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# Peroxide Chemistry

## Mechanistic and Preparative Aspects of Oxygen Transfer

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Research Report

### 6.1 Introduction

Carbonyl C-oxides **1** were proposed as reactive intermediates in the ozonolysis of alkenes by Crager et al. in 1949 [1, 2]. Although a large number of trapping experiments are consistent with the formation of **1** as short-lived intermediates, the direct spectroscopic characterization of **1** during an ozonolysis reaction has not been successful, so far. The only route to the spectroscopic characterization of **1** is the oxidation of diazo compounds, either directly with  $^{18}\text{O}_2$  (single route) [3-7] or via the corresponding carbene with  $^{18}\text{O}_2$  (triple route) [8-14] (Scheme 6.1). Two techniques have been shown to be particularly useful for the characterization of **1**: the matrix



## 6 Carbonyl *O*-Oxides and Dioxiranes – From Laboratory Curiosities to Useful Reagents

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### Abstract

Carbonyl *O*-oxides **1** and the isomeric dioxiranes **2** are highly reactive oxidation reagents. While the chemistry of dimethyldioxirane and several other semi-stable dioxiranes has been established over the last years, many aspects of the carbonyl oxide reactivity are still unknown. We here describe the synthesis of kinetically stabilized carbonyl oxides **1** and dioxiranes **2** via oxidation of diazo compounds or carbenes. Thus, dimesityldioxirane **2b** is in substance stable and could be characterized by X-ray crystallography. As expected, the reactivity of **2b** is much lower than that of dimethyldioxirane. Dimesitylketone *O*-oxide could be generated in a variety of solvents and is stable in the dark at temperatures below  $-70\text{ }^{\circ}\text{C}$ . The influence of substituents on the stability and reactivity of **1** and **2** is discussed.

### 6.1 Introduction

Carbonyl *O*-oxides **1** were proposed as reactive intermediates in the ozonolysis of alkenes by Criegee et al. in 1949 [1, 2]. Although a large number of trapping experiments are consistent with the formation of **1** as short-lived intermediates, the direct spectroscopic characterization of **1** during an ozonolysis reaction has not been successful, so far. The only route to the spectroscopic characterization of **1** is the oxidation of diazo compounds, either directly with  $^1\text{O}_2$  (singlet route) [3–7] or via the corresponding carbenes with  $^3\text{O}_2$  (triplet route) [8–14] (Scheme 6.1). Two techniques have been shown to be particularly useful for the characterization of **1**: the matrix isola-

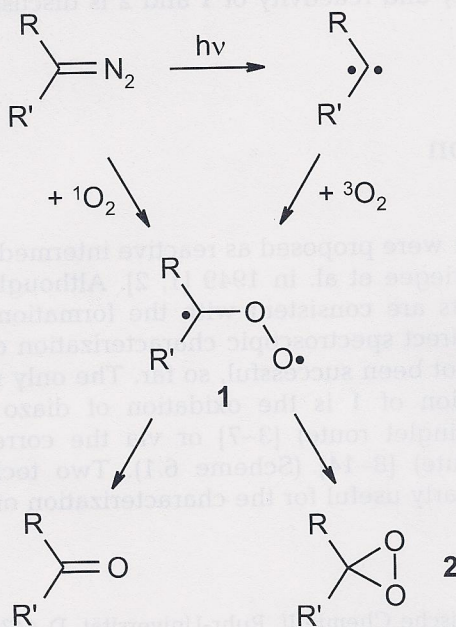
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tion in inert gases at cryogenic temperatures, and laser flash photolysis (LFP) in solution with nanosecond time resolution.

In typical matrix isolation experiments diazo compounds (or the isomeric diazirines) are isolated in 0–1% oxygen-doped argon matrices at 10 K [14, 15]. Photolysis produces the carbenes, which in many cases are completely stable under these conditions. Subsequent annealing at 30–40 K allows the diffusion of the O<sub>2</sub> molecules and thermal reaction with the carbene to produce **1** on a time scale of several minutes (triplet route). Singlet oxygen is rapidly deactivated in solid argon, and thus the singlet route can not be used in matrices. The advantage of matrix isolation is that the reactive intermediates (carbenes, carbonyl oxides and photoproducts of the carbonyl oxides) are produced step by step and characterized by IR and UV/VIS spectroscopy.

LFP allows to directly monitor carbonyl oxides in solution as transient species [5, 16–21]. The lifetime of typical carbonyl oxides is in the order of milliseconds. Both the singlet and the triplet route have been used for the synthesis of **1**. While the UV/VIS and IR spectra from LFP experiments show a lower resolution than the matrix spectra, the advantage of LFP is that kinetic data under "normal" laboratory conditions (solution, room temperature) are obtained. Thus, the combination of LFP and matrix spectroscopy provides the full range of spectroscopic and kinetic data.

The most pronounced spectroscopic features of **1** is the intense O–O stretching vibration around 900 cm<sup>-1</sup> and a strong and broad absorption in the visible region of the spectrum ( $\lambda_{\text{max}} = 400\text{--}500\text{ nm}$ ), assigned to a  $\pi \rightarrow \pi^*$  transition [14]. Molecule **1** is formally a closed-shell molecule, but possesses



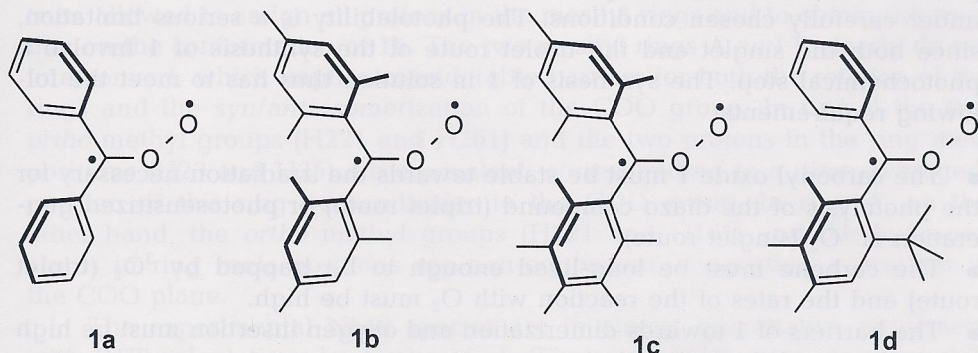
Scheme 6.1

also significant biradical character [22] and, consequently, single determinant methods with little dynamic electron correlation such as second or third order Møller–Plesset perturbation theory (MP2, MP3) fail to describe **1** adequately [23]. With methods that include a larger amount of electron correlation effects such as Coupled Cluster theory with single and double excitations and a perturbative inclusion of triple excitations, CCSD(T), or density functional theory (DFT) with hybrid functionals as, e.g. B3LYP, better results are obtained so that calculated and experimental IR spectra are in good agreement [24].

Apart from their role in the ozonolysis reaction, the chemistry of carbonyl oxides **1** is not very well known, although Murray and others demonstrated that **1** are powerful oxidizing reagents [4, 25]. One of the most interesting reactions of **1** is the insertion of oxygen into non-activated CH bonds. Thus, benzophenone *O*-oxide **1a** oxidizes toluene to a mixture of cresols and *N*-acetyl-phenylalanine to *N*-acetyl-tyrosin [25]. The latter reaction is reminiscent to the reactivity of monooxygenases in biological systems.

Dioxiranes **2** were postulated first as intermediates in the Baeyer–Villiger oxidation [26], however, isotopic labeling experiments later clearly revealed that the two oxygen atoms are not equivalent, and thus the symmetrical intermediate **2** was excluded [27, 28]. Under the conditions of matrix isolation dioxiranes **2** are readily obtained by long wavelength photolysis ( $\lambda > 500$  nm) of **1**, and this method has been used for the first spectroscopic characterization of a dioxirane [11, 29]. A breakthrough in dioxirane chemistry was the synthesis of dimethyldioxirane (**2**, R = CH<sub>3</sub>) in acetone solution, which is fairly stable at room temperature [30, 31]. Meanwhile, dimethyldioxirane has found many applications as mild oxygen transfer reagent [32–35].

In contrast to carbonyl oxides **1**, dioxiranes **2** do not exhibit characteristic IR and visible absorptions. The O–O stretching vibration leads to a weak absorption around 750 cm<sup>-1</sup>, and the asymmetrical and symmetrical CO stretching vibrations are found around 900 and 1300 cm<sup>-1</sup>, respectively [36–38]. Solutions of dimethyldioxirane (**2**, R = CH<sub>3</sub>) in acetone are weakly yellow, however, the origin of this color is not yet clear. Due to the lack of



Structure 6.1a–d

characteristic absorptions, transient dioxiranes **2** can only be detected by matrix isolation spectroscopy, but not by the less sensitive LFP technique.

HF theory fails to describe the electronic structure of dioxiranes **2** accurately. Since the structure of the parent dioxirane (**2**, R = H) could be determined by microwave spectroscopy [39, 40], the calculated geometrical data can be directly compared to the experiment. In a recent systematic study Cremer et al. demonstrated that very expensive CCSD(T) calculations including large basis sets with f functions are necessary to reproduce the microwave structure within the experimental errors [41]. However, the far less demanding DFT methods, and in particular the B3LYP functional, perform reasonably well and are thus the method of choice for the theoretical description of larger dioxiranes.

The combination of matrix isolation spectroscopy, laser flash photolysis, and theoretical methods allowed the detailed study of unstable and under "normal" laboratory conditions transient carbonyl oxides **1** and dioxiranes **2**. The next step is now the synthesis of derivatives which are stable enough to be studied by conventional methods and especially allow to investigate the rich chemistry of these species.

## 6.2 Dimesitylketone O-oxide

### 6.2.1 Synthesis

A successful technique for the stabilization of reactive molecules is the introduction of sterically demanding groups such as *tert.*-butyl or mesityl groups. However, even kinetically stabilized carbonyl oxides **1** are expected to be thermally labile, reactive towards many solvents, and in addition extremely photolabile. Therefore, the synthesis of **1** in solution has to be carried out under carefully chosen conditions. The photolability is a serious limitation, since both the singlet and the triplet route of the synthesis of **1** involve a photochemical step. The synthesis of **1** in solution thus has to meet the following requirements:

- The carbonyl oxide **1** must be stable towards the irradiation necessary for the photolysis of the diazo compound (triplet route) or photosensitized generation of  $^1\text{O}_2$  (singlet route).
- The carbene must be long-lived enough to be trapped by  $^3\text{O}_2$  (triplet route) and the rates of the reaction with  $\text{O}_2$  must be high.
- The barriers of **1** towards dimerization and oxygen insertion must be high to avoid a rapid decay in solution.
- The solvent has to be inert towards the highly oxidizing **1**.

A carbonyl oxide that meets all these requirements is dimesitylketone *O*-oxide **1b**, which Scaiano et al. generated (LFP) as a transient species in solution from dimesityldiazomethane **3b** both via the singlet and the triplet routes [5]. In acetonitrile at room temperature the half-life of carbonyl oxide **1b** is 374 ms, considerably longer than that of other carbonyl oxides.

Dimesitylcarbene **4b** is a sterically hindered carbene, which in the absence of oxygen in solution is long-lived, while the reactivity towards  $O_2$  is only one order of magnitude smaller than that of diphenylcarbene. The absorption maximum of **3b** is at 493 nm, and 515 nm irradiation results in a rapid loss of nitrogen. If **3b** is irradiated in oxygen saturated solvents ( $CCl_3F$ , acetonitrile, THF) at  $-80\text{ }^\circ\text{C}$ , an intense yellow solution of **1b** with an absorption maximum  $\lambda_{\text{max}} = 398\text{ nm}$  is obtained [42–44]. The yield of **1b** is estimated to 20–25%. As expected, **1b** is very photolabile and irradiation with  $\lambda > 475\text{ nm}$  rapidly results in the decolorization of the solution and formation of dioxirane **2b** as the major product.

Alternatively, carbonyl oxide **1b** was synthesized by the reaction of diazo compound **3b** with  $^1O_2$  in a variety of solvents with small amounts of photosensitizers. Good results were obtained in  $CCl_3F$ /octafluoroporphyrin, THF/rose bengal, or pentane/ $C_{60}$  at temperatures below  $-80\text{ }^\circ\text{C}$  and  $\lambda > 570\text{ nm}$  excitation.

### 6.2.2 Spectroscopic Characterization

Carbonyl oxide **1b** is the first carbonyl oxide that could be characterized by  $^1\text{H}$  and – after  $^{13}\text{C}$  isotopic labeling –  $^{13}\text{C}$  NMR spectroscopy (Figure 6.1) [43]. The chemical shift of the “carbonyl” carbon atom of **1b** was found at 211.0 ppm, 8.5 ppm shifted downfield from dimesitylketone. The deshielding suggests polarization with a partial positive charge at this carbon atom although paramagnetic effects may also determine the chemical shift of the carbonyl carbon.

The determination of the long range H,H couplings in the  $^1\text{H}$  NMR spectrum allowed to assign all protons in the mesityl rings and to obtain information on the conformation of **1b**. The two mesityl rings A and B clearly do not interconvert, which implies considerable barriers for both the rotation of the rings and the *syn/anti*-isomerization of the COO group. In ring B the two *ortho* methyl groups (H221 and H261) and the two protons in the ring *meta* positions (H23 and H25) are equivalent, corresponding to a (time-averaged) position of this ring perpendicular to the COO group. In ring A, on the other hand, the *ortho* methyl groups (H121 and H161) and the hydrogen atoms in ring *meta* positions are non-equivalent, suggesting a position in the COO plane.

The experimental NMR spectra are in almost quantitative agreement with DFT calculations by Kraka et al. (Figure 6.1) [45]. The chemical shift of the “carbonyl” carbon atom is calculated to be 210.6 ppm, only 0.4 ppm

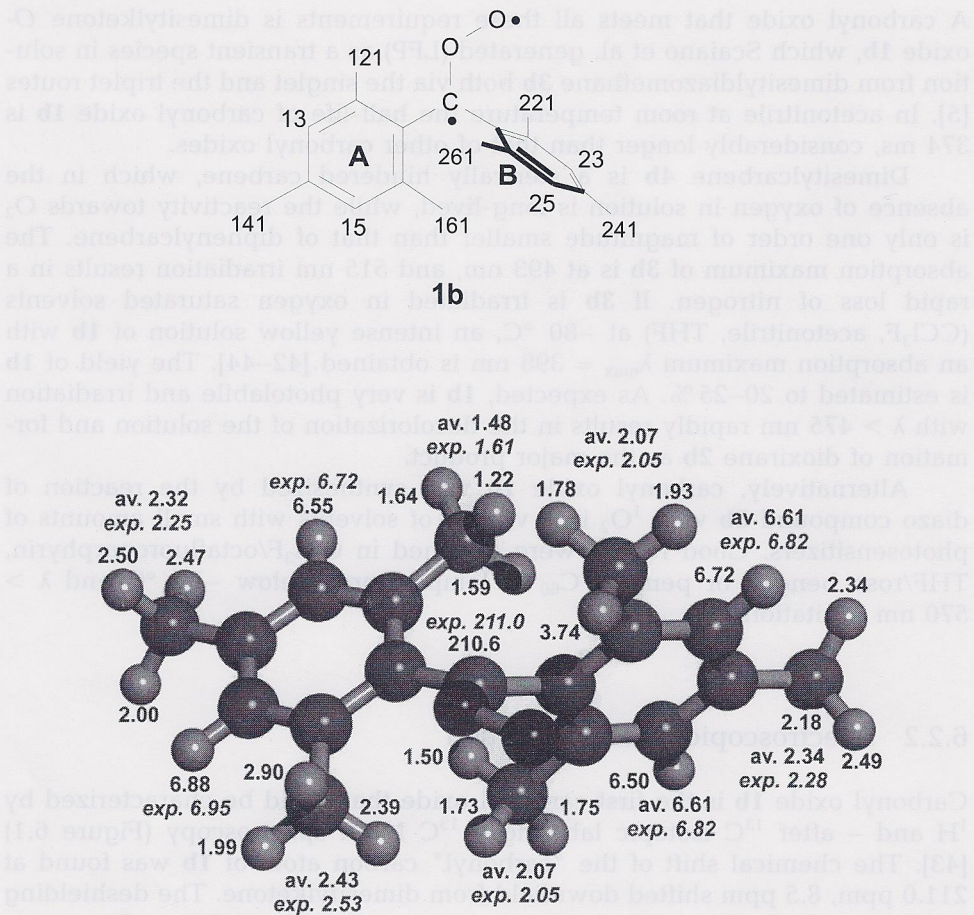
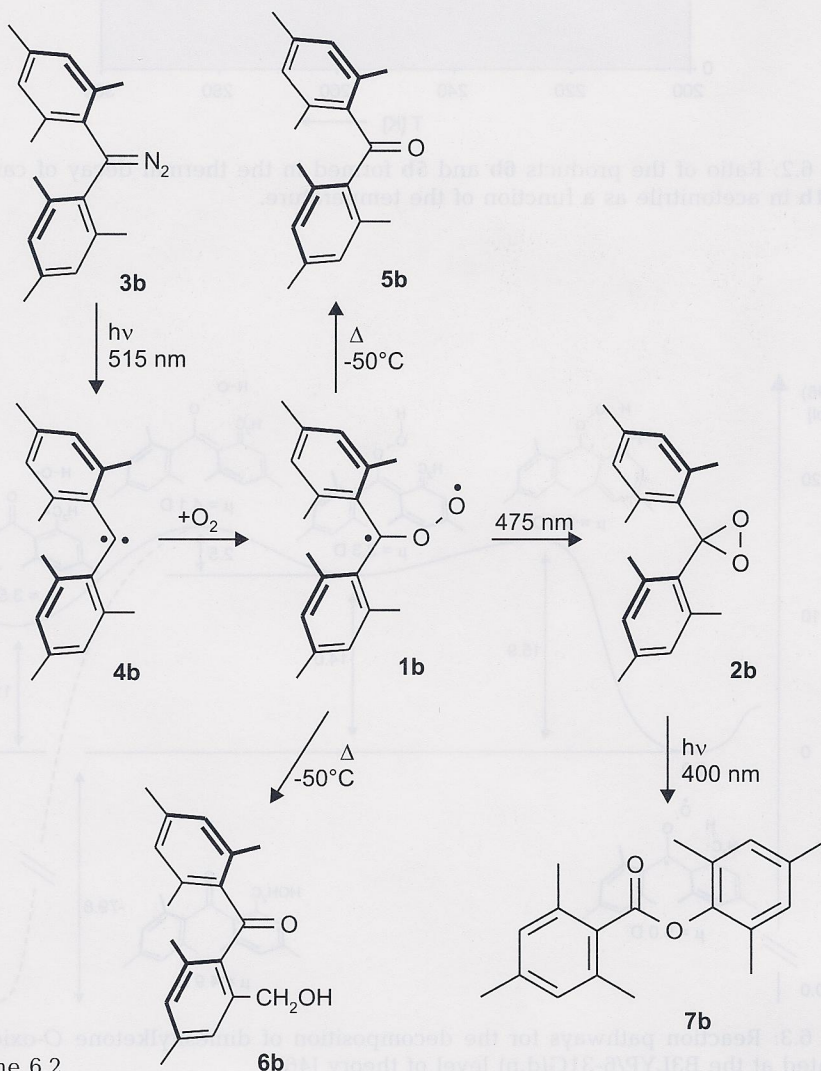


Figure 6.1: Experimental and calculated NMR data of dimesitylketone *O*-oxide **1b**. The calculated chemical shifts are given at the individual atoms. Experimental chemical shifts (exp., in italics) are compared to calculated shifts, averaged over symmetry-equivalent positions (av.) [43, 45].

from the experimental value. The chemical shifts of the individual protons in the *ortho* methyl groups in ring B range from 1.50 to 3.74 ppm, however, the average over all six protons (2.07 ppm) almost exactly matches the experimental value (2.05 ppm). A similar agreement of theory and experiment is observed for the other protons.

## 6.2.3 Thermal Decay

At  $-80\text{ }^{\circ}\text{C}$  carbonyl oxide **1b** is thermally stable, while above  $-50\text{ }^{\circ}\text{C}$  a rapid decay following first order kinetics with an activation enthalpy at 300 K of  $13.3 \pm 1\text{ kcal/mol}$  is observed. This is in contrast to benzophenone oxide (**1**, R = Ph), which decays with a second order kinetics to give the dimer as the principal product. The major products of the decay of **1b** are dimesitylketone **5b**, formed by loss of the terminal oxygen atom, or the benzyl alcohol **6b**, the insertion product of an oxygen atom into one of the *ortho* methyl groups (Scheme 6.2). The latter reaction is of interest as a model for the inser-



Scheme 6.2



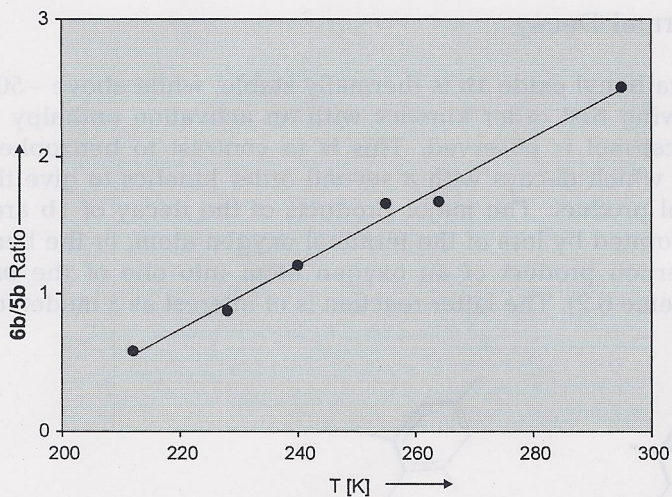


Figure 6.2: Ratio of the products **6b** and **5b** formed in the thermal decay of carbonyl oxide **1b** in acetonitrile as a function of the temperature.

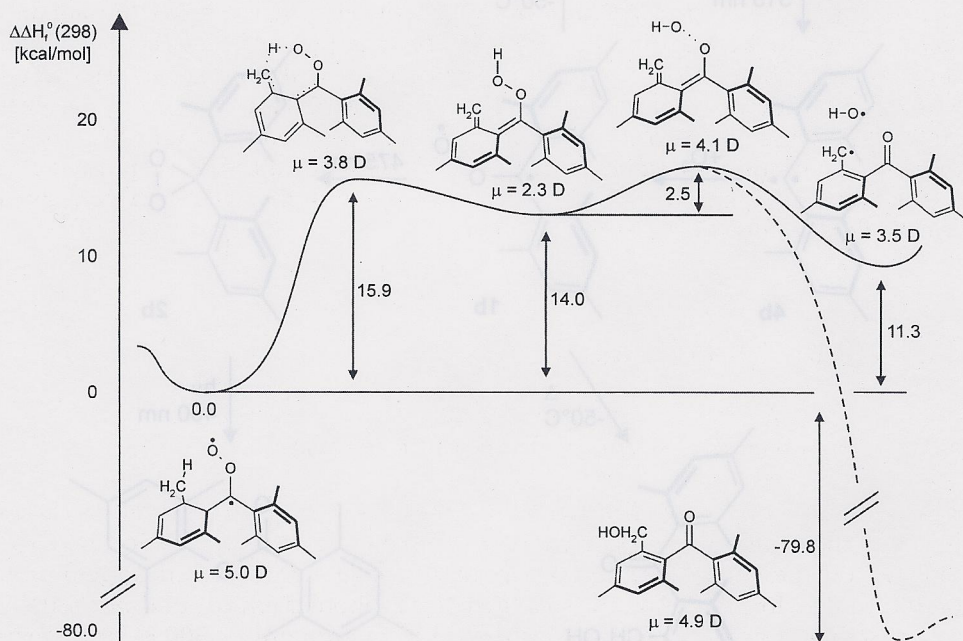


Figure 6.3: Reaction pathways for the decomposition of dimesitylketone O-oxide **1b**, calculated at the B3LYP/6-31G(d,p) level of theory [46].

tion of an oxygen atom into a non-activated CH bond and clearly demonstrates the oxidative power of carbonyl oxides.

The ratio of **5b/6b** depends both on the solvent and the temperature. Thus, in  $\text{CCl}_3\text{F}$  at room temperature the major product is alcohol **6b** ( $\mathbf{6b/5b} = 2.51$ ), while at  $-60\text{ }^\circ\text{C}$  the ketone **5b** is the main product ( $\mathbf{6b/5b} = 0.58$ ). Within this temperature range the  $\mathbf{6b/5b}$  ratio linearly decreases with decreasing temperature. In acetonitrile just the opposite behaviour is observed: the  $\mathbf{6b/5b}$  ratio increases from 0.1 at  $-6\text{ }^\circ\text{C}$  to 1.28 at  $-39\text{ }^\circ\text{C}$ , again with a linear temperature dependence (Figure 6.2). In hexane the  $\mathbf{6b/5b}$  ratio shows a peculiar behaviour: at  $-10\text{ }^\circ\text{C}$  the ketone **5b** is the major product ( $\mathbf{6ab/5b} = 0.31$ ). A decrease of the temperature to  $-35\text{ }^\circ\text{C}$  increases the ratio to 1.09, while the further decrease to  $-53\text{ }^\circ\text{C}$  again results in a smaller  $\mathbf{6b/5b}$  ratio (0.66 at the lowest temperature). Since the melting point of acetonitrile is at  $-44\text{ }^\circ\text{C}$ , it was not possible to measure the  $\mathbf{6b/5b}$  ratio in acetonitrile in this temperature range. The temperature dependence of the product ratio suggests that the products are formed in parallel reactions with different temperature dependence.

A mechanism of the thermal reaction of **1b** based on DFT calculations was proposed by Cremer and Kraka [46] (Figure 6.3). The key step of the thermal decomposition of **1b** is the abstraction of an *ortho* H-atom resulting in the formation of a very labile vinylhydroperoxide. The calculated activation enthalpy at 300 K for this step is 15.9 kcal/mol, close to the experimental value. The hydroperoxide either directly rearranges to **6b** or decomposes to OH and a benzyl radical, which by hydrogen abstraction from the solvent could generate ketone **5b**. Both processes will proceed via the transition state for O–O bond cleavage, which according to calculations is associated with an activation enthalpy of 2.5 kcal/mol at 300 K. However, in perdeuterated acetonitrile or hexane no deuterium was incorporated into **6b**, which rules out hydrogen abstraction from the solvent. An alternative pathway is the oxidation of the solvent via oxygen transfer from **1b**, which competes with the intramolecular oxygen transfer.

## 6.3 Dimesityldioxirane

### 6.3.1 Synthesis and Structural Characterization

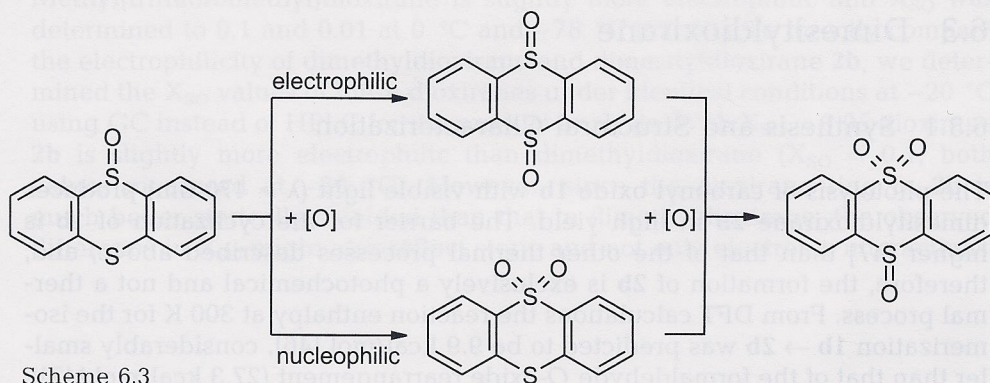
The photolysis of carbonyl oxide **1b** with visible light ( $\lambda > 470\text{ nm}$ ) produces dimesityldioxirane **2b** in high yield. The barrier for the cyclization of **1b** is higher [47] than that of the other thermal processes described above, and, therefore, the formation of **2b** is exclusively a photochemical and not a thermal process. From DFT calculations the reaction enthalpy at 300 K for the isomerization  $\mathbf{1b} \rightarrow \mathbf{2b}$  was predicted to be 9.9 kcal/mol [46], considerably smaller than that of the formaldehyde *O*-oxide rearrangement (27.3 kcal/mol [47]).

For the preparative scale synthesis of dioxirane **2b** a specially designed photoreactor using a Hg/Cd arc lamp and a  $\text{CuCl}_2/\text{HCl}$  filter solution was developed (Figure 6.4). The irradiation was carried out in  $\text{CCl}_3\text{F}$  purged with  $\text{O}_2$  at  $-70^\circ\text{C}$  and allowed to synthesize up to 300 mg of **2b** per run in 50–60% yield in the crude mixture. Since dioxirane **2b** is labile towards irradiation with short-wavelength visible light ( $\lambda < 420\text{ nm}$ ), the control of the photolysis wavelength is very critical.

After chromatographic purification the dioxirane is obtained as colorless crystals which at room temperature decompose within several days but at  $-20^\circ\text{C}$  are indefinitely stable. The X-ray structure of dimesityldioxirane **2b** reveals a comparatively short O–O distance of  $1.503\text{ \AA}$ , which is responsible for the stability of **2b** at room temperature [44] (Figure 6.5). The steric repulsion of the two mesityl groups leads to a widening of the central C–C–C angle ( $119.2^\circ$ ), which in turn results in a smaller O–C–O angle ( $64.2^\circ$ ) and thus O–O distance. For the parent dioxirane an O–O bond distance of  $1.516\text{ \AA}$  was determined by microwave spectroscopy [39], and for difluorodioxirane the O–O distance is even  $1.576\text{ \AA}$  [48, 49].

### 6.3.2 Reactivity

Compared to dimethyldioxirane (**2**,  $\text{R} = \text{CH}_3$ ), the reactivity of **2b** is to a great extent reduced. Thus, even electron rich olefins are only very slowly epoxidized, if at all. Triphenylphosphine and phenyl methyl sulfide, on the other hand, are readily oxidized. Thianthrene 5-oxide has been introduced by Adam et al as a sensitive chemical probe of the chemoselectivity of carbonyl oxides, dioxiranes, and other oxygen transfer agents [50–52] (Scheme 6.3). The ratio of the various thianthrene dioxides and trioxides defines the  $X_{\text{SO}}$  scale of the philicity of oxygen transfer reagents. Nucleophilic reagents such as peracid anions predominantly oxidize the sulfoxide functionality which results in  $X_{\text{SO}}$  values close to 1. Electrophilic reagents, on the other



Scheme 6.3

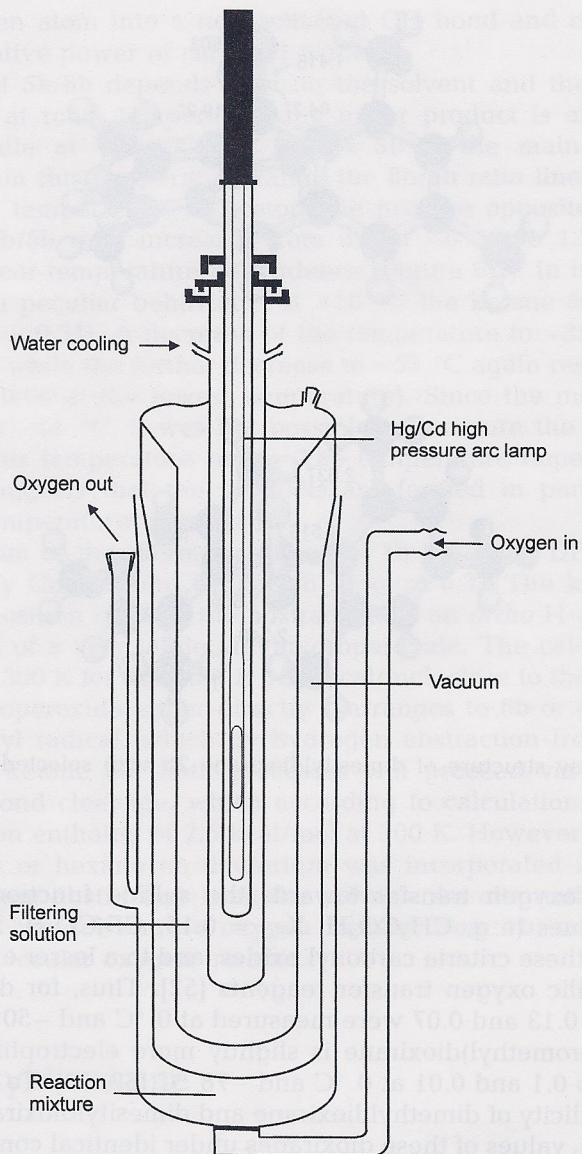


Figure 6.4: Photoreactor for the preparative scale synthesis of stable dioxiranes.

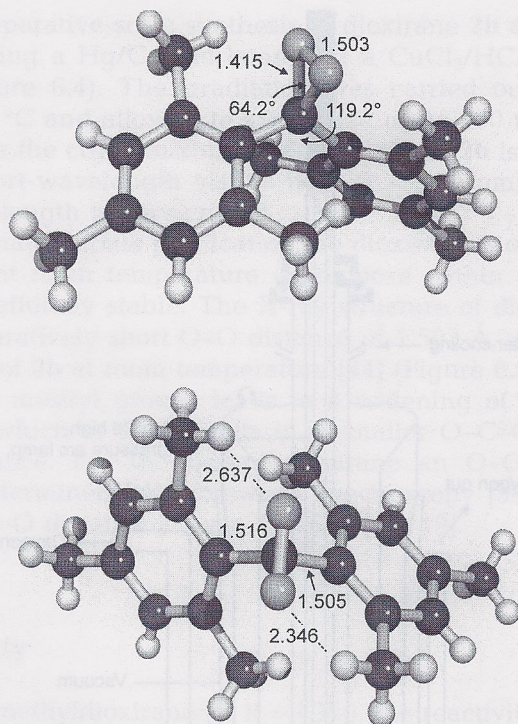


Figure 6.5: X-ray structure of dimesityldioxirane **2b** with selected bond lengths and angles.

hand, prefer oxygen transfer towards the sulfide functionality leading to small  $X_{SO}$  values (e.g.  $\text{CH}_3\text{CO}_3\text{H}$ ,  $X_{SO} = 0.16$ ;  $\text{CF}_3\text{CO}_3\text{H}$ ,  $X_{SO} = 0.01$ ) [53]. According to these criteria carbonyl oxides, and to a lesser extend dioxiranes, are electrophilic oxygen transfer reagents [52]. Thus, for dimethyldioxirane  $X_{SO}$  values of 0.13 and 0.07 were measured at 0 °C and -50 °C, respectively. Methyl(trifluoromethyl)dioxirane is slightly more electrophilic and  $X_{SO}$  was determined to 0.1 and 0.01 at 0 °C and -78 °C [52, 53]. To directly compare the electrophilicity of dimethyldioxirane and dimesityldioxirane **2b**, we determined the  $X_{SO}$  values of these dioxiranes under identical conditions at -20 °C using GC instead of HPLC for the product analysis. With  $X_{SO} = 0.05$  dioxirane **2b** is slightly more electrophilic than dimethyldioxirane ( $X_{SO} = 0.1$ , both values measured at -20 °C). However, since the dioxirane ring in **2b** is much better sterically shielded than that in dimethyldioxirane, the observed difference in  $X_{SO}$  might also reflect steric and not only electronic interactions.

## 6.4 Other Stable Carbonyl Oxides and Dioxiranes

Other in solution stable carbonyl oxides synthesized in our laboratory are mesityl(pentamethylphenyl) ketone *O*-oxide **1c** and (6-*tert.*-butyl-2,3,4-trimethylphenyl)phenylketone *O*-oxide **1d**. The carbonyl oxides **1c** and **d** were obtained from the corresponding diazo compounds as yellow solutions, stable at temperatures below  $-80$  °C. The UV/VIS spectra of **1c** and **d** with absorption maxima at 390 and 380 nm, respectively, are very similar to that of **1b**. A major difference between **1b** and the other carbonyl oxides **1c** and **d** is that for the latter *syn* and *anti* conformers of the COO group may be formulated. So far, **1c** and **d** were not characterized by NMR spectroscopy and thus the conformation in solution was not determined.

The structures of **1a**, **1b**, and **1d**, calculated at the B3LYP/6-31G(d) level of theory, are shown in Figure 6.6. Most noticeable is the short nonbonding O...H distance of 2.164 Å in **1a**, 2.093 Å in **1b**, and 2.050 Å in **1d** between the terminal COO oxygen atom and a neighbouring hydrogen atom. This interaction demonstrates the high polarity of the COO group and leads to a stabilization of the carbonyl oxide. To achieve a close interaction between the terminal oxygen atom and one of the *ortho* phenyl hydrogen atoms the out of the COO plane twisting of the phenyl groups is reduced from 29.3° in **1a** to just 9.5° in **1d**. The bulky *tert.*-butyl group in **1d** results in a almost perpendicular conformation of the second aryl ring. In **1b** the twisting of the mesityl groups is as expected larger than that of the phenyl rings in **1a**, and the terminal COO oxygen atom now interacts with one of the hydrogen atoms in an *ortho*-methyl group.

The decay of **1d** follows first order kinetics, the products have not yet been identified. The half life in  $\text{CCl}_3\text{F}/(\text{CBrF}_2)_2$  (1:1) drops from 194 min at  $-84$  °C to just 4 min at  $-48$  °C (Figure 6.7), which corresponds to an activation enthalpy of 5.8 kcal/mol. Thus, **1d** is considerably less stable than **1b** with lifetimes of 12,300 and 23 min at the same temperatures and an activation enthalpy for the thermal decay of 13.3 kcal/mol. Obviously, the less efficient shielding of the phenyl substituent in **1d** – compared to the mesityl group in **1b** – is not compensated by the additional *tert.*-butyl group in the second aryl ring.

The carbonyl oxides **1c** and **d** are photolabile and on visible light irradiation rearrange to the corresponding dioxiranes **2c** and **d**. The dioxiranes could be separated using reversed phase HPLC and showed a similar thermal and chemical stability as **2a**. Dioxirane **2c** was characterized by UV irradiation results in the rearrangement to esters **6**.

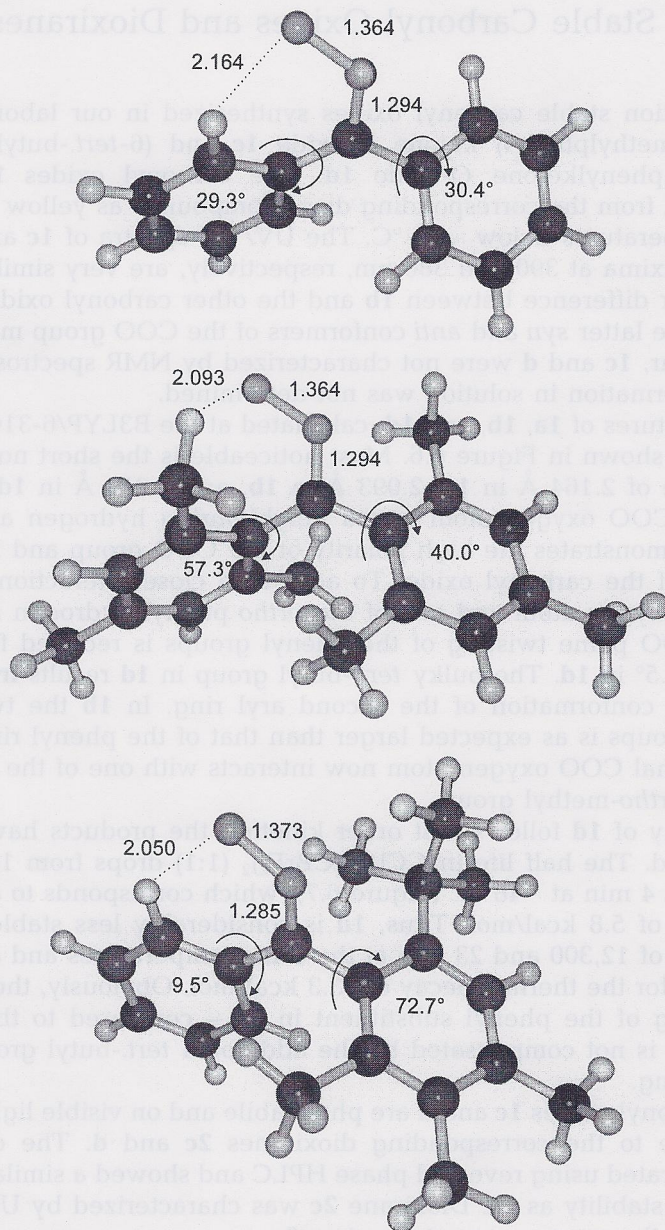


Figure 6.6: Structures and some geometrical data of carbonyl oxides **1a**, **1b**, and **1d**, calculated at the B3LYP/6-31G(d) level of theory.

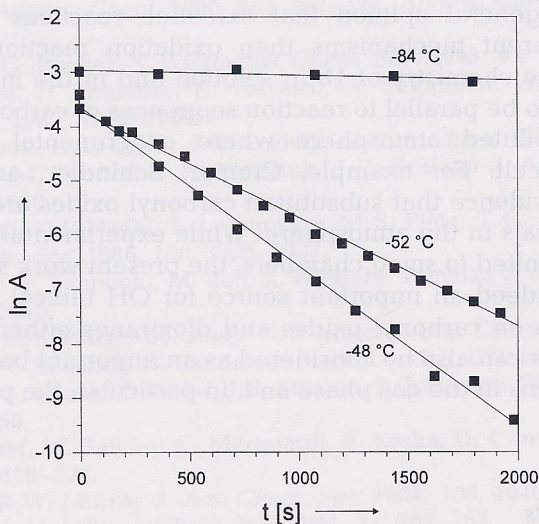


Figure 6.7: Kinetic data of the decay of carbonyl oxide **1d** in  $\text{CCl}_3\text{F}/(\text{CBrF}_2)_2$  (1:1) at various temperatures.

## 6.5 Conclusion

The synthesis of stable carbonyl oxides in solution at low temperature for the first time allows the detailed study of the chemistry of these species. Prerequisite for the successful synthesis of kinetically stabilized carbonyl oxides **1** and dioxiranes **2** was the knowledge of the reaction mechanisms from matrix isolation, LFP, and theoretical studies. The main advantage of stable – compared to transient – **1** and **2** is that other highly reactive oxidizing species, such as ozone, ozonides, peroxides, singlet oxygen etc., are excluded. The intramolecular insertion of the terminal oxygen atom of **1b** into one of the *ortho* methyl groups with a low activation barrier clearly demonstrates the power of carbonyl oxides as oxidizing reagents. The stable dioxiranes **2**, on the other hand, are much less reactive and more selective oxygen transfer reagents. Accordingly, **2** and related aryldioxiranes are suitable oxidants to study regio- and stereoselective epoxidation reactions of alkenes by dioxiranes, which despite their frequent use in synthetic chemistry are not well understood, with experimental and theoretical means in detail. Dioxiranes with sterically less demanding groups than mesityl are now synthesized in our laboratory and should fill the gap between dimesityl- and dimethyldioxirane so that regio- and stereoselectivity in dependence of steric bulk can be investigated.



There is the general opinion that oxidation reactions in condensed phases follow different mechanisms than oxidation reactions in the gas phase. However, the chemistry of **1b** in solution and in the matrix has been found in this work to be parallel to reaction sequences of carbonyl oxides discussed for the polluted atmosphere where experimental investigations become more difficult. For example, Cremer, Schindler, and co-workers [54, 55] provided evidence that substituted carbonyl oxides are an important source for OH radicals in the atmosphere. While experimental verification of OH production is limited to smog chambers, the present work shows that carbonyl oxides are indeed an important source for OH radical production. In this sense, research on carbonyl oxides and dioxiranes either in the matrix or in solution phases can also be considered as an important basis for probing oxidation mechanisms in the gas phase and, in particular, the polluted atmosphere.

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