Optical Modulation Spectroscopy: A Study of the Self-Reaction of Benzophenone Oxide¹

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The bimolecular self-reaction of benzophenone oxide was investigated by optical modulation spectroscopy and by product studies. The transient decayed to give benzophenone and oxygen and the rate constants for its disappearance, 2k, are described by the expression log $(2k) = (9.1 \pm 0.2) - (1.8 \pm 0.3)/\theta$ where $\theta = 2.30RT$ kcal mol⁻¹. The significance of these parameters is discussed in terms of the orientational requirements for self-reaction. Benzophenone oxide was found to react with octanal with a rate constant 2.0 \times 10⁴ M⁻¹ s⁻¹.

Carbonyl oxides, I, have long been recognized as being important intermediates in the ozonolysis of olefins, eq $1-3.^2$ Evidence for their existence came largely from the fact that they could be intercepted by the addition of aldehydes or ketones, eq 4. to give 1,2,4-trioxalanes which were quite different to those normally obtained from the starting olefin.² Much of the pioneering work in the area was carried out by Criegee and his colleagues and, in recognition of this fact, these interesting transients are often referred to as "Criegee" intermediates.²



From the synthetic point of view, carbonyl oxides are best made via reactions 1 and 2. However, they can be produced by a more direct route. Photolysis of diazo compounds in the presence of oxygen gives carbonyl oxides via a simple carbene addition, eq 5.3-9 Studies of these reactions have provided mechanistic support in favor of Criegee's proposal that carbonyl oxides were intermediates in ozonolysis chemistry¹⁰ and, at the same time, they have formed the basis of a method for the direct detection of these transients.11-15

$$\left\langle cN_{2} \xrightarrow{h\nu} c + N_{2} \xrightarrow{O_{2}} c = 0 - \bar{0} \right\rangle$$
 (5)

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Laser flash photolysis^{11,13,15} and matrix isolation infrared studies¹² of the carbene-oxygen reaction have provided direct spectroscopic evidence for the existence of carbonyl oxides as discrete intermediates. Indeed, the laser flash photolysis approach made it possible to measure the kinetics for some reactions of I. However, carbonyl oxides were found to be long lived on the time scale (maximum ca. 50 μ s) of the laser flash photolysis apparatus,^{11,13,15} so that the kinetics for their decay could not be studied.

In this work, we have used the slower technique of optical modulation spectroscopy^{16,17} (time scale $1-10^{-5}$ s) to monitor the behavior of benzophenone oxide, II, in solution. Through a

$$Ph_2C=O^+-O$$

II

combination of kinetic and product studies, we have been able to build a fairly comprehensive picture of the reactions which lead to its decay and have been able to measure the rate constant for its reaction with a typical aldehyde.

Experimental Section

Materials. Diphenyldiazomethane was prepared from benzophenone following the literature procedure¹⁸ and was purified by vacuum sublimation before use. Acetonitrile was purified by distillation from calcium hydride and octanal (Aldrich, 99%) was used as received.

Apparatus. The optical modulation spectrometer used in this work has been described in detail elsewhere¹⁹ and follows on the design originally developed by Huggenberger and Fischer.¹⁶ Briefly, samples were irradiated in a UV flow cell (Starna, 43Q, 5-mm path length) with a 1000-W mercury-xenon lamp (Hanovia 997B001). The light from the lamp was modulated with a mechanical chopper fitted with irises. The design of the chopper system was such that the intensity of the light at the sample cell rose and fell as a sine wave. Accordingly, the concentration of transient generated by the photolysis was also sinusoidally modulated.

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Figure 1. Optical absorption spectrum of benzophenone oxide recorded 298 K and at a modulation frequency of 258 rad s^{-1} .

An optical detection system was arranged at right angles to the photolysis direction. In addition to lenses, irises, etc., this consisted of a low-power, xenon monitoring lamp and a monochromator fitted with a photomultiplier tube detector. In simple terms, the output of the photomultiplier tube consisted of a large dc signal and a very small ac signal due to the absorption of the transient. The amplitude and phase of the oscillating signal was analyzed with a lock-in amplifier (PAR 124A), which was driven by a reference signal from the mechanical chopper. The ratio of the ac signal to the dc was taken with a voltage divider (Adalab) and was equal to the oscillating part of optical density due to the transient.^{16,17}

Spectra were obtained by recording the optical density due to the transient as a function of wavelength and kinetic data were obtained by monitoring the phase dependence of the transient signal as a function of modulation frequency (vide infra).^{16,17}

Analysis. In a typical run, an acetonitrile solution of diphenyldiazomethane $(1 \times 10^{-3} \text{ M})$ was saturated with oxygen via a fritted gas bubbler. For kinetic studies, the solution was pumped through the sample chamber of the spectrometer at a rate which ensured that the conversion of the starting diazo compound was small (<10%). The extent of depletion was monitored by taking the UV-visible spectra of the solutions before and after photolysis. Kinetic data were obtained at a fixed wavelength and neutral density filters, as well as a band-pass filter (364-464 nm), were placed in the monitoring beam to ensure that there was no significant photolysis of the sample from this light source.

For product studies, the flow rate was reduced so as to achieve higher conversions of the starting material. However, care was taken to ensure that the photolysis time did not extend beyond that sufficient to achieve this goal, i.e. photolysis of the reaction products was minimized.

After photolysis, the products were analyzed by GC/mass spectrometry (Hewlett-Packard 1995) and were quantified by GC (Hewlett-Packard 5890A) with 10 m, 0.2 mm diameter crosslinked methylsilicon columns. Isolated yields were obtained by separation of the reaction products on thin layer chromatography plates.

Results and Discussion

Benzophenone oxide, II, was generated by modulated photolysis of an oxygen-saturated solution of diphenyldiazomethane $(1 \times 10^{-3} \text{ M})$ in acetonitrile, cf. eq 5. The absorption spectrum (Figure 1) was recorded at a fixed modulation frequency and was, within error, identical with that previously reported for benzophenone oxide, with $\lambda_{max} = 410$ nm. The shape of the spectrum was essentially independent (vide infra) of the phase setting of the lock-in amplifier indicating that the lifetime of the transient was the same at all wavelengths and therefore that the spectrum was due to a single transient.^{16,17} Moreover, the form of the spectrum was independent of reagent flow rate indicating that it was not



Figure 2. Plot of $-\tan \phi$ vs. ω used to measure the lifetime of benzophenone oxide at 298 K.

due to a secondary photolysis product.

The fact that benzophenone oxide was detected rather than its precursor, triplet diphenylcarbene, is consistent with very high rate constant ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)¹³ for the carbene-oxygen reaction. This process is spin allowed, there being a 1/9th probability that the two triplet molecules will combine to give the singlet product, II. Even at the relatively low concentrations of oxygen (ca. 10^{-3} M) attainable in saturated acetonitrile, the lifetime for this reaction is ca. 0.2 μ s, which is well below the time resolution of the modulation spectrometer.

Kinetic data for the disappearance of the carbonyl oxide were obtained by two methods. In the first approach, the absorption spectrum of the transient was monitored at a wavelength (410 nm) where there was no absorption due to the starting diazo compound or the reaction products. The amplitude of the signal due to the carbonyl oxide was resolved into components which were out-of-phase and in-phase with respect to the modulated photolysis. The ratio of these components is, by definition,^{16,17} equal to the tangent of the phase angle, ϕ , which is in turn related to the transient lifetime, τ , and the modulation frequency, ω , eq 6. The phase angle was measured as a function of modulation

$$-\tan\phi = \omega\tau \tag{6}$$

frequency at a given temperature. The data were then plotted via eq 6, which is applicable for values of $\tan \phi > 1$. Plots of this kind were linear and the transient lifetimes, τ , were obtained from the slopes. A typical example is shown in Figure 2.

The kinetic order for the decay of the transient signal was measured at fixed frequency by monitoring changes in the phase angle as the intensity of the modulated photolysis beam was reduced by a factor of 2.5 by using neutral density filters. A high flow rate was sustained so as to ensure that the measurements were made at low conversions (<10%) of diazo compound. It was found that τ was directly proportional to the square root of the maximum rate of initiation, I_0 , over the temperature range 238–298 K, demonstrating that the benzophenone oxide decayed with second-order kinetics. The relationship between τ and I_0 under these conditions is given in eq 7, where 2k is the bimolecular rate constant for the self-reaction of II.^{16,17}

$$\tau = (4kI_0)^{-1/2} \tag{7}$$

In addition to the data for the transient lifetimes, values of the average rate of photochemical initiation, $I_0/2$, were required for the determination of the second-order rate constants for decay,

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eq 7. These were obtained by sustaining solution flow rates at a relatively high level so that <10% of the starting diazo compound was destroyed by photolysis in the sample cell. The extent of conversion was accurately measured spectrophotometrically and was combined with data for the solution flow rate and sample cell volume to yield I_0 in units of M s⁻¹.

An Arrhenius plot of the data is represented by eq 8, where $\theta = 2.30RT$ kcal mol⁻¹. The rate constant for bimolecular decay of benzophenone oxide at 300 K was found to be 6×10^7 M⁻¹ s⁻¹.

$$\log (2k) = (9.1 \bullet 0.2) - (1.8 \pm 0.3)/\theta \tag{8}$$

While the phase angle data yield the kinetics for bimolecular decay of II, its extinction coefficient, ϵ , can only be evaluated by making use of the optical density, ΔOD , due to the modulated signals.^{16,17} These are obtained from the vector sum of the in-phase and out-of-phase signals due to the transient. Following the analysis of Huggenberger and Fischer,¹⁶ a plot of $(\Delta OD)^{-2}$ vs. ω^2 for the data obtained at 300 K gave a straight line of slope *a* and intercept *b* which are defined in eq 9 and 10. In these expressions, *l*, is the pathlength of the cell in the direction of the monitoring beam.

$$a = 4(\epsilon I I_0)^{-2} \tag{9}$$

$$b = 4(\epsilon l I_0 \tau)^{-2} \tag{10}$$

The average rate of transient generation was obtained by measuring the optical absorption of the solution of diazo compound before and after its passage through the sample cell, the volume of the cell, and the flow rate. The latter was maintained at a high level so that sample depletion was $\leq 10\%$. This ensured that the sample was homogeneous, to a good approximation, which is a necessary condition for reliable measurement. Substitution of the value for $I_0/2$ into eq 9 gave $\epsilon(410 \text{ nm}) = 1850 \pm 450 \text{ M}^{-1} \text{ cm}^{-1}$.

The equations described above, which were used to analyze the results of the modulation experiment, are valid under the limiting conditions stated, i.e. for values of $\omega \tau > 1$ and at wavelengths where the starting materials and products do not absorb the monitoring light. Under these conditions, I_0 , and hence ϵ have to be evaluated by some form of actinometry, e.g. by measuring the rate of consumption of the starting material.

Recently, Chen and Paul²⁰ have developed a method for measuring ϵ that completely eliminates actinometry. In essence, they have solved the modulation equations for regions where the transient, its precursor, and products absorb the monitoring light. Measurements in these regions allow the extinction coefficient of the transient, $\epsilon_{\rm T}$, to be related to those for the starting materials, $\epsilon_{\rm S}$, and products, $\epsilon_{\rm P}$, which, in turn, can be easily obtained in a simple UV experiment.

In a region where the starting material, transient, and products absorb the monitoring light, the phase angle, ϕ , measured for the total modulated optical density is dependent upon the extinction coefficients for each component, i.e. ϵ_S , ϵ_T , and ϵ_P , respectively²⁰

$$\tan \phi = \frac{\epsilon_{\rm S} - \epsilon_{\rm P}}{\epsilon_{\rm T} - \epsilon_{\rm P}} \frac{1}{F\tau\omega} - \left\{ f - \frac{\epsilon_{\rm S} - \epsilon_{\rm P}}{\epsilon_{\rm T} - \epsilon_{\rm P}} \frac{1}{F} \right\} \tau\omega \qquad (11)$$

where

$$F = g[(1 + \tau^2 \omega^2) / (1 + f^2 \tau^2 \omega^2)]^{1/2}$$
(12)

$$g = 1 + 0.2 \exp(-2.67\tau\omega) \tag{13}$$

$$f = 1 + \exp\{-3.08(\tau\omega)^{0.46}\}$$
(14)

These equations are valid for all values of $\omega \tau$ and, in experiments where the signal-to-noise levels are high, they can be solved by computer fitting using τ and the extinction coefficient of the transient, $\epsilon_{\rm T}$, as independent variables.

The approach was not feasible in this work since the signalto-noise levels were not high enough. To overcome the problem, we measured the frequency dependence of $\tan \phi$ at two wavelengths using a single sample mixture. At the first (410 nm) only benzophenone oxide absorbed and so τ was determined by using eq 6. At the second (460 nm) both the transient and starting material absorbed the light so that the data contained information about the relative values of ϵ_T and ϵ_S . The reaction product, benzophenone (vide infra), has no significant absorption at this wavelength. By combining the data obtained at 460 nm with the value of τ determined at 410 nm we were able to solve eq 11–14 directly and found $\epsilon_T/\epsilon_S = 11.6 \pm 1.3$ at 460 nm. In fact the data which best define this ratio are those obtained at very low modulation frequencies, i.e. $\omega \tau \rightarrow 0$, and these were more heavily weighted in the analysis. Since $\epsilon_S(460 \text{ nm}) = 38 \text{ M}^{-1} \text{ cm}^{-1}$, it follows that $\epsilon_T(460 \text{ nm}) = 441 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$.

In order to find the extinction coefficient for the transient at the maximum of its absorption band one cannot simply take the amplitudes of the transient spectrum at the two wavelengths and apply a simple scaling factor. This is because the amplitude at 460 nm is not due to the transient alone but contains a contribution from the starting material. However, the necessary scaling factor was obtained from eq 15, where D is the amplitude of the modulated signal. The value of $\epsilon(410 \text{ nm})$ was found to be 1216 ± 150 M⁻¹ cm⁻¹ in fair agreement with that found in the first experiment using actinometry.

$$D(\text{out of phase}) = \frac{I_0 l}{4\omega} \left(\frac{\tau^2 \omega^2}{1 + \tau^2 \omega^2} \epsilon_{\rm T} - \epsilon_{\rm S} \right)$$
(15)

This value was used in conjunction with the data obtained at 410 nm and gave $2k = 3.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the bimolecular self-reaction of benzophenone oxide, eq 7 and 9, which was again in reasonable agreement with the result obtained in the initial experiment.

In order to fully characterize the reaction products, photolyses were carried out by reducing the flow rate to the point where the characteristic pink color of the diazo compound could no longer be detected in the cell effluent. Analysis by GC and GC/mass spectrometry showed that the only products obtained were benzophenone and benzophenone ketazine, eq 16–19. These were

$$Ph_2CH_2 \xrightarrow{n\nu} Ph_2C: + N_2$$
 (16)

$$\begin{array}{l} Ph_2C: + O_2 \rightarrow Ph_2CO_2 \\ II \end{array} \tag{17}$$

$$2II \rightarrow 2Ph_2CO + O_2 \tag{18}$$

$$Ph_2C: + Ph_2CN_2 \rightarrow Ph_2C=N-N=CPh_2$$
 (19)

isolated by thin layer chromatography in yields of 97 and 3%, respectively. No evidence was obtained for the formation of the diperoxide, III, eq 20, although this product has been obtained in 15% yield in similar reactions carried out at -78 °C.⁴

$$2II \longrightarrow Ph_2 C O O CPh_2 (20)$$

III

A labeling study⁴ originally led to the conclusion that benzophenone could not have been formed directly in the self-reaction of II. In that experiment, reactions 16-18 were investigated by using an atmosphere of isotopically labeled oxygen. The conclusion was based on the fact that no scrambling of the labeled oxygen was detected as the reaction progressed. However, this is a very narrow interpretation of the results since it assumes that the molecules of carbonyl oxide orient themselves in "head-to-head" formation, IV.

In fact, IV is likely to be an unfavored orientation since benzophenone oxide has a dipole moment of 4.0 D,¹⁴ implying that arrangements such as V are preferred. All that is then required

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to explain the results is that benzophenone be formed in a process²¹ which preserves the labeling pattern of the original oxygen molecules, eq 21.

$$\Sigma \longrightarrow Ph_2 C^{\circ} CPh_2$$
 (21)

The value for the rate constant, k_{18} , is ca. 2-3 orders of magnitude lower than that characteristic of a diffusion-controlled process.²² For such reactions A factors in the range 10^{10} to 10^{11} M⁻¹ s⁻¹ are typical; activation energies are normally 1-3 kcal mol⁻¹ and depend upon the solvent viscosity.²² Clearly, the important difference between the parameters for decay of II and those for diffusion-controlled processes is in the magnitude of the reaction A factor itself.

The value of the A factor is fairly typical of those for many relatively simple, bimolecular processes²³ implying that the reacting fragments must adopt a prefered orientation with respect to one another, in contrast to a diffusion-controlled process where entry into the same solvent cage is a sufficient requirement for reaction. However, the entropy loss in achieving the transition state is not as great as that observed for the self-reactions of nitroxides where strong dipolar interactions lead to A factors which are typically ca. $10^4 \text{ M}^{-1} \text{ s}^{-1}.^{24,25}$

There is an important distinction between the self-reactions of nitroxides and those of carbonyl oxides which may account for this substantial difference. In general, the nitroxide self-reaction is a disproportionation process. The dipolar interaction is thought to lead to formation of a complex which, for structural reasons, disfavors hydrogen transfer so that dissociation rather than product formation is its dominant fate, eq 22.²⁶ For carbonyl oxides the

$$2RR'NO^{\bullet} \rightleftharpoons complex \rightarrow RR'NOH + RR'(-H)NO \qquad (22)$$

dipolar interaction is likely to provide relative orientations of the molecules which are condusive to product formation so that

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dissociation of the encounter pair is relatively unimportant. Thus, self-reactions of molecules with strong dipole moments cannot a priori be expected to show very low A factors.

In addition to the self-reaction described above, we measured the rate constant for the reaction of II with a typical carbonyl oxide scavenger.

Aldehydes react readily with carbonyl oxides to form secondary ozonides. We therefore measured the rate constant for an example of this reaction and used octanal as a scavenger of benzophenone oxide, eq 23. The carbonyl oxide was generated by the method

$$Ph_2 C\overline{OO} + RC(O)H \longrightarrow Ph_2 C \xrightarrow{O} H (23)$$

R = octyl

described above and its lifetime was measured as a function of octanal concentration up to 6 mM. Addition of the aldehyde caused a significant decrease in the signal intensity and a reduction in the lifetime of the carbonyl oxide. The observed pseudo-first-order rate constants for this process, k_{obsd} , are related within a good approximation to that of interest, k_{23} , and to τ_0 which represents the lifetime of the carbonyl oxide in the absence of octanal, eq 7 and 24.²⁷ A plot of the data gave $k_{23} = 2.0 \times 10^4$

$$k_{\text{obsd}} = \frac{1}{\tau_0} + k_{23}[\text{octanal}]$$
(24)

 M^{-1} s⁻¹ at 298 K. This value is ca. 2 orders of magnitude less than that for the related reaction of fluorenylidene oxide with octanal.¹⁵

Summary

Benzophenone oxide was investigated by the technique of optical modulation spectroscopy. This Criegee intermediate undergoes bimolecular self-reaction in the absence of quenchers with a rate constant which is ca. 2 orders of magnitude less than the diffusion-controlled limit. The activation energy for the process was only 1.8 ± 0.3 kcal mol⁻¹ and its relative slowness was found to be due to the entropic requirements for the reaction. The reaction kinetics and the high yields of benzophenone as product are consistent with the dipolar nature of the intermediates and the results of early ¹⁸O labeling studies. Benzophenone oxide was scavenged relatively slowly by octanal.

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Registry No. Benzophenone oxide, 90-47-1; octanal, 124-13-0; diphenyldiazomethane, 883-40-9.

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