Fluorenone Oxide: Transient Spectroscopy and Kinetics of Its Formation and Reactions[1]

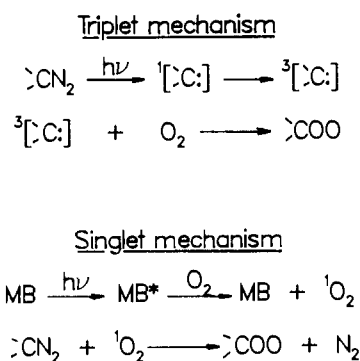H. L. Casal, M. Tanner,[2] N. H. Werstiuk,[3] and J. C. Scaiano*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. Received November 23, 1984

Abstract: Fluorene oxide has been characterized in solution at room temperature with laser flash photolysis techniques. This intermediate ($\lambda_{max} = 450$ nm) can be generated by reaction of fluorenylidene with oxygen, or by reaction of singlet oxygen (via methylene blue sensitization) with diazofluorenone. In Freon-113 solutions the lifetime of the carbonyl oxide is well in excess of 100 μs; aldehydes readily quench fluorenone oxide, as expected from the well-documented Criegee mechanism of ozonolysis. For example, reaction with acetaldehyde occurs with a rate constant at 1.2×10^9 M^{-1} s^{-1} in Freon-113 at 27 °C. The effect of carbene or singlet oxygen quenchers (depending on the reaction used) on the yield of carbonyl oxide can be used to obtain kinetic and mechanistic data on these precursors.

Carbonyl oxides, frequently referred to as "Criegee intermediates", are well established intermediates in organic chemistry.[4,5] They are generated in the ozonolysis of olefins,[4] in the reaction of carbenes with molecular oxygen,[6] and by reaction of singlet oxygen with diazo compounds.[7] There is also evidence suggesting that they may play a role in biological processes.[8] In spite of their well-recognized importance, their direct detection was achieved only recently. Two reports have dealt with cyclopentadienone oxide at low temperatures in matrices, where this intermediate was detected with infrared spectroscopy.[9,10] Two recent communications from our laboratory have demonstrated that benzophenone oxide can be readily generated and detected with laser flash photolysis techniques, by either the carbene[11] or the singlet oxygen route[12] (Scheme I). An independent report has also shown that 10,10-dimethyl-10-siloanthracen-9(10H)-one oxide can also be detected with flash techniques.[13,14]

We have now started a detailed study of the formation, spectroscopy, and reactions of a number of carbonyl oxides derived from aromatic substrates; in particular we are examining the two routes shown in Scheme I. In the early stages of this study it became evident that fluorenone oxide presents very specific problems, which justify its separate examination. To a considerable extent these differences with the other aromatic ketone oxides reflect differences in the behavior of the carbene precursor, fluorenylidene in this case. Several reports from Schuster's[15] and

(1) Issued as NRCC-24326.
(2) NRCC summer student, 1984.
(3) NRCC visiting scientist. Permanent address: Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.
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(14) Fluorenone oxide has been recently detected in matrices at low temperature in Professor I. R. Dunkin's laboratory. The spectral data appear to agree quite well with that reported herein.

Scheme I

our laboratory[16] have discussed in detail the chemistry of fluorenylidene, which while complex is now well understood.

In this paper we report on the kinetics and mechanism of the formation of fluorenone oxide by the two mechanisms of Scheme I, and we examine its spectroscopy and the kinetics of representative reactions. In addition, this study led to a few more kinetic details on the behavior of fluorenylidene itself. Studies in ylide-forming solvents (such as acetone and acetonitrile) led to complications due to the competitive formation of these ylides[16,17] and the carbonyl oxide, but at the same time this combination provides mechanistic insights not available in the case of other carbene precursors.

Results and Discussion

Unless otherwise indicated all experiments were carried out under an oxygen atmosphere at 27 °C and with a flow system. A nitrogen laser (337.1 nm) was used for the carbene-mediated reaction (triplet route) and a dye laser (582 or 587 nm) for the singlet-oxygen-mediated reaction (singlet route).

Triplet Fluorenylidene. The triplet carbene (^{3}Fl) was readily characterized in deaerated solutions by its sharp absorption band at 470 nm.[15,16] In addition to reproducing the data in solvents already examined in earlier reports (such as acetonitrile), we found that measurements in benzene were also straightforward and led to $\tau_3 = 16$ ns (lifetime for ^{3}Fl). Interestingly, earlier attempts to measure this lifetime in aromatic solvents had been system-

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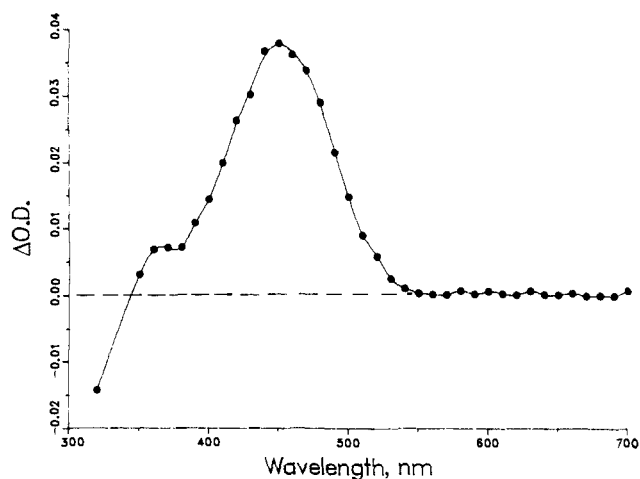
Figure 1. Transient spectrum obtained by 337-nm excitation of a 1 mM solution of diazofluorene in Freon-113 containing 2.5×10^{-2} M O_2 at 300 K. Signal monitored $\sim$1 μs after excitation.

atically unsuccessful. We now find that the use of a flow system is absolutely essential; even a decrease in the flow rate readily causes the accumulation of a fluorescent product that makes this measurement impossible. Most likely this was the problem in earlier attempts in our and other laboratories with static cells.

Spectroscopic Characterization of Fluorenone Oxide. Laser photodecomposition of diazofluorene leads to the essentially instantaneous formation of the singlet carbene, ^{1}Fl, which can undergo its characteristic reactions (such as O–H or C–H insertion) in competition with intersystem crossing to the triplet ground state, ^{3}Fl. The two states are sufficiently close that singlet reactions can be detected even after singlet–triplet intersystem crossing, reflecting the presence of a significant concentration of thermally populated ^{1}Fl.[15,16,18]

We find Freon-113 to be a convenient solvent for many of our experiments; this is in agreement with earlier measurements where the longest carbene lifetime was recorded in this solvent.[16] Further, oxygen solubility is high in fluorinated solvents.[19] The transient spectrum obtained by excitation of a 1 mM solution of diazofluorene in oxygen-saturated ($[O_2]= 2.5 \times 10^{-2}$ M) Freon-113 is illustrated in Figure 1. This spectrum demonstrates the presence of a transient species (other than the carbene) with fairly strong absorption at 450 nm. The 450-nm species can also be generated in a singlet-oxygen-mediated reaction described under a separate heading. Further, kinetic studies (vide infra) also demonstrate that the formation of this transient occurs concurrently with the decay of the carbene or singlet oxygen, as applicable. These results make us confident that the species detected is the carbonyl oxide. Virtually identical transient spectra were also obtained in other solvents, such as benzene, isooctane, or acetone, although in the latter we observed significant yields of the acetone carbonyl ylide. The details of this competition are also discussed separately.

Kinetics of Carbonyl Oxide Formation. Triplet Route. The kinetics of carbonyl oxide formation by reaction of the triplet carbene with molecular oxygen were studied by monitoring the formation of carbonyl oxide at 450 nm following laser excitation of solutions of diazofluorene (typically 1 mM) containing various concentrations of oxygen. The buildup of the signal followed clean pseudo-first-order kinetics (see insert in Figure 2). The experimental rate constant, k_{ex}, derived from the analysis of these traces is related to the rate constant for carbene scavenging by oxygen according to

$$k_{ex} = \tau_3^{-1} + k_{O_2}[O_2] \qquad (1)$$

The corresponding plot is shown in Figure 2 and leads to $k_{O_2} =$
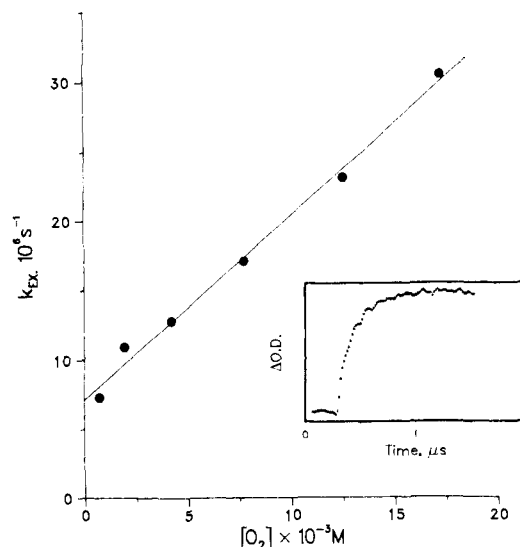
Figure 2. Plot of the growth rate of fluorene oxide as a function of oxygen concentration in Freon-113 solution. Inset: growth of fluorenone oxide signal (450 nm) in a 1×10^{-3} M solution of diazofluorene in Freon-113 containing 7.1×10^{-4} M oxygen.

$(1.4 \pm 0.2) \times 10^9$ M^{-1} s^{-1} (errors as $\pm 2\sigma$ throughout) and $\tau_3 \sim$ 200 ns. The value of k_{O_2} is comparable to that recently reported for diphenylcarbene (5×10^9 M^{-1} s^{-1}).[11] The carbene lifetime is in good agreement, and probably more accurate, than the value of 290 ns reported earlier in this solvent.[16] The agreement between the lifetime measured directly and the extrapolated value based on the 450-nm transient provides further support for the assignment of this species as the carbonyl oxide.

Singlet Route. It has been proposed that the reaction of singlet oxygen, $^1O_2$, with diazo compounds leads to the formation of the corresponding carbonyl oxide.[7] In the case of diphenyldiazomethane, work from our laboratory has already established that the reaction intermediate produced is the same as that formed by reaction of the triplet carbene with molecular (triplet) oxygen (see Scheme I).[12] We have used methylene blue (MB) as a sensitizer, which has been established to be a good singlet oxygen source,[20] and its absorption spectrum ($\lambda_{max} \sim 650$ nm; $\epsilon = 89125$ M^{-1} cm^{-1})[21] does not overlap significantly with the absorptions (transient or ground state) of the other components in the system. MB was excited with the 587-nm pulses from a flash pumped dye laser, typically operated at about 1 J/pulse. The solutions of MB ($\sim$4 μM) were sufficiently dilute that only a small fraction of this energy was actually absorbed by the sensitizer. The diazo compound was shown not to photodecompose under these experimental conditions; for example, 587-nm excitation of 1 mM diazofluorene in acetonitrile does not yield any detectable signals at $\sim$400 nm, where the corresponding nitrile ylide has a strong absorption band.[15,16]

Experiments in this section were carried out under 1 atm of oxygen, which ensures the fast deactivation of the MB triplet. The formation of the carbonyl oxide was then monitored at 450 nm for various concentrations of diazofluorene (FlN$_2$). The values of k_{ex} are now related to the various rate constants according to

$$k_{ex} = \tau_0^{-1} + k_D[FlN_2] \qquad (2)$$

where τ_0 is the lifetime of singlet oxygen in the solvent and k_D is the rate constant for singlet oxygen scavenging by diazofluorene. The corresponding plot for acetonitrile as solvent is shown in Figure 3 and leads to $k_D = (6.6 \pm 0.4) \times 10^7$ M^{-1} s^{-1}; this value is in good agreement with that measured by Bethell,[22] using an independent approach. For comparison, the value of k_D for di-

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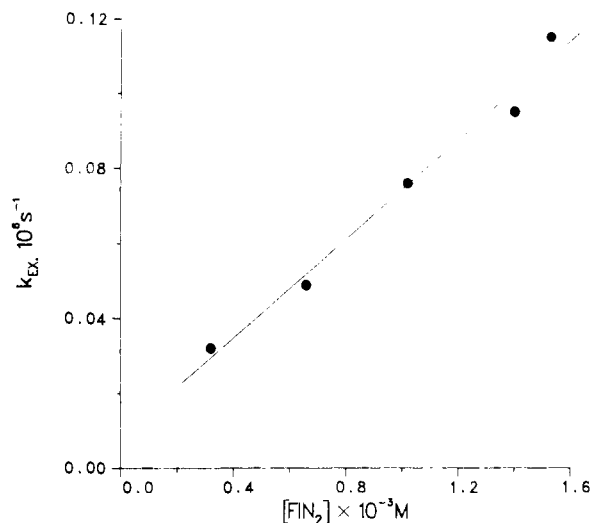
Figure 3. Plot of the growth rate of fluorenone oxide from the "singlet route" as a function of diazofluorene concentration in acetonitrile containing 7.7×10^{-3} M oxygen.

Table I. Rate Constants for Reaction of Fluorenylidene in Freon-113 at 300 K, Using the Carbonyl Oxide Signals as a Probe

substrate	$k_a/M^{-1} s^{-1}$
diethyl ether	$(1.3 \pm 0.2) \times 10^8$
1,4-cyclohexadiene	$(1.1 \pm 0.2) \times 10^9$
β-pinene	$(1.2 \pm 0.4) \times 10^9$
isooctane	$(9 \pm 1) \times 10^6$

phenyldiazomethane in acetonitrile is $k_D = (1.0 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.[12] The value of τ_0^{-1} was too small to be significant, indicating that under our experimental conditions nonreactive decay of singlet oxygen is not an important process.

Further and conclusive confirmation that the 450-nm band results from a reaction of singlet oxygen can be obtained by adding a known $^1O_2$ scavenger to a solution containing a fixed concentration of the diazo precursor. The singlet oxygen scavenger selected for these experiments was 2,3-dimethyl-2-butene (TME) for which the reactivity toward $^1O_2$ is well documented in many solvents.[23] Under these conditions the value of k_{ex} will be determined by

$$k_{ex} = \tau_0^{-1} + k_D[FlN_2] + k_{TME}[TME] \qquad (3)$$

The corresponding plot led to $k_{TME} = 3.7 \times 10^7$ M^{-1} s^{-1} in acetonitrile, in excellent agreement with the reported value.[23] This approach, using the carbonyl oxide as a probe, could possibly find other applications in the study of singlet oxygen kinetics.

Carbene Reactivities from Carbonyl Oxide Studies. While a few rate constants for carbene reactions have been determined in the case of fluorenylidene, these are generally difficult to obtain. Carbonyl oxides produced by the triplet route discussed above provide a convenient probe for the study of carbene reactions. Thus, when oxygen and a substrate "A" are present in a sample, the rate constant associated with the signal buildup at 450 nm will be given by

$$k_{ex} = \tau_3^{-1} + k_{O_2}[O_2] + k_a[A] \qquad (4)$$

where k_a is the rate constant for reaction of the carbene with A.

We have used Freon-113, in which fluorenylidene is relatively long lived, and maintained $[O_2] = 5.23 \times 10^{-3}$ M by using air-saturated solutions. Table I gives values of k_a, and representative plots are shown in Figure 4. With the exception of β-pinene, all other rate constants are likely to be dominated by a combination of hydrogen abstraction by the triplet carbene, with contribution from C–H insertion by the thermally populated singlet carbene.

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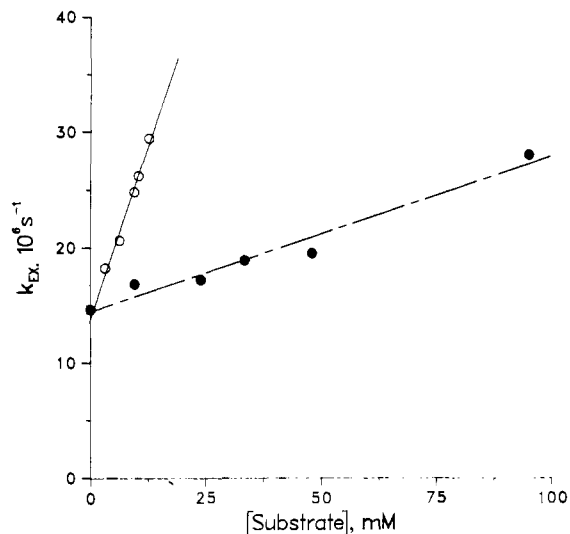
Figure 4. Plot of k_{ex} for fluorenone oxide formation (measured at 450 nm) in Freon-113 solution containing 5.23×10^{-3} M oxygen, for diethyl ether (●) and β-pinene (○).
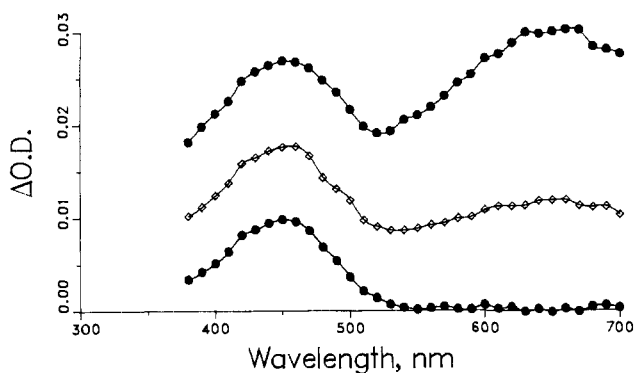
Figure 5. Transient spectra obtained by 337-nm excitation of diazofluorene (1×10^{-3} M) in acetone containing 1.1×10^{-2} M oxygen monitored at 1 (A), 8 (B), and 12 (C) μs after excitation. The top spectra (A and B) have been shifted by 0.015 and 0.0065 OD units, respectively.

Competition for Ylide Formation: The Case of Acetone. Fluorenylidene readily reacts with ketones and nitriles to yield the corresponding ylides.[15-18] Studies with nitriles (such as acetonitrile) are difficult in this case due to the extensive spectral overlap between the carbonyl oxide and nitrile ylides. In the case of aliphatic ketones (acetone in particular), the carbonyl ylide signals ($\lambda_{max} = 640$ nm) are well separated from those of the carbonyl oxide (see Figure 1).[17]

Figure 5 shows the spectra obtained following 337-nm laser excitation of 1 mM diazofluorene in oxygen-saturated acetone. At short times (<1 μs) we detect two bands, clearly those of the carbonyl oxide ($\lambda_{max} = 450$ nm) and to the red the carbonyl ylide ($\lambda_{max} = 640$ nm). As the delay between excitation and detection is increased we see a gradual decrease and eventual disappearance of the 640-nm band, reflecting the much shorter lifetime of the carbonyl ylide under oxygen as compared with the lifetime of fluorenone oxide. Under these conditions (oxygen-saturated acetone, $[O_2] = 1.14 \times 10^{-2}$ M) the carbonyl ylide is short lived; it reacts with oxygen with $k = (7.2 \pm 0.3) \times 10^7$ M^{-1} s^{-1}, while the carbonyl oxide does not react with oxygen; this latter observation also applies to benzophenone oxide.

Similar experiments to the one used to record the spectra of Figure 5 were carried out for several oxygen concentrations. The ratio of transient optical densities monitored at 650 and 450 nm before significant transient decay occurred was a function of the oxygen concentration, as expected. In order to use these data in a Stern–Volmer type of analysis, it is necessary to take into account spectral overlap. The 650-nm absorption is entirely due to the
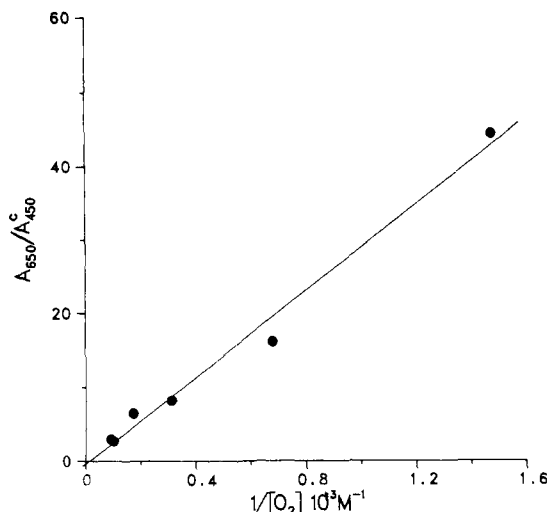
Figure 6. Plot of A_{650}/A_{450}^c vs. $[O_2]^{-1}$ obtained from a 1×10^{-3} M solution of diazofluorene in acetone (see eq 8).

carbonyl ylide, since the carbonyl oxide (see Figure 1) is transparent at this wavelength; thus, no correction is necessary for the 650-nm measurement. The absorption at 450 nm is mostly, but not entirely, due to the carbonyl oxide, since the carbonyl ylide does show some absorption at this wavelength.[17] The spectrum of the ylide, obtained under identical experimental conditions, shows that the absorption of 450 nm corresponds to 15% of that at 650 nm. Since the latter is known in all cases, it is straightforward to introduce the correction, i.e.

$$A_{450}^c = A_{450} - 0.15 \times A_{650} \tag{5}$$

If we assume (as concluded in an earlier report) that no trapping by the ketone occurs prior to carbene intersystem crossing,[24] then yields of carbonyl oxide, Φ_{FlOO}, and of carbonyl ylide, Φ_{CY}, will be given by

$$\Phi_{FlOO} = \Phi_3 \frac{k_{O_2}[O_2]}{k_{O_2}[O_2] + k_{CY}[\text{acetone}]} \tag{6}$$

$$\Phi_{CY} = \Phi_3 \frac{k_{CY}[\text{acetone}]}{k_{O_2}[O_2] + k_{CY}[\text{acetone}]} \tag{7}$$

where k_{CY} is the rate constant for carbene scavenging by acetone, and it has been further assumed that all carbenes decay by reaction with either acetone or oxygen.

Assuming that A_{650} and A_{450}^c are proportional to the concentration of carbonyl ylide and oxide, respectively, the following relationship is found

$$\frac{A_{650}}{A_{450}^c} = c \frac{k_{CY}[\text{acetone}]}{k_{O_2}[O_2]} \tag{8}$$

where the constant c is the ratio of extinction coefficients for the two transients. Figure 6 illustrates the dependence of A_{650}/A_{450}^c according to eq 8. Introducing the known values of k_{CY} and k_{O_2}, we obtain $c = 0.3 = (\epsilon_{CY}/\epsilon_{FlOO})$.

The linearity of the plot in Figure 6 suggests that neither acetone nor oxygen trap significant amounts of carbene prior to singlet–triplet intersystem crossing.

We note that in earlier studies of the carbonyl ylide we usually detected a sharp band at 500 nm,[17] due to the 9-fluorenyl radical. This signal was not detected in the experiments described above; this must be the result of scavenging of 9-fluorenyl by O_2.

As we mentioned above, fluorenylidene reacts with acetonitrile to form the corresponding nitrile ylide. When fluorenone oxide is formed in acetonitrile, its absorption overlaps the absorptions due to the nitrile ylide. As in the case of the carbonyl ylide with
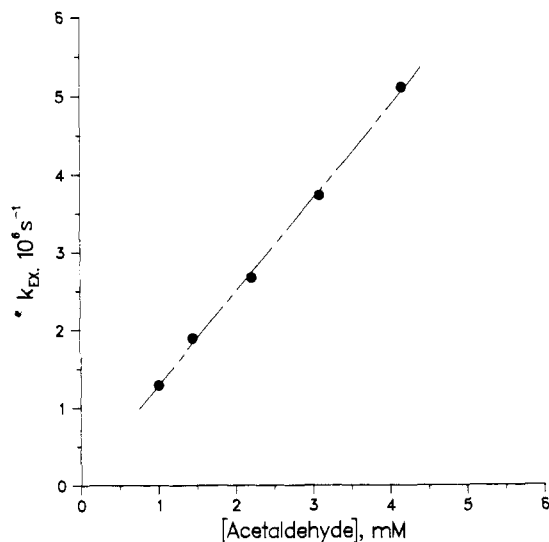

Figure 7. Plot of the rate of decay of the fluorenone oxide signal (450 nm) as a function of added acetaldehyde in Freon-113 solution containing 1×10^{-3} M diazofluorene and 2.5×10^{-2} M oxygen.

Table II. Rate Constants for Reaction of Fluorenone Oxide with Aldehydes in Freon-113 at 300 K

scavenger	$k_S/M^{-1} s^{-1}$
acetaldehyde	$(1.21 \pm 0.04) \times 10^9$
phenylacetaldehyde	$(5.0 \pm 1.0) \times 10^8$
n-octanal	$(4.5 \pm 0.5) \times 10^7$
5-norbornene-2-carboxaldehyde	$\sim 1.5 \times 10^7$

acetone, the nitrile ylide is shorter lived than fluorenone oxide under these conditions. The nitrile ylide dominates the transient spectrum at short time intervals after the laser pulse but at longer times only fluorenone oxide is evident. Due to this extensive overlap it is impractical to attempt an anlysis similar to that for the carbonyl ylide, eq 8.

Scavenging of the Carbonyl Oxide. Carbonyl oxides can be trapped by a wide range of substrates including aldehydes, alkenes, and aromatic compounds. In this section we examine the kinetics of these reactions. Their mechanism is generally well known; for example, the reaction with aldehydes yields ozonides.[4,5] In all cases fluorenone is expected among the products, and our own experiments show its formation in high yields.

We have studied the reaction of fluorenone oxide with several aldehydes. In general, when a carbonyl oxide scavenger is added, the lifetime of the signal at 450 nm decreases, reflecting its scavenging by the substrate. Similar to studies mentioned above, the pseudo-first-order rate constant for carbonyl oxide decay, k_{ex}, is given by

$$k_{ex} = \tau_{FlOO}^{-1} + k_S[S] \tag{9}$$

where k_S is the rate constant for reaction of the carbonyl oxide with the scavenger S. Figure 7 shows the corresponding plot for acetaldehyde as the scavenger. The rate constant derived from these data is $(1.21 \pm 0.04) \times 10^9$ M^{-1} s^{-1} in Freon-113 at 300 K. Table II summarizes the rate constants for aldehydes as scavengers.

When 2,5-dimethyl-2,4-hexadiene (DMHD) is used instead of a carbonyl oxide scavenger and the signal at 450 nm is monitored, we observed a decrease in the absorption intensity at 450 nm "immediately" after laser excitation. We attribute this effect to the trapping of the carbene by DMHD, a reaction which is well documented. If this conclusion is correct, the values of A_{450} should follow a Stern–Volmer type of dependence with the concentration of DMHD; this is indeed found to be the case. In this case, analysis of the data similar to that presented earlier leads to

$$(A_{450})^{-1} = d + d \frac{k_{diene}[\text{DMHD}]}{k_{O_2}[O_2]} \tag{10}$$

(24) Such a process would lead to a "jump" in the buildup traces; this is not observed.[17]

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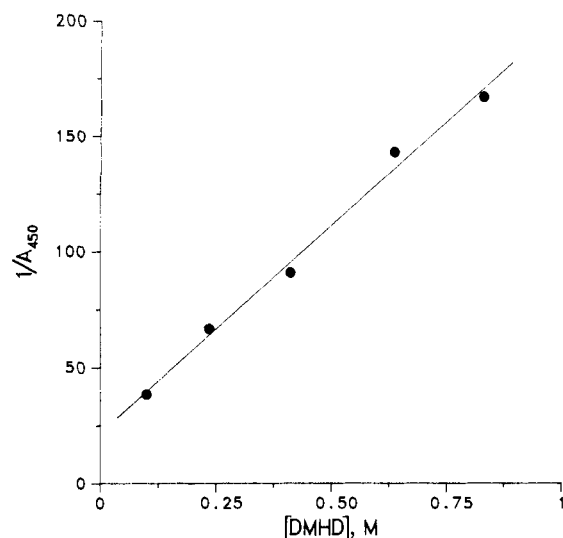
Figure 8. Plot of $1/A_{450}$ as a function of added 2,5-dimethyl-2,4-hexadiene in Freon-113 solution containing 1×10^{-3} M diazofluorene and 2.5 $\times 10^{-2}$ M oxygen (see eq 10).

where d is a constant and k_{diene} refers to the reaction of the carbene, not the carbonyl oxide. Figure 8 shows the corresponding plot at constant oxygen ($[O_2] = 2.49 \times 10^{-2}$ M), which leads to $k_{diene}/k_{O_2} = 0.21$ in Freon-113 at 300 K. The ratio is in good agreement with the value of k_{diene} of 6.7×10^8 M^{-1} s^{-1} reported in acetonitrile solution[15] and fits nicely with the overall reaction mechanism proposed in this report.

In the case of 2,3-dimethyl-2-butene (TME), the absorption at 450 nm (A_{450}) also decreased as the TME was added to the solution. In this case, analysis according to eq 10 yields $k_{TME} = 1.4 \times 10^8$ M^{-1} s^{-1} for reaction of fluorenylidene with TME in Freon-113. This value compares well with that measured directly in acetonitrile-d_3 (5×10^8 M^{-1} s^{-1}).[16]

Early studies with DMHD suggested that this diene was a good quencher of the carbonyl oxide (preliminary rate constants were around 10^6 M^{-1} s^{-1}). However, our measurements did not seem to be as reproducible as for other substrates. Careful purification of DMHD, use of fast flow in the reaction cell, and minimization of contact time between the components in the sample showed that $k < 10^4$ M^{-1} s^{-1}. The apparent higher preliminary rates were probably due to oxidation-produced impurities (perhaps unsaturated aldehydes). These problems, of which we were not aware before, could have led to some overestimation of rate constants for reaction of benzophenone oxide with DMHD.[11,12]

Lifetime of Fluorenone Oxide in Various Reactive Solvents. The lifetime of fluorenone oxide in Freon-113 was usually in excess of 100 μs. Our experiments show that while carbonyl oxides are quite reactive toward aldehydes, the rates of reaction with other substrates are not particularly high, and kinetic measurements are sometimes difficult with laser techniques (in fact we would anticipate them to be easier by conventional flash photolysis). In order to examine a few more carbonyl oxide reactivities, we measured the lifetime of fluorenone oxide in a variety of solvents, hoping that the high concentration would make the lifetimes short enough for accurate measurements. Values in acetonitrile and alcohols were obtained by using the "singlet route" in order to eliminate carbene reactions that could interfere (acetonitrile) or completely eliminate (alcohols) the fluorenone oxide signals.

Our data have been summarized in Table III. We have preferred to report these results in the form of half-lives, $t_{1/2}$, reflecting the difficulties in fitting the data accurately with a single

Table III. Half-Life of Fluorenone Oxide in Different Solvents

solvent	$t_{1/2}$, μs	solvent	$t_{1/2}$, μs
CH$_2$Cl$_2$	9	toluene	270[b]
Freon-113	370	chlorobenzene	$\geq$500
cyclohexane	$\geq$500	CCl$_4$	35
acetone	26	2-propanol[a]	$\geq$55
benzene	$\geq$800	acetonitrile[a]	35

[a] Measured by using the single oxygen route (Scheme I); to avoid scavenging of the carbene by the hydroxilic solvent (isopropanol) or by formation of the nitrile ylide (acetonitrile). [b] In this case we also observed a faster decay occurring with $t_{1/2} \sim 8$ μs.

exponential. The reasons for these problems were not pursued, but self-reactions of carbonyl oxides, or reactions with other transients likely to be present or generated in the system (e.g., free radicals), are candidates for interference. The "true" lifetimes may be somewhat longer than the value in Table III. We also note that Table III includes half-lives, not lifetimes (i.e., based on e^{-1}) as in other places; lifetimes are always represented by τ.

Concluding Remarks. More than three decades have elapsed since Criegee[25] proposed that carbonyl oxides were discrete intermediates of the ozonolysis reaction. The existence of these intermediates had indeed been demonstrated over the years.[5] However, we are now able to detect and study them in solution at ambient temperatures. In this report we have produced fluorenone oxide by two independent routes and have studied its formation and reaction kinetics. At the same time, we have demonstrated that the transient signals can be used to determine the yield of fluorenone oxide under differing conditions. The yields of transient can then be used to measure the kinetics of the precursors (carbene or singlet oxygen) in situations which are otherwise complicated. More studies are now in progress in attempts to establish structure–reactivity relationships for these intermediates.

Experimental Section

All experiments were carried out by flowing the solutions through a 7×7 mm^2 cell made of Suprasil quartz. The concentration of oxygen in the solutions was varied by bubbling N$_2$/O$_2$ mixtures of known composition through the solutions with a Matheson Model 610 gas mixing system. The concentration of oxygen in the different solvents was calculated from its reported solubility.[19]

For excitation, a Molectron UV-24 N$_2$ laser (337 nm, up to 10 mJ, 8–10 ns) and a flash-pumped dye laser (Candela UV-500M) operated with Rhodamine 6G delivering 587-nm pulses (up to 1 J, $\sim$250 ns) were used. Details of the laser facility have been given elsewhere.[27]

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(27) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.