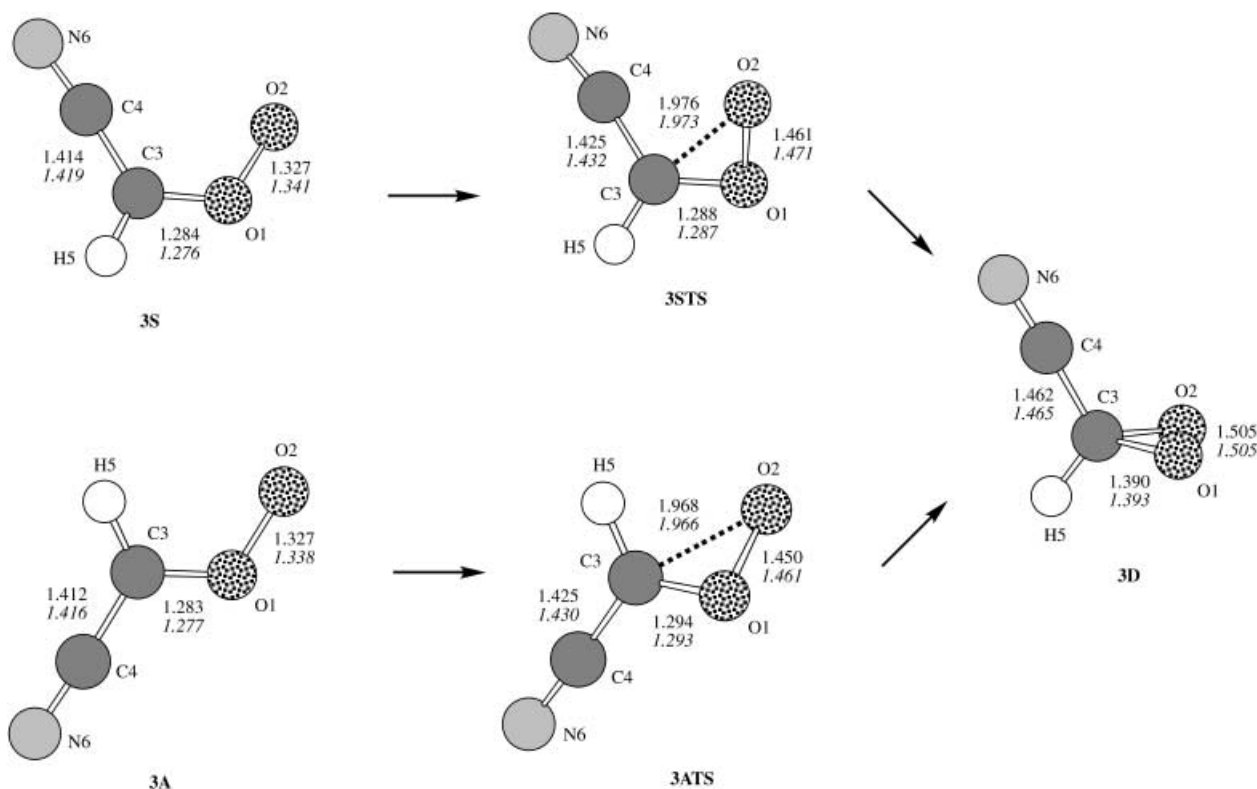


Table 1 Total electronic energies, E_{ELEC} , (in Hartrees) and zero-point energies, ZPE, (in kcal mol⁻¹) of the compounds calculated in gas phase ($\epsilon=1$) and in solution ($\epsilon=78.5$) with B3LYP/6-31G(d,p)

Compound	$\epsilon=1$		$\epsilon=78.5$	
	E_{ELEC}	ZPE	E_{ELEC}	ZPE
1	-189.5799146	19.60	-189.5910236	19.70
1TS	-189.5456450	18.65	-189.5562073	18.80
1D	-189.6182807	20.43	-189.6237613	20.48
2S	-228.9160896	37.38	-228.9273044	37.37
2STS	-228.8763054	36.46	-228.8872872	36.44
2A	-228.9112018	37.25	-228.9243161	37.24
2ATS	-228.8823599	36.22	-228.8945445	36.23
2D	-228.9495849	38.08	-228.9549354	38.05
3S	-281.8135264	19.12	-281.8248285	19.16
3STS	-281.7757130	17.98	-281.7870670	18.08
3A	-281.8137125	18.98	-281.8233038	19.00
3ATS	-281.7788192	17.95	-281.7878224	18.01
3D	-281.8461662	19.48	-281.8538005	19.54
4S_o	-304.1177645	40.58	-304.1395720	40.93
4S_oTS	-304.0876365	39.77	-304.1085001	39.94
4A_o	-304.1173462	40.34	-304.1368577	40.36
4A_oTS	-304.1047955	39.97	-304.1233555	40.20
4D_o	-304.1565276	41.10	-304.1643244	41.03
4S_i	-304.1247923	40.71	-304.1376903	40.79
4S_iTS	-304.1039252	40.14	-304.1163734	40.35
4A_i	-304.1238527	40.76	-304.1406211	40.89
4A_iTS	-304.1104122	40.26	N	N
4D_i	-304.1635372	41.33	-304.1681465	41.22
5	-268.2459164	54.88	-268.2584836	54.89
5TS	-268.2099637	53.94	-268.2218884	53.77
5D	-268.2774896	55.44	-268.2827375	55.41
6	-374.0383408	18.15	-374.0465584	18.14
6TS	-374.0000769	16.95	-374.0076989	16.97
6D	-374.0642270	18.13	-374.0708455	18.16

N: Not optimized

Fig. 3 Optimized structures and some selected atomic distances for the conversion of cyano carbonyl oxide to cyano dioxirane with B3LYP/6-31G(d,p). The parameters in solution are shown in *italics*

MP4(SDQ)/6-31G(d) and MP2/6-31G(d) levels [15] then at the CCSD(T)/DZ+P level [9, 33]. Their CCSD(T)/DZ+P calculations indicate a barrier of 20.3 kcal mol⁻¹ for ring closure and 44.4 kcal mol⁻¹ for ring opening [9, 33]. The same barriers were calculated with B3LYP/6-31G(d,p) to be 20.6 kcal mol⁻¹ and 43.8 kcal mol⁻¹, respectively, in perfect agreement with higher level CC results [9, 32, 33]. These B3LYP results are reproduced in this study.

In solution, the barrier for ring closure increased slightly, on the other hand ring opening is favored by 3.1 kcal mol⁻¹. In solvated media, the conversion of carbonyl oxide to dioxirane is less favored, although the possibility of ring opening is higher. Compounds **1** and **1TS** are stabilized in polar medium more than compound **1D** because of the higher dipole moments of the former compounds in comparison with those of the latter. The difference between the charge separation for compounds **1** and **1D** can be stated as the main reason for the decrease in the reaction energy, ΔE_{RXN} , in solution (Table 3).

Fig. 4 Optimized structures and some selected atomic distances for the conversion of (a) the *anti* methoxy carbonyl oxide to methoxy dioxirane with B3LYP/6-31G(d,p) and (b) the *syn* methoxy carbonyl oxide to methoxy dioxirane with B3LYP/6-31G(d,p). The parameters in solution are shown in *italics*

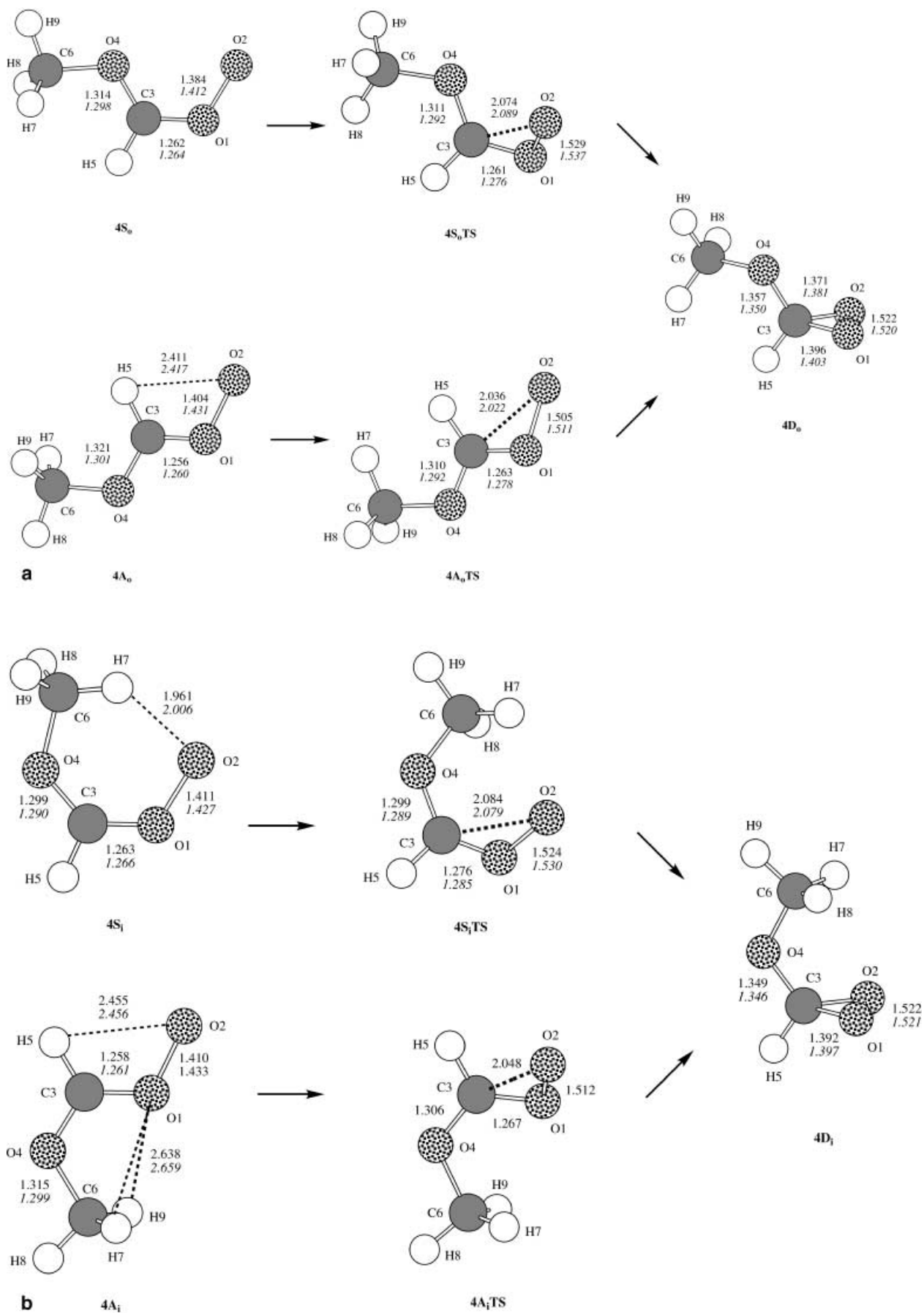


Fig. 4 Legend see p. 73

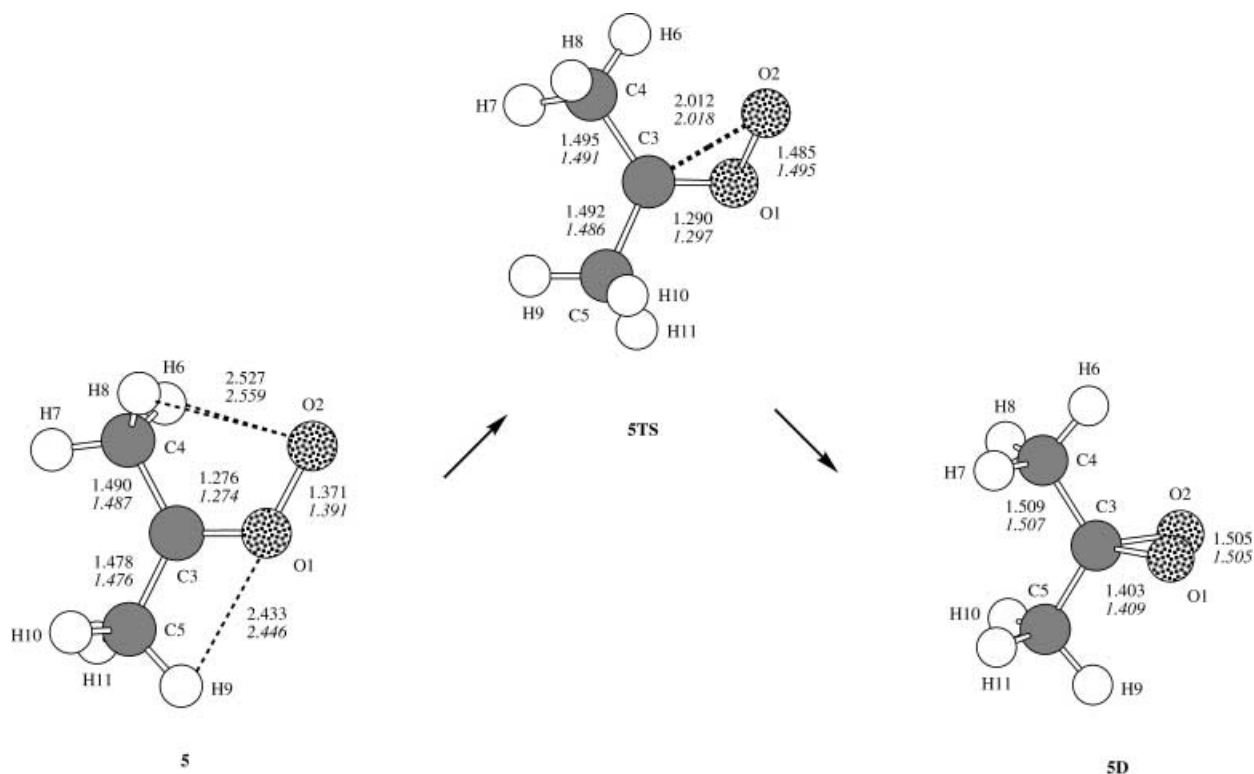


Fig. 5 Optimized structures and some selected atomic distances for the conversion of dimethyl carbonyl oxide to dimethyl dioxirane with B3LYP/6-31G(d,p). The parameters in solution are shown in *italics*. Gas phase geometries are taken from [33]

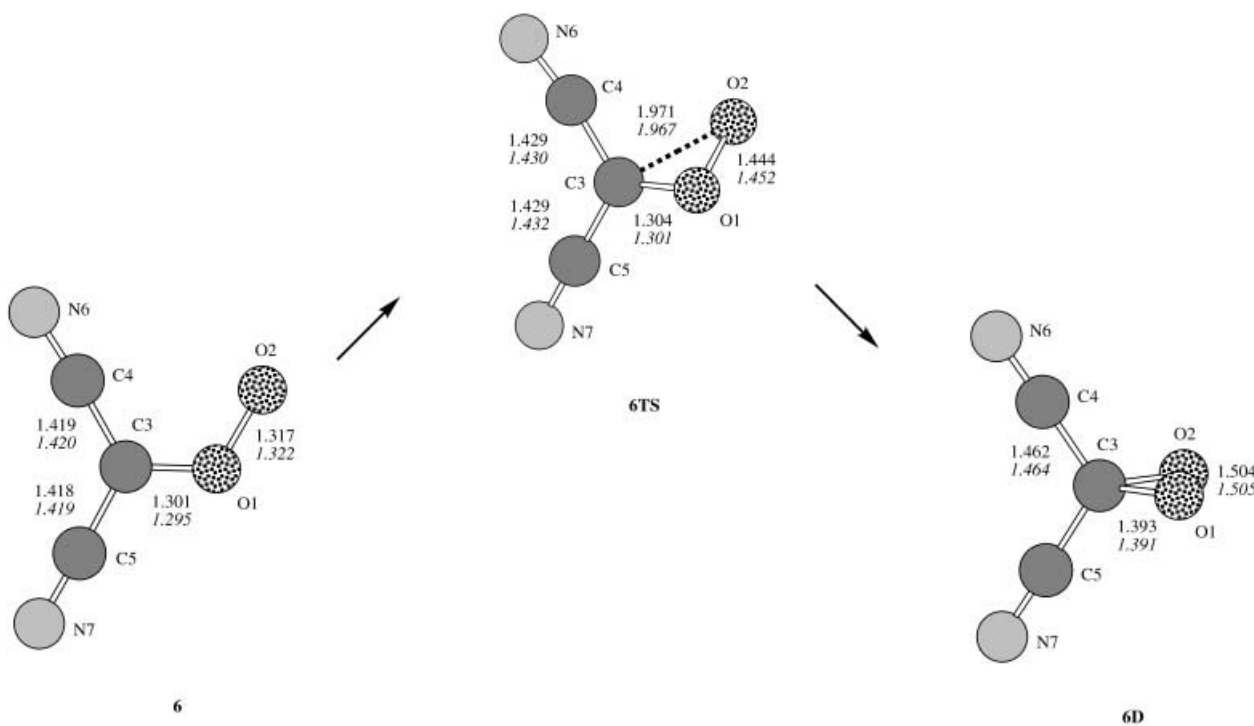


Fig. 6 Optimized structures and some selected atomic distances for the conversion of dicyano carbonyl oxide to dicyano dioxirane with B3LYP/6-31G(d,p). The parameters in solution are shown in *italics*

Previous studies have shown that the CO bond in the carbonyl oxide resembles a double bond, whereas the OO bond is almost like a single bond [6, 9, 32, 33, 46]. The transition structure (**1TS**) located in this study is half way between the reactant carbonyl oxide and the product dioxirane.

Table 2 Calculated dipole moments, μ , (in D), relative energies, E_{REL} , and heats of formation, ΔH_f , (in kcal mol⁻¹) for the compounds studied

	Dipole moment (μ)		E_{REL}^a				ΔH_f
			e=1		e=78.5		
	$\epsilon=1$	$\epsilon=78.5$					
1	3.91	5.30	24.08	<i>23.24</i>	20.54	<i>19.76</i>	-16.37
1TS	3.65	4.74	45.58	<i>43.80</i>	42.39	<i>40.71</i>	-
1D	2.53	3.07	0.00	<i>0.00</i>	0.00	<i>0.00</i>	-40.45
2S	4.19	5.61	21.02	<i>20.32</i>	17.34	<i>16.66</i>	-31.78
2STS	4.06	5.39	45.98	<i>44.36</i>	42.45	<i>40.84</i>	-
2A	4.87	6.58	24.09	<i>23.26</i>	19.21	<i>18.41</i>	-28.71
2ATS	4.63	5.88	42.18	<i>40.33</i>	37.90	<i>36.08</i>	-
2D	2.80	3.42	0.00	<i>0.00</i>	0.00	<i>0.00</i>	-52.80
3S	3.80	5.12	20.48	<i>20.12</i>	18.18	<i>17.79</i>	19.27
3STS	3.55	4.68	44.21	<i>42.71</i>	41.88	<i>40.41</i>	-
3A	1.83	2.47	20.37	<i>19.86</i>	19.14	<i>18.60</i>	19.16
3ATS	2.02	2.71	42.26	<i>40.73</i>	41.40	<i>39.87</i>	-
3D	2.49	3.17	0.00	<i>0.00</i>	0.00	<i>0.00</i>	-1.21
4S_o	6.81	9.11	28.72	<i>27.97</i>	17.93	<i>17.64</i>	-82.34
4S_oTS	6.61	8.69	47.63	<i>46.07</i>	37.43	<i>36.15</i>	-
4A_o	6.81	9.03	28.99	<i>28.00</i>	19.63	<i>18.77</i>	-82.08
4A_oTS	6.71	8.46	36.86	<i>35.50</i>	28.11	<i>27.09</i>	-
4D_o	3.76	4.75	4.40	<i>4.18</i>	2.40	<i>2.21</i>	-106.67
4S_i	4.03	5.37	24.31	<i>23.69</i>	19.11	<i>18.68</i>	-86.75
4S_iTS	3.86	5.03	37.41	<i>36.22</i>	32.49	<i>31.62</i>	-
4A_i	5.27	6.98	24.90	<i>24.34</i>	17.27	<i>16.94</i>	-86.16
4A_iTS	5.08	N	33.34	<i>32.27</i>	N	N	-
4D_i	1.72	2.06	0.00	<i>0.00</i>	0.00	<i>0.00</i>	-111.06
5	4.85	6.52	19.81	<i>19.25</i>	15.22	<i>14.70</i>	-43.21
5TS	4.61	6.09	42.37	<i>40.87</i>	38.18	<i>36.54</i>	-
5D	2.90	3.62	0.00	<i>0.00</i>	0.00	<i>0.00</i>	-63.02
6	0.77	1.13	16.24	<i>16.26</i>	15.24	<i>15.22</i>	60.44
6TS	1.32	1.82	40.25	<i>39.07</i>	39.63	<i>38.44</i>	-
6D	0.82	1.00	0.00	<i>0.00</i>	0.00	<i>0.00</i>	44.20

^a E_{REL} has been calculated separately for each compound; values in italics include ZPE corrections
N: Not optimized

Table 3 Calculated energy differences with B3LYP/6-31G(d,p) for the steps from carbonyl oxides to transition structures (ΔE_I), from transition structures to dioxiranes (ΔE_{II}) and reaction ener-

Carbonyl oxide	ΔE_I		ΔE_{II}				ΔE_{RXN}					
			$\epsilon=1$		$\epsilon=78.5$		$\epsilon=1$	$\epsilon=78.5$				
	$\epsilon=1$	$\epsilon=78.5$										
1	21.50	<i>20.56</i>	21.85	<i>20.95</i>	-45.58	<i>-43.80</i>	-42.39	<i>-40.71</i>	-24.08	<i>-23.24</i>	-20.54	<i>-19.76</i>
2S	24.96	<i>24.04</i>	25.11	<i>24.18</i>	-45.98	<i>-44.36</i>	-42.45	<i>-40.84</i>	-21.02	<i>-20.32</i>	-17.34	<i>-16.66</i>
2A	18.09	<i>17.07</i>	18.69	<i>17.67</i>	-42.18	<i>-40.33</i>	-37.90	<i>-36.08</i>	-24.09	<i>-23.26</i>	-19.21	<i>-18.41</i>
3S	23.73	<i>22.59</i>	23.70	<i>22.62</i>	-44.21	<i>-42.71</i>	-41.88	<i>-40.41</i>	-20.48	<i>-20.12</i>	-18.18	<i>-17.79</i>
3A	21.89	<i>20.87</i>	22.34	<i>21.27</i>	-42.26	<i>-40.73</i>	-41.40	<i>-39.87</i>	-20.37	<i>-19.86</i>	-19.14	<i>-18.60</i>
4S_o	18.91	<i>18.11</i>	19.50	<i>18.51</i>	-43.23	<i>-41.89</i>	-35.03	<i>-33.94</i>	-24.32	<i>-23.79</i>	-15.53	<i>-15.43</i>
4A_o	7.87	<i>7.50</i>	8.48	<i>8.32</i>	-32.46	<i>-31.32</i>	-25.71	<i>-24.88</i>	-24.59	<i>-23.82</i>	-17.23	<i>-16.56</i>
4S_i	13.10	<i>12.53</i>	13.38	<i>12.94</i>	-37.41	<i>-36.22</i>	-32.49	<i>-31.62</i>	-24.31	<i>-23.69</i>	-19.11	<i>-18.68</i>
4A_i	8.44	<i>7.93</i>	-	-	-33.34	<i>-32.27</i>	-	-	-24.90	<i>-24.34</i>	-17.27	<i>-16.94</i>
5	22.56	<i>21.62</i>	22.96	<i>21.84</i>	-42.37	<i>-40.87</i>	-38.18	<i>-36.54</i>	-19.81	<i>-19.25</i>	-15.22	<i>-14.70</i>
6	24.01	<i>22.81</i>	24.39	<i>23.22</i>	-40.25	<i>-39.07</i>	-39.63	<i>-38.44</i>	-16.24	<i>-16.26</i>	-15.24	<i>-15.22</i>

Substituent effect on carbonyl oxides

Methyl carbonyl oxide exists as two different conformers: the *anti* (**2A**) and *syn* (**2S**) compounds. It is worth noting that **2S** is more stable than **2A** both in the gas phase (2.9 kcal mol⁻¹) and in solution (1.8 kcal mol⁻¹). As mentioned earlier [6, 9, 31, 32, 33, 46, 47], long-range attractive interactions between the hydrogens on the methyl group and the terminal oxygen stabilize compound **2S** over **2A**. The O1O2 bond is longer than the corresponding one in compound **1**; this difference amounts to 0.017 Å for **2S** and to 0.014 Å for **2A**. Earlier results on methyl carbonyl oxide have also shown bond elongation and increase in dipolar character relative to the parent carbonyl oxide [9, 31, 32, 33, 46].

Consideration of the *anti* (**3A**) and *syn* (**3S**) isomers of cyano carbonyl oxide has revealed that the *anti* isomer **3A** is more stable than the *syn* isomer **3S** by 0.3 kcal mol⁻¹ in the gas phase. Because of its higher dipole (3.80 D), however, **3S** is more stable than **3A** (1.83 D) by 0.8 kcal mol⁻¹ in solution. The *anti* and *syn* conformers of cyano carbonyl oxide **3A** and **3S** have almost identical bond lengths. Because of its electron-withdrawing properties, the cyano group weakens the O1C3 bond which is longer than that in the parent compound **1**. On the other hand, in both conformers the O1O2 bond is shorter than that in **1**. This behavior is more significant with MP2/6-31+G(d) calculations, with which we have investigated the ozonolysis of acrylonitrile [48]. We have discovered that the O1O2 bond has quasi double-bond character and the O1C3 bond has quasi single-bond character, thus the charges are localized on oxygens O1 and O2 instead of O1 and C3.

The methoxy group can be either *syn* or *anti* to the terminal oxygen; furthermore, for each position two different orientations of the methyl group around the C3O4 are possible. Thus four different conformers, **4S_o**, **4S_i**, **4A_o**, and **4A_i** have been optimized. In the gas phase, the relative energies (in kcal mol⁻¹) of these compounds have been determined as $E_{4S_i}(0.0) < E_{4A_i}(0.7) < E_{4S_o}(4.3) < E_{4A_o}(4.3)$. The energetic preference for the **4S_i** conformer over the others is because of its small dipole mo-

gies for the isomerization of carbonyl oxides to dioxiranes (ΔE_{RXN}); all values are in kcal mol⁻¹, values in italics include the ZPE corrections

ment and the attractive interactions between the terminal oxygen (O2) and H7 of the methyl group. Also note that in **4S_i** and **4A_i** the methoxy group points towards the carbonyl oxygens and because of this stabilizing interaction the inner isomers "i" are more stable than the outer isomers "o". In solution, the relative stability of these compounds can be shown as $E_{4A_i}(0.0) < E_{4S_o}(0.7) < E_{4S_i}(1.7) < E_{4A_o}(1.8)$. Conformer **4A_i** is stabilized in polar medium more than **4S_i**, because of its higher dipole moment. Also it is worth noting that conformer **4S_o** is stabilized the most in polar environments, because of its high dipole moment. In these compounds (**4S_i**, **4S_o**, **4A_i**, and **4A_o**), the O1C3 bond is shorter and the O1O2 bond is longer than the corresponding bonds in carbonyl oxide. Electron donation from the methoxy group shortens the O1C3 bond. In **4A_i**, **4A_o**, **4S_i** the O1O2 bond lengthens by almost 5% in comparison with **1**, partly because of the stabilizing interactions between the terminal oxygen and either H5 or the hydrogens of the methyl group. In **4S_o**, although the O1O2 bond is ~3% longer than that in **1**, the O2–O4 repulsion inhibits stabilization of this compound.

In dimethyl carbonyl oxide (**5**), the hydrogens of the two methyl groups are staggered relative to each other. The hydrogens of the *syn* methyl group are directed towards the terminal oxygen, because of the stabilizing interactions between them. The properties and geometry of dimethyl carbonyl oxide, **5**, have been discussed in previous studies at different levels [6, 9, 31, 32, 33, 46].

In dicyano carbonyl oxide, **6**, the O1C3 and O1O2 bonds have quasi single-bond character, supporting the diradicaloid character of this structure as suggested earlier [11]. Among all the compounds studied dicyano carbonyl oxide is the one in which the shortening of the O2O3 bond (2%) and the lengthening of the O1C3 bond are maximum (3%). The presence of two electron-withdrawing groups induces motion of electrons from the terminal oxygen towards C3.

Substituent effect on transition states

Two transition structures, **2ATS** and **2STS**, have been located for the conversion of **2A** and **2S** to **2D**. In the gas phase, **2STS** is slightly earlier than **2ATS** as indicated by the length of the critical bond O2C3, which is 0.010 Å shorter in the former than in the latter. This observation can be interpreted by the fact that the O1C3 bond is longer in **2S** than in **2A**, and **2S** is closer to **2STS** than **2A** is to **2ATS**. Additionally, the methyl group is *syn* to the end oxygen in **2S** and the end Hs are polarized: the C3C4 bond is stronger and the O1C3 bond is weaker than in **2A**. In solution, the situation is reversed; **2ATS** is formed before **2STS**.

The transition state **3ATS** is formed slightly before **3STS** in both media; the O2C3 bond of **3ATS** is 0.008 Å shorter in the gas phase and this difference reduces to 0.007 Å in solution. Both **3STS** and **3ATS** have the O1O2 bond shorter than **1TS**. As in **3S** and **3A** the cyano group induces the motion of electrons from O2 towards O1.

Four different transition structures corresponding to the four different conformers (**4S_iTS**, **4S_oTS**, **4A_iTS**, and **4A_oTS**) have been located for the methoxy substituent. Except for **4S_oTS**, the O1C3 bond shortens and the O1O2 and O2C3 bonds lengthen in comparison with **1TS**.

The transition structure **5TS** is formed after **2ATS** and **2STS**. In the polar medium, however, this structure resembles the more polar carbonyl oxide rather than dioxirane. **6TS** has a longer O1C3 bond than **1TS** (2%) but a shorter O1O2 bond (2%) than **1TS**, and resembles the reactant, **6**.

Substituent effect on dioxiranes

The main feature in all the dioxirane compounds is the elongation of the C3X4 (X=C, O) bond in comparison with that in carbonyl oxides.

Methyl dioxirane (**2D**) has only one conformer in which the hydrogens of the methyl group are *gauche* to the ring.

Cyano dioxirane (**3D**) has also one conformer and the CC bond has lengthened in comparison with those in **3S** and **3A**, because of the repulsive interactions between the lone pairs of ring oxygens and the π orbitals of the cyano group.

Depending on the position of the methyl group relative to the three-membered ring, two different conformers for methoxy dioxirane, **4D_o** and **4D_i**, have been located. The C3O4 bond is longer in methoxy dioxiranes, mainly because of the repulsion between the dioxirane ring and the substituent. This elongation is greater in **4D_i**, because of the bulkiness and position of the substituent. In compound **4D_o**, the methoxy group orients itself such that the torsional angle C6O4C1H5 is 36.5°; in this way, the lone pairs of the ring oxygens and the oxygen of the methoxy group do not repel each other.

In compound **5D**, as in the single-substituted dioxirane (**2D**), the methyl groups are *gauche* to the dioxirane ring and minimize steric interactions. As noted earlier by Cremer [15], the presence of geminal methyl groups increases the stability of the three-membered ring (Table 2).

The presence of two cyano groups in **6D** does not alter the geometric features of the dioxirane ring, **1D**.

Substituent effect on the energetics of the conversion reaction

The interconversion of carbonyl oxide (**1**) to dioxirane (**1D**) is an exothermic reaction ($-23.2 \text{ kcal mol}^{-1}$) with a forward barrier of $20.5 \text{ kcal mol}^{-1}$ and a reverse barrier of $43.8 \text{ kcal mol}^{-1}$. In solution, although the forward barrier does not change; the reverse barrier is reduced by $3.1 \text{ kcal mol}^{-1}$ and the reaction energy decreases by $3.5 \text{ kcal mol}^{-1}$.

Comparison of the *syn*- and *anti*-substituted carbonyl oxides shows that the interconversion mechanism is easi-

er for the *anti* conformer, **2A**, for which the destabilizing steric effects caused by the presence of the methyl group is minimized. The forward barrier is reduced by 7.0 kcal mol⁻¹ in the gas phase. The energy profile changes only slightly in solution. The *syn* position of the methyl group in **2S** inhibits somewhat (2.9 kcal mol⁻¹) the cyclization of carbonyl oxide to dioxirane. The ΔE_I (24.0 kcal mol⁻¹) and ΔE_{II} (44.4 kcal mol⁻¹) values are in excellent agreement with those calculated by Cremer (23.8, 44.0 kcal mol⁻¹, respectively) [30, 32, 33] but lower than the results of Anglada et al. [31].

For cyano carbonyl oxide the isomerization is favored for **3A**, as for the methyl substituent. This is probably because of steric hindrance created by the bulkiness of the substituent when it is *syn* to the terminal oxygen, resulting in repulsive interactions between the π orbitals of the cyano group and the lone pairs of the terminal oxygen. Nevertheless, ΔE_I and ΔE_{II} for the *anti* conformer are slightly smaller in solution (1.4 kcal mol⁻¹ and 0.5 kcal mol⁻¹, respectively). The change in barrier heights mostly stems from the higher stabilization of **3ATS** compared with **3STS**. There is only one conformer for cyano dioxirane, namely **3D**. The reaction energy for **3S** is 0.3 kcal mol⁻¹ smaller than the reaction energy of **3A** in the gas phase; ΔE_{RXN} for **3A** is, however, larger by 0.8 kcal mol⁻¹ in solution.

The energy barrier for the isomerization reactions, ΔE_I , is lower for the *anti* conformers, as expected, because of small steric interactions of the methyl group with the terminal oxygen. This behavior is also manifested in the lengths of the O1O2 bonds in **4A_oTS** (1.505 Å) and **4S_oTS** (1.529 Å). The same is true for **4A_iTS** (1.512 Å) and **4S_iTS** (1.524 Å) except that we were unable to locate **4A_iTS** in solution. The barriers for **4S_i** and **4S_o** are lower for the **4S_i** conformer in both media (5.58 kcal mol⁻¹ in the gas phase and 5.57 kcal mol⁻¹ in solution). It seems that the stabilizing interactions between the methyl group and the terminal oxygen facilitate the formation of the dioxirane ring. On the other hand, in the gas phase conversion of **4S_o** to **4D_o** is slightly more exothermic than conversion of **4S_i** to **4D_i**. This behavior changes in solution, however, and conversion of **4S_i** to **4D_i** is 3.3 kcal mol⁻¹ more exothermic than the conversion of **4S_o** to **4D_o**.

The forward barrier for the conversion of compound **5** to **5D** is slightly higher than that for carbonyl oxide, **1**. The energetics for the barriers for dimethyl carbonyl oxide (21.6, -40.9 kcal mol⁻¹) are identical with those calculated by Cremer (21.4, -40.6 kcal mol⁻¹) [30, 33] but lower than those with MP2/6-31G(d,p) (23.8, -56.7 kcal mol⁻¹) [49] and Anglada's MRDCI results [31]. Dimethyl substitution destabilizes compound **5D** and the reverse barrier increases by ~4 kcal mol⁻¹. Also note that in both media isomerization of the *anti* conformer of methyl carbonyl oxide, **2A**, is much easier than conversion of **5**.

The ΔE_I value for the isomerization of dicyano carbonyl oxide (**6**) is slightly higher than the barriers of **3A** and **3S** whereas the ΔE_{II} and ΔE_{RXN} values are lower in

both media. Although there are two electron-withdrawing groups on the carbonyl oxide the change in ΔE_{RXN} between the two media is small (1.0 kcal mol⁻¹) because of the polar nature of **6**, **6TS** and **6D** which are almost identically stabilized in solution.

Optimizations in solution (Table 1) have shown that ZPE are medium independent. Differences between E_{ELEC} for the two media stem from different electrostatic interactions in a polar environment.

The calculated heats of formation (Table 2) reflect the relative stability of the substituted carbonyl oxides and dioxiranes. It is noteworthy that ΔH_f values are highly dependent on the level and reactions used in the calculations, as indicated by Cremer et al. [33], and they are used for qualitative support of the discussion on the relative stabilities of the compounds studied. The methoxy substituent with its electron-donor character stabilizes carbonyl oxide and dioxirane with a preference for the inner position. The cyano group is a representative of electron-withdrawing groups and destabilizes both carbonyl oxide and dioxirane. Dicyano carbonyl oxide is more unstable than its mono cyano counterpart. Among the methyl-substituted carbonyl oxides and dioxiranes **2S** is more stable than **2A** because the end methyl group interacts somewhat with the terminal oxygen. Also note that **4D_i** is more stable than **4D_o** because of the interactions of the hydrogens of the methyl group with the ring oxygens.

Conclusion

Our computational results have shown that the conversion of carbonyl oxides to dioxiranes depends mainly on the electronic nature of the substituents and somewhat on the polarity of the medium. The geometries of the carbonyl oxides and the transition states depend on the type of the substituent whereas the structure of dioxirane is not affected by the substituent except for the methoxy group. The *syn* isomers of carbonyl oxides are always more stable than the *anti* isomers except for the cyano group. It can be concluded that the stability of *syn* isomers is a result of attractive interactions between hydrogens and the terminal oxygen, which are absent in cyano carbonyl oxide. Changing the polarity of the medium causes drastic changes in the geometries of carbonyl oxides and transition states; the structures with higher dipoles are stabilized more in polar environments. The simple SCIPCM method used cannot reflect the complex situation that can occur by coordination of the solvent to carbonyl oxides. For all dioxiranes, the CO bonds are in the range of 1.390–1.400 Å, the OO bonds are approximately 1.505 Å except for the methoxy group which has longer OO bonds (1.522 Å).

The energetics of the reactions considered are substituent-dependent; in particular a methoxy group in the *anti* position reduces the barrier considerably. In general, the conversion of *anti*-substituted carbonyl oxides into dioxiranes is found to be easier than conversion of *syn*-

substituted carbonyl oxides. Disubstitution favors the ring-opening reaction of dioxiranes. All ring closure reactions are found to be exothermic in both media; the reaction energies (ΔE_{RXN}) are lower by 1 to 8 kcal mol⁻¹ in solution, depending on the substituent. As a result, it can be stated that the conversion of carbonyl oxides to dioxiranes seems to be the major process in the gas phase but alternative reactions such as reactions between carbonyl oxides and the solvent molecules might dominate over ring closure in solution. Polar environment can stabilize other intermediates energetically, and the possibility of ring closure reaction can be very low [3].

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