Supplementary Material Available: Description of X-ray data collection parameters, positional and thermal parameters for all atoms, a complete listing of bond distances and angles, and observed and calculated structure factors for **3** and $(Ph_4P)_2Mo_2O_2As_4S_{14}$ (55 pages). Ordering information is given on any current masthead page.

Study of Carbonyl Oxide Formation in the Reaction of Singlet Oxygen with Diphenyldiazomethane[1]

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Carbonyl oxides are believed to be important reaction intermediates in the ozonolysis reaction. Criegee was the first to make this suggestion,[2,3] and carbonyl oxides are frequently referred to as Criegee intermediates. More recently it has been proposed[4] that they may be involved in the metabolic activation of carcinogenic polycyclic aromatic hydrocarbons to yield arene oxides.[5] In spite of their importance, carbonyl oxides have only recently been detected in a handful of examples. Cyclopentadienone oxide has been detected by IR spectroscopy in matrices at low temperatures,[6] while in solution only the intermediates produced by reaction of oxygen with 10,10-dimethyl-10-silaanthracen-9-(10*H*)-ylidene,[7] diphenylcarbene,[8] and fluorenylidene[9] have been detected by using laser flash photolysis.

Murray et al., in a detailed series of studies,[10-14] showed that carbonyl oxides can be conveniently produced by reaction of singlet oxygen with diazo compounds. However, we do not know of any examples where the carbonyl oxide produced in this manner has been detected directly. In this communication (a) we report the spectrum of the carbonyl oxide produced by reaction of singlet oxygen with diphenyldiazomethane, (b) we show that this intermediate is identical with that produced by reaction of triplet carbenes with oxygen,[15] thus providing conclusive proof of the mechanism proposed by Murray,[10-14] and (c) we have examined the kinetics of the reaction of singlet oxygen with the diazo precursor.

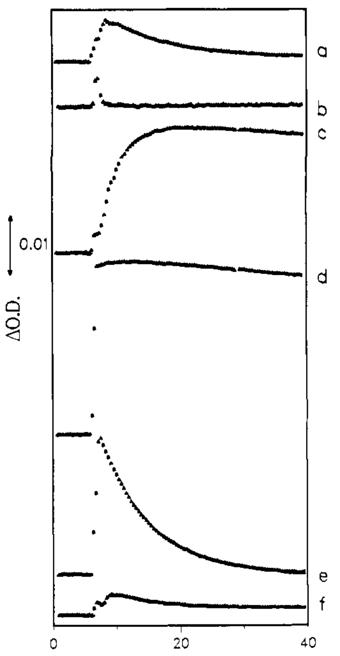

Figure 1. Time profiles obtained at 410 nm in acetonitrile at 300 K from a sample with 4 μM MB: (a) under N_2, λ_{ex} = 587 nm; (b) containing 7.7 mM O_2, λ_{ex} = 587 nm; (c) same as b with 1 mM Ph_2CN_2, λ_{ex} = 587 nm; (d) same as c, excited at 337.1 nm; (e) same as d containing 0.21 M 2,5-dimethyl-2,4-hexadiene, λ_{ex} = 337.1 nm; (f) same as e, λ_{ex} = 587 nm, note the initial "blip" due to MB^{*}.

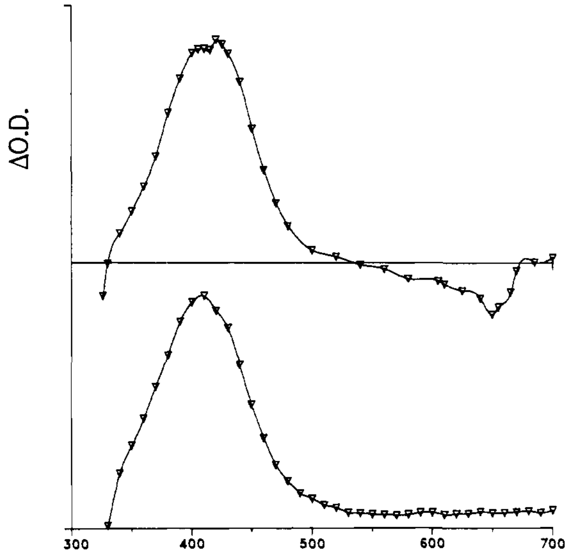

Figure 2. Transient spectrum (top) obtained by 587-nm excitation of an acetonitrile solution containing 4 μM MB, 1 mM Ph_2CN_2, and 7.7 mM O_2, at 300 K. Signal monitored between 8 and 12 μs after excitation. The bottom spectrum corresponds to benzophenone oxide produced by reaction of diphenylcarbene and oxygen,[8] under comparable conditions (λ_{ex} = 308 nm).

Singlet oxygen was generated by using methylene blue (MB) as a sensitizer in oxygen-saturated acetonitrile. MB, typically 4 μM, was excited with 587-nm pulses from a flash pumped dye laser.[16] The MB triplet ($\lambda_{max} \sim 430$ nm) was very long lived (≥10 μs) in deaerated solutions, but decayed essentially during

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(16) A flash-pumped dye laser (Candela UV-500M) operated with rhodamine 6G delivering 587-nm pulses (up to 1 J, ~250 ns) was used as excitation source. The concentration of MB used, 4 μM, ensures that the amount of energy absorbed by the sample is much less than that available during the laser pulse. Diphenyldiazomethane in acetonitrile does not yield any signals when irradiated under the same conditions in the absence or presence of oxygen. Details of our laser facility have been reported elsewhere.[17] All experiments were carried out using a flow system employing solutions saturated with O_2, N_2, or O_2/N_2 mixtures of known composition.

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the laser pulse (~250 ns) in oxygenated solution (Figure 1a,b, at 410 nm). Addition of 1 mM diphenyldiazomethane led to a well-resolved signal buildup which occurs with a lifetime of 3 μs (Figure 1c) and leads to the spectrum of Figure 2 (top). The 410-nm band in this spectrum is identical with that of the carbonyl oxide recently characterized in the reaction of diphenylcarbene with oxygen (Figure 2, bottom).[8] The same spectrum can also be obtained in the reaction mixture described above, when the laser excitation wavelength is 337.1 nm[18] instead of 587 nm. However, in this case the formation of the carbonyl oxide is much faster (see Figure 1d) reflecting the rapid reaction of oxygen with diphenylcarbene ($k_{O_2} = 5 \times 10^9$ M^{-1} s^{-1}).[8] The small buildup that follows the jump in trace d, Figure 1, reflects minor light adsorption by MB at 337.1 nm. We suggest that the same intermediate is produced by two different reaction mechanisms depending on the excitation wavelength, according to Scheme I

Scheme I

587 nm, singlet route

$$MB \xrightarrow{h\nu} \rightarrow MB^*$$

$$MB^* + O_2 \rightarrow MB + {}^1O_2$$

$${}^1O_2 + Ph_2CN_2 \rightarrow N_2 + Ph_2COO$$

337 nm, triplet route

$$Ph_2CN_2 \xrightarrow{h\nu} {}^1(Ph_2C:) \rightarrow {}^3(Ph_2C:)$$

$${}^3(Ph_2C:) + O_2 \rightarrow Ph_2COO$$

(where all secondary reactions and nonreactive decay modes have been excluded). We note that the MB mechanism (Figure 2, top) also leads to weak, irreversible bleaching at 650 nm, presumably due to side reactions leading to some MB consumption.

The kinetics of the reaction $^1O_2$ with diphenyldiazomethane were monitored by examining the pseudo-first-order growth at 410 nm as a function of diazo concentration and led to $k \sim 6 \times 10^8$ M^{-1} s^{-1} in agreement with the value reported by Bethell et al.[19] The long-lived carbonyl oxide (>100 μs) can be trapped by aldehydes and electron-deficient and electron-rich olefins;[20] in the case of 2,5-dimethyl-2,4-hexadiene (DMHD), the rate constant observed was $\sim 1 \times 10^6$ M^{-1} s^{-1}, in agreement with the value obtained earlier from the carbene route.[8] Traces e and f in Figure 1 illustrate the effect of the diene; in both cases the carbonyl oxide lifetime is significantly shortened. In the carbene mechanism (trace e) the decrease in signal intensity is minor; however, in trace f we observe a drastic decrease, which we attribute to singlet oxygen scavenging by the diene,[21] and possible triplet MB quenching. We have also examined the trapping of the carbonyl oxide by aldehydes; these reactions are well characterized[10,22] and yield the corresponding ozonides. The rate constants in acetonitrile are $(2.1 \pm 0.2) \times 10^6$ and $(3.1 \pm 0.4) \times 10^6$ M^{-1} s^{-1} for phenylacetaldehyde and acetaldehyde, respectively.

We also examined the effect of 2,3-dimethyl-2-butene (TME) on the yield of carbonyl oxide produced by the singlet route. Stern-Volmer analysis of these data yields the rate constant for reaction of $^1O_2$ with TME as 3.5×10^7 M^{-1} s^{-1} in acetonitrile in excellent agreement with reported values.[23]

It has been proposed[10] that $^1O_2$ reacts with diazo compounds via the intermediacy of the five-membered ring azo peroxide. If such an intermediate is involved,[24] it must be short lived in the time scale of our experiments, since the 410-nm band is identical with that produced via the carbene and its generation rate is linearly dependent on diazo concentration.

Note Added in Proof. The reaction of fluorenone oxide with DMHD has now been studied. The results suggest that oxidation products generated in situ can lead to somewhat overestimated rates for DMHD. This may also apply to benzophenone oxide.

Registry No. Ph_2CN_2, 883-40-9; O_2, 7782-44-7; $Ph_2C:$, 3129-17-7; $Ph_2CO\text{-}O$, 86508-70-5.

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(24) This proposal[10] is based on the detection of N_2O among the reaction products. An alternate route to this product may be the reaction of Ph_2COO with Ph_2CN_2 which occurs with $k \sim 4 \times 10^5$ M^{-1} s^{-1}.[8]

Principal Component Analysis Applied to 1-Phenyl-2-(2-naphthyl)ethene Fluorescence. Four Components not Two

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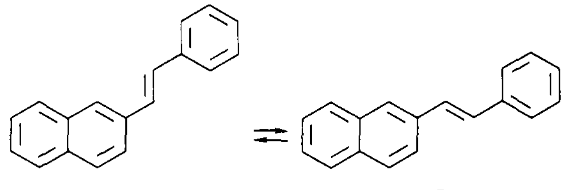
The complex photophysical behavior of 1-phenyl-2-(2-naphthyl)ethene (2-NPE) has been attributed to the presence of an equilibrium mixture of aryl-rotational conformers:



2-NPE$_1$ 2-NPE$_2$

Electronic excitation increases the double-bond character in the aryl-vinyl bonds "freezing" ground-state conformers into noninterconverting populations of excited-state species.[1] The dependence of fluorescence spectral shape on excitation wavelength, λ_{exc}, and fluorescence decay results requiring multiexponential fits[1,2] are accounted for since the spectra and excited-state lifetimes of such conformers should differ. Such properties are exhibited by 1,2-diarylethenes capable of existing in multiple, nearly isoenergetic, ground-state conformers[3] and are absent in olefins substituted with symmetrical aryl groups or in olefins in which a single conformer predominates for steric reasons.[1,4] We have employed two approaches in an effort to determine conclusively the role of 1-α aryl rotation in the 2-NPE system, to obtain pure component spectra, and to assign their structure and lifetime(s).[6] The first was treatment of *t*-2-NPE fluorescence spectra obtained under varying conditions of λ_{exc}, T, η, and quencher, Q, in terms

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