Generation and Transient Spectroscopy of Substituted Diaryl Carbonyl Oxides[1]

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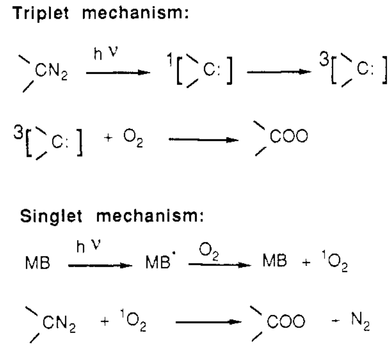
Received March 31, 1988

Spectroscopic and kinetic parameters for a variety of substituted diaryl carbonyl oxides in solution at room temperature are reported. These species are generated by direct reaction of oxygen with the triplet carbene derived from the corresponding diazo compound or by reaction of the diazo compound with singlet oxygen. Typically, diaryl-substituted carbonyl oxides have absorption maxima in the 400–450-nm region and decay with second-order kinetics. For example, the parent benzophenone oxide (λ_{max} 410 nm) can be formed by reaction of the carbene with oxygen (k_{O_2} 5.0×10^9 M^{-1} s^{-1}) or by reaction of singlet oxygen with the diazo precursor ($k_D = 1.0 \times 10^9$ M^{-1} s^{-1}). It decays by self-reaction with $k = 1.33 \times 10^7$ M^{-1} s^{-1} in acetonitrile and can be readily scavenged by aldehydes, e.g. for acetaldehyde $k_3 = 3.1 \times 10^6$ M^{-1} s^{-1}.

Carbonyl oxides have been postulated as reaction intermediates in the ozonolysis of olefins for several decades.[2-4] Recently, there has been renewed interest in these intermediates, largely as a result of their successful detection and identification in low-temperature matrices,[5-14] as well as in solution at ambient temperatures.[15-18] Carbonyl oxides can be readily generated from diazo compounds via a triplet mechanism, i.e. photolysis of the diazo compounds leads to triplet carbene, which reacts directly with ground-state molecular oxygen to yield the carbonyl oxide[16] (Scheme I). Alternatively, the same species can be generated via reaction of singlet oxygen with the diazo precursor[18] (singlet mechanism); in this case it is necessary to use a single oxygen sensitizer, such as methylene blue (MB in Scheme I).

Scheme I



We have previously reported a detailed laser flash photolysis study of fluorenone oxide[17] generated by the two routes indicated in Scheme I and in preliminary form we have also reported on benzophenone oxide.[18] In this paper we report the results of studies on a variety of diaryl-substituted carbonyl oxides, which demonstrate the generality of the spectroscopic properties observed for benzophenone oxide and fluorenone oxide and also illustrate some of the differences in their kinetic behavior.

Experimental Section

Materials. Unless otherwise noted, all chemicals were from Aldrich or BDH and were purified prior to use. Solvents were Aldrich Gold label (benzene), BDH spectrophotometric grade (acetonitrile), and Fluka puriss (Freon 113) and were dried and distilled prior to use. Diazo compounds with the exception of dimesityldiazomethane (V) and diazofluorene (VI) were prepared by standard literature procedures[19] and were vacuum sublimed prior to use. Diazofluorene was prepared according to the method of Moss and Joyce.[20] Dimesityldiazomethane was synthesized by the method reported by Zimmerman and Paskovich.[21]

Laser Flash Photolysis. Laser flash photolysis experiments were carried out on oxygen containing solutions of the diazo compound (~10^{-4}–10^{-3} M). For experiments in which the rate constant for reaction of oxygen with carbenes was determined, varying concentrations of oxygen in nitrogen were bubbled through the solution. The N_2/O_2 mixtures were prepared with a Matheson Model 610 gas mixing system. All other experiments were carried out on solutions under a continuously replenished atmosphere of oxygen. All experiments used a flow system in order to ensure that each laser pulse irradiated a fresh volume of solution. Lasers used were either a Lumonics TE-860-2 excimer laser (308 nm, ~4 ns, ~40 mJ/pulse) or a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, <10 mJ/pulse). In the experiments requiring methylene blue sensitization, the pulses from a Candela 500M flashlamp-pumped dye laser were used [590 nm (Rhodamine 6G), ~250 ns, <500 mJ/pulse]. Quenchers were added as aliquots to the reservoir containing the oxygen saturated solutions. Further details of the laser photolysis system are given elsewhere.[22]

Conventional Flash Photolysis. Conventional flash photolysis experiments were performed on oxygen-saturated solutions of the diazo compound (~10^{-4} M). Solutions contained in a reservoir were flowed into a cylindrical jacketted quartz cell (path length 10 cm) before each pulse. The jacket of the cell was filled with an aqueous solution of K_2CrO_4 (0.77 g/L) and Na_2CO_3 (1 g/L), which acts as a filter transmitting light in the 290–340-nm range, with λ_{max} 310 nm. This filter thus allows the transmission of light of wavelengths comparable to either excimer or nitrogen

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[1] Issued as NRCC No. 29829.

[2] Criegee, R.; Wenner, G. *Justus Liebigs Ann. Chem.* **1943**, *564*, 9.

[3] Criegee, R. *Rec. Chem. Prog.* **1957**, *18*, 111.

[4] Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

[5] Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213.

[6] Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1842.

[7] Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 725.

[8] Dunkin, I. R.; Bell, G. A. *Tetrahedron* **1985**, *41*, 339.

[9] Bell, G. A.; Dunkin, I. R.; Shields, C. J. *Spectrochim. Acta* **1985**, *41A*, 1221.

[10] Sander, W. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 255.

[11] Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

[12] Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154.

[13] Sander, W. *Spectrochim. Acta* **1987**, *43A*, 637.

[14] Sander, W. *J. Org. Chem.*, in press.

[15] Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* **1983**, 1261.

[16] Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391.

[17] Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

[18] Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623.

[19] Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 351.

[20] Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475.

[21] Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2145.

[22] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

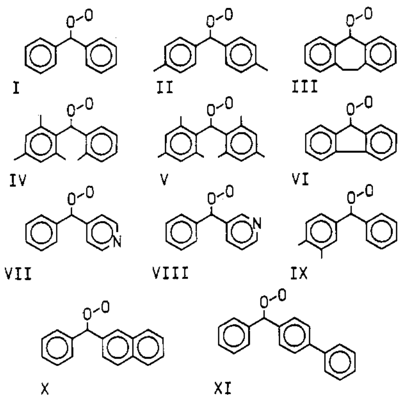
0022-3263/89/1954-1612$01.50/0

Table I. Spectroscopic and Kinetic Parameters for Various Aryl-Substituted Carbonyl Oxides

carbonyl oxide	solvent	λ_{max}, nm	k_{O_2}, M^{-1} s^{-1}	k_D, M^{-1} s^{-1}	$(2k/\epsilon l)$,[a] s^{-1}
I	acetonitrile	410	$(5.0 \pm 0.1) \times 10^9$	$(1.0 \pm 0.4) \times 10^9$[b]	$(1.44 \pm 0.01) \times 10^3$
II	acetonitrile	409	$(2.2 \pm 0.6) \times 10^9$		$(1.99 \pm 0.04) \times 10^3$
III	acetonitrile	401			$(8.10 \pm 0.4) \times 10^3$
IV	acetonitrile				$(3.0 \pm 0.04) \times 10^2$
V	acetonitrile	390	$(3.4 \pm 0.2) \times 10^8$	1.2×10^7	1.85[d]
V	benzene		$(1.3 \pm 0.3) \times 10^8$		
VI	Freon-113	450	$(1.4 \pm 0.2) \times 10^9$	$(6.6 \pm 0.4) \times 10^7$[c]	
VII	Freon-113	418			
VIII	acetonitrile	428			$(3.10 \pm 0.06) \times 10^3$
IX	acetonitrile	415			
X	acetonitrile	405			$(1.87 \pm 0.04) \times 10^3$
XI	acetonitrile	410			$(1.25 \pm 0.02) \times 10^3$

[a] For l = 10 cm throughout. [b] From ref 18. [c] From ref 17. [d] First-order rate constant (s^{-1}). Fit is poor for second order.

Chart I



lasers. The photolysis system was a PRA FP-1000 unit and consisted of two colinear 10 cm Xe quartz flash lamps [~250 to ~700 nm; 10 μs pulse duration, ~12 J/pulse (at 2.5 kV)]; a 75-W Xenon monitoring lamp; and a monochromator–photomultipler detection system. Signals from the photomultiplier were captured with a Tektronix 2230 digital storage oscilloscope equipped with an RS-232 interface. Waveforms were transferred to a PDP11-73 computer for kinetic analysis and storage.

Results and Discussion

All experiments described in this study have been carried out in solution at room temperature. Studies leading to the measurement of rate constants for carbene reactions with oxygen were carried out in the presence of variable oxygen concentrations, while all other studies were carried out in oxygen saturated solutions. All experiments were carried out with use of a flow system to avoid extensive depletion of the diazo precursor.

Transient Spectroscopy of Carbonyl Oxides. Chart I shows the structures of the carbonyl oxides examined in this and in earlier work.[16-18] Figure 1 shows spectra of representative carbonyl oxides generated by the triplet (carbene) route, as indicated in Scheme I; they agree with those generated by the singlet route. The solvents in these experiments were acetonitrile or Freon 113, although it should be noted that the spectra of carbonyl oxides do not show any extensive solvent dependence, a rather interesting observation in view of their large dipole moment.[23] Typical diazo concentrations were 1×10^{-4} M. In the case of V the carbene–oxygen reaction is rather slow (vide infra), and the spectrum shown in Figure 1 also shows some carbene absorption at $\lambda \leq 340$ nm.

Current knowledge of carbene chemistry suggests that intersystem crossing (singlet–triplet) is a very fast process. For example, for diphenylmethylene k_{ISC} ~3×10^9 s^{-1} in acetonitrile.[24] Fast intersystem crossing and relatively unreactive behavior of singlet carbenes toward oxygen supports the mechanism indicated in Scheme I, where carbonyl oxide formation is indicated as an exclusive triplet reaction.

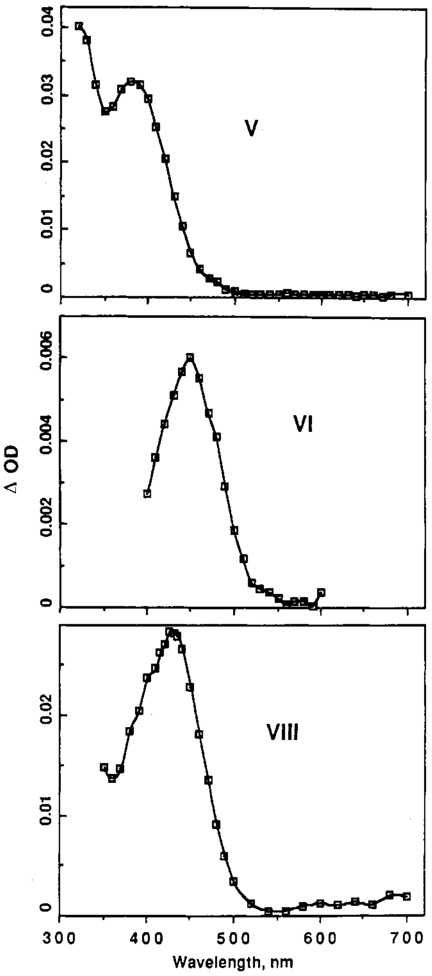


Figure 1. Transient absorption spectra for carbonyl oxides V and VIII in acetonitrile and for VI in Freon-113 at room temperature. In the case of V some carbene is still present and is responsible for most of the absorption at $\lambda \leqslant 340$ nm.

Table I lists the observed maxima for absorption of all carbonyl oxides studied. In all cases except VI the absorption maximum is at 410 ± 20 nm even though there must be considerable differences in the geometry of the various carbonyl oxides. For example in V the conformation must be such that the phenyl rings deviate from

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(23) Fessenden, R. W.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *117*, 103.

(24) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.

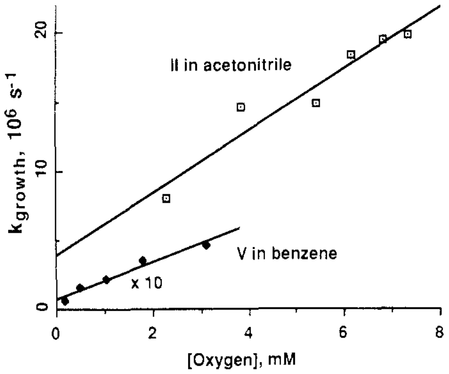

Figure 2. Kinetic data for the generation of II in acetonitrile and of V in benzene by the triplet mechanism, plotted according to eq 1. In the case of V the data have been expanded vertically (×10).

coplanarity even more than in the case of I. Nevertheless, their absorption maxima are very similar. This suggests that the COO groups interact with only one phenyl ring and therefore this interaction is similar for all (except VI). At the same time, III, which has a small deviation from coplanarity, has a spectrum similar to the others. This suggests that such a small deviation is enough to give λ_{max} similar to that for V. The contrasting case is that of VI for which λ_{max} is 450 nm. This carbonyl oxide is the only one in which bonding forces coplanarity of the phenyl rings, and it could be proposed that in such a situation there is enhanced interaction between *both* phenyl rings and the COO chromophore. Recent matrix infrared studies of VI[8] and I[10] show that the stretching vibration involving mainly C–O is at a lower wave number for VI than for either I or indenone oxide. This is compatible with a "weaker" C–O bond and might result from the forced coplanarity of VI. A red shift of the fluorenylidene with respect to the diphenylcarbene ylide has also been observed in the case of thiocarbonyl ylides.[25]

The reactions of singlet oxygen with the corresponding diazo compounds lead to the same transients as those obtained by the carbene reaction. The reactions involving singlet oxygen were carried out with methylene blue (MB) as a sensitizer. Excitation of the sensitizer was carried out at 590 nm with the pulses from a dye laser.

Kinetics of Carbonyl Oxide Formation by the Triplet Mechanism. The kinetics of carbonyl oxide formation were studied by monitoring their formation at their corresponding absorption maxima following laser excitation at 337 or 308 nm. Typical diazo concentrations were in the 10^{-4}–10^{-3} M range. The build-up of the signal followed pseudo-first-order kinetics (k_{growth}) and was monitored for several concentrations of oxygen, which was adjusted by bubbling with O_2/N_2 mixtures of known composition. The bimolecular rate constant, k_{O_2}, was determined from plots of k_{growth} vs $[O_2]$, according to eq 1 where τ_3 is the carbene lifetime in the absence of oxygen

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

in the solvent employed for the experiment, and k_{O_2} is the rate constant for the reaction of the carbene with oxygen (see Scheme I). Figure 2 shows representative plots according to eq 1; the rate constants obtained in this way have been included in Table I.

The rate constant for generation of V is 3.4×10^8 M^{-1} s^{-1} in acetonitrile, i.e., about 1 order of magnitude smaller than for the less hindered precursors, probably reflecting a combination of steric and geometric restrictions in the reaction leading to V. Analysis according to eq 1 also yields the carbene lifetimes, τ_3. The values determined are compatible with the triplet lifetimes determined directly.

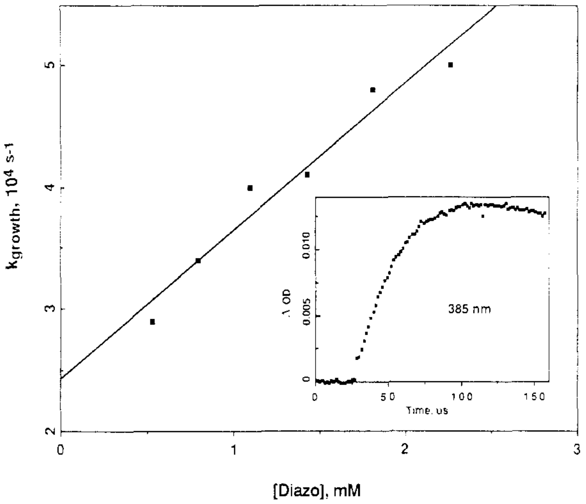

Figure 3. Kinetic data for the formation of V in acetonitrile via the singlet mechanism, plotted according to eq 2. Insert: Trace showing the formation of V monitored at 385 nm for a solution containing 1.8 mM diazo compound.

Kinetics of Carbonyl Oxide Formation by the Singlet Route. The singlet route (Scheme I) offers more than just an alternative pathway for producing carbonyl oxides. Carbenes are extremely reactive species, and quite frequently the choice of the solvent used for the carbene reactions is dictated simply by the extent of carbene reactivity in that solvent. For example, the carbene route is useless in alcohols, as a result of fast carbene insertion into the O–H bond. The singlet-oxygen method does not have this restriction and is only limited by the reactivity of singlet oxygen toward the solvent. This is not a severe restriction, however, given the fact that diazo compounds are efficient singlet-oxygen scavengers (vide infra) and therefore compete favorably with most solvents in spite of the large differences in concentration (10^{-3} M vs ~10 M). Many of our experiments have been carried out in the same solvents with both reactions in Scheme I, simply to facilitate direct comparison of results.

Methylene blue (MB) was used as a singlet-oxygen sensitizer, at a concentration of approximately 1 μM, in oxygen-saturated solutions. In the case of acetonitrile, saturation corresponds to $[O_2] = 7.7 \times 10^{-3}$ M.[26] Under these conditions the rate constant for carbonyl oxide formation can be determined by measuring its growth at the corresponding absorption maximum, as a function of diazo concentration. In this case the experimental rate constants, k_{growth}, are given by:

$$k_{growth} = \tau_0^{-1} + k_D[Ar_2CN_2] \qquad (2)$$

where τ_0 is the lifetime of singlet oxygen in the solvent used in the absence of diazo compound and k_D is the bimolecular rate constant for singlet-oxygen scavenging by the diazo compound. Carbonyl oxides produced by the singlet route were I, V, and VI. The values of k_D derived from these measurements have also been included in Table I. A representative plot (for V) according to eq 2 is shown in Figure 3. The insert in Figure 3 shows a typical growth

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[25] McGimpsey, W. G.; Scaiano, J. C. *Tetrahedron Lett.* **1986**, *27*, 547.

[26] Coetzee, J. F.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1957**, *79*, 6110. Battino, R. *Solubility Data Series*; *Oxygen and Ozone*; Pergamon Press: Oxford, 1981; Vol. 7.

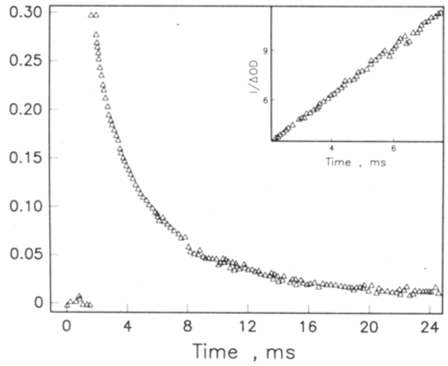


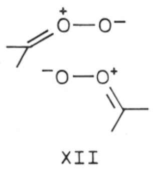
Figure 4. Decay of I in acetonitrile monitored at 410 nm obtained by coventional flash photolysis. Insert: Second-order fit of the decay data.

curve from which the individual values of k_{growth} were derived. In the few cases where a comparison is possible, the values of k_D are in agreement with literature values obtained by other techniques.[27]

Carbonyl Oxide Decay Kinetics. The time domain of our laser flash photolysis detection system is $\sim 10^{-9}$ to $\sim 10^{-4}$ seconds. Since the decay of carbonyl oxides studied in inert solvents involves decay times longer than these, this technique was not adequate for accurate kinetic measurements. For this reason, we have used conventional flash photolysis techniques to study carbonyl oxide decay processes. With this setup it is possible to measure decay times of 10^{-5}–10^{0} s.

Conventional flash photolysis of oxygen-saturated acetonitrile solutions of the diazo compound ($\sim 10^{-4}$–10^{-5} M) resulted in the production of the corresponding carbonyl oxide which was monitored at the absorption maximum determined in the laser flash experiments. This species was produced within the duration of the lamp pulse. The decay of the carbonyl oxide was found to be second order (see Figure 4 for an example) in all cases except V. For V the decay was several orders of magnitude slower than that recorded for the other carbonyl oxides and was best fit to a first order decay. Second-order fitting of transient absorption data yields $2k/\epsilon l$ values, where $2k$ is the self reaction rate constant, ϵ the extinction coefficient, and l the optical path. The $2k/\epsilon l$ values obtained for several carbonyl oxides are given in Table I. The actual $2k$ value for benzophenone oxide can be estimated by using the value for ϵ (410 nm) determined by optical modulation methods[28] ($\epsilon = 1850 \pm 450$ M^{-1} cm^{-1}). This leads to $k \sim 1.33 \times 10^7$ M^{-1} s^{-1} in excellent agreement with the value of 1.8×10^7 M^{-1} s^{-1}, reported by Girard and Griller.[28]

The second-order decay of carbonyl oxides is expected to take place via the orientation shown in XII,[28] ultimately leading to the formation of benzophenone and oxygen.



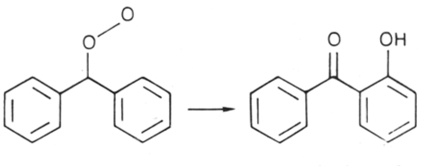
XII

The first-order decay of V may simply be the result of an inefficient process, which becomes the dominant reaction pathway when the formation of XII becomes very slow. The first-order process may reflect secondary photolysis by the monitoring beam. Presumably intramolecular oxygen atom migration similar to that reported by Kumar and Murray[29] for I and VI (eq 3) would not be feasible for V.

Table II. Rate Constants for Reaction of Aryl-Substituted Carbonyl Oxides with Aldehydes

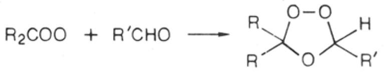
carbonyl oxide	solvent	aldehyde	k_s, M^{-1} s^{-1}
I	acetonitrile	acetaldehyde	$(3.1 \pm 0.4) \times 10^6$
		phenylacetaldehyde	$(2.1 \pm 0.1) \times 10^6$
		mesitaldehyde	$\sim 1 \times 10^7$
II	acetonitrile	acetaldehyde	$(4.5 \pm 0.6) \times 10^6$
III	acetonitrile	acetaldehyde	$(4.7 \pm 0.4) \times 10^5$
		phenylacetaldehyde	$(2.9 \pm 0.2) \times 10^5$
VI[a]	Freon-113	acetaldehyde	$(1.21 \pm 0.04) \times 10^9$
VI[a]	Freon-113	phenylacetaldehyde	$(5.0 \pm 1.0) \times 10^8$
VI[a]	Freon-113	*n*-octanal	$(4.5 \pm 0.5) \times 10^7$

[a] From ref 17.



(3)

Reaction of Carbonyl Oxides with Aldehydes. The reaction of carbonyl oxides with aldehydes to yield the corresponding ozonide is well documented, and the mechanism of this reaction was proposed by Criegee[3] to explain the mechanism of the ozonolysis of olefins.



(4)

The rate constants for the scavenging of carbonyl oxides by various aldehydes were determined by recording the decay of the carbonyl oxide as a function of aldehyde concentration. The reactions of carbonyl oxides frequently follow complex kinetics (vide supra) in the absence of quenchers or at very low quencher concentration. However, once a sufficient concentration of scavenger has been added, the decays can be adequately fitted with a monoexponential expression. The experimental pseudo-first-order rate constant for decay, k_d, follows the following expression:

$$k_d = k_d{}^0 + k_s[\text{aldehyde}] \qquad (5)$$

where k_s is the rate constant for the reaction of aldehyde with the carbonyl oxide, and $k_d{}^0$ is the rate of carbonyl oxide decay in the absence of scavenger ($k_d{}^0 = \tau^{-1}$). The corresponding rate constants have been summarized in Table II and include the values determined previously for fluorenone oxide. The measurements involving mesitylaldehyde were somewhat more difficult, presumably as a result of competitive light absorption and photoenolization[30] of the aldehyde. Only an approximate value could be determined.

Summary

This paper reports a spectroscopic and kinetic study of a variety of diaryl-substituted carbonyl oxides in solution at room temperature. As was previously reported the production of these species may take place via a triplet mechanism involving the direct reaction of molecular oxygen with triplet carbene generated by photolysis of the corresponding diazo precursor. The rate constants for

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[27] Bethell, D.; McKeivor, R. *J. Chem. Soc., Perkin Trans. 2* **1977**, *327*.

[28] Girard, M.; Griller, D. *J. Phys. Chem.* **1986**, *90*, 6801.

[29] Kumar, S.; Murray, R. W. *Tetrahedron Lett.* **1980**, *21*, 4781.

[30] Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.

these reactions have been determined. Alternatively, methylene blue sensitized production of singlet oxygen leads to reaction with the diazo precursor, again giving the carbonyl oxide. Rate constants for this reaction for several different diazo compounds have also been determined.

Carbonyl oxides decay almost exclusively by a second-order process involving recombination and ultimately ketone production. Severely hindered carbonyl oxides (IV and especially V) decay more slowly than less hindered species, thus giving indirect support for the recombination mechanism. In addition aldehyde quenching has been shown for I–III in agreement with the results of Criegee.

Finally, we have been interested in the photochemistry of reaction intermediates induced by subjecting photochemically produced transients to a second laser pulse.[31] In a two-laser experiment in which the first laser is used to produce the carbonyl oxide (I) and a dye laser tuned to ~430 nm is used to photolyze I, we observed efficient irreversible bleaching associated with the dye laser pulse. This bleaching indicates that permanent chemical change takes place following excitation of I. Whether the products associated with this bleaching are benzophenone or the aryl ester, phenyl benzoate, will be the subject of future work.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance and to Professor W. Sander for the communication of unpublished results (ref 14).

Registry No. I, 20387-24-0; II, 91669-23-7; III, 118797-91-4; IV, 118797-92-5; V, 118797-93-6; VI, 118797-94-7; VII, 118797-95-8; VIII, 118797-96-9; IX, 118797-97-0; X, 118797-98-1; XI, 118797-99-2; O_2, 7782-44-7; diphenyldiazomethane, 883-40-9; bis(4-methylphenyl)diazomethane, 1143-91-5; bis(2,4,6-trimethylphenyl)diazomethane, 61080-14-6; 9-diazofluorene, 832-80-4; diphenylcarbene, 3129-17-7; bis(4-methylphenyl)carbene, 32076-77-0; bis(2,4,6-trimethylphenyl)carbene, 85236-86-8; 9*H*-fluoren-9-ylidene, 2762-16-5; acetaldehyde, 75-07-0; phenylacetaldehyde, 122-78-1; mesitaldehyde, 487-68-3.

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(31) See for example: McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2179. Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 5487.

Reactions of Phenylmagnesium Chloride and Phenyllithium with Thianthrene Cation Radical Perchlorate. Evidence for Electron Transfer: Formation and Decomposition of 5-Substituted Thianthreniumyl Perchlorates

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Received November 28, 1988

Reaction of thianthrene cation radical perchlorate (Th$^{\bullet+}$ClO$_4^-$), suspended in either ether or THF, with PhMgCl, and reaction of Th$^{\bullet+}$ClO$_4^-$, suspended in ether, with PhLi in C_6H_{12}/ether, gave largely benzene and Th. 5-Phenylthianthreniumyl perchlorate (**1a**) was formed in the Grignard reactions but was not obtained in the PhLi reaction. Diphenyl sulfide (Ph$_2$S) and dibenzothiophene (DBT) were obtained with PhMgCl and PhLi in ether, but not with PhMgCl in THF. Small amounts of ethyl 1-phenylethyl ether and 2-phenyltetrahydrofuran (PhTHF) were also formed. Reaction with PhMgCl in THF-d_8 and with PhLi in $(C_2D_5)_2O$ gave a mixture of C_6H_6 and C_6H_5D. These results show that phenyl radical (Ph$^\bullet$) was formed in the cation radical reactions and abstracted H(D) atom from the solvent. The results suggest also that Ph$^\bullet$ was trapped by Th$^{\bullet+}$, leading to **1a**. However, as shown with control reactions, **1a** reacted further with PhMgCl (slowly) and PhLi (rapidly) and was converted into Ph$_2$S and DBT. Control reaction of PhLi with **1a** gave Ph$_2$S and DBT in high, approximately equal yields. Reaction with 5-(*p*-tolyl)thianthreniumyl perchlorate (**1b**) analogously gave phenyl *p*-tolyl sulfide and DBT. Reaction of PhMgCl with **1a** was slow and incomplete and gave not only Ph$_2$S and DBT but also some 2-phenyl-2′-(phenylthio)diphenyl sulfide (**2a**) and a mixture of 1- and 2-phenylthianthrene (together designated as **3a**). An analogous reaction occurred between PhMgCl and **1b**. Reaction of **1a** with BuMgCl gave BuSPh and DBT, some 2-(phenylthio)diphenyl sulfide (**4**), and some 2-(butylthio)-2′-phenyldiphenyl sulfide (**5a**). In contrast, reaction of PhMgCl with 5-butylthianthreniumyl perchlorate (**1e**) gave mainly benzene and Th, while reaction of BuMgCl with **1e** gave mainly butane, octane, and Th along with a small amount of 2-butyl-2′-(butylthio)diphenyl sulfide (**5e**). Reaction of PhLi with **1e** and its analogues 5-methyl- and 5-ethylthianthreniumyl perchlorate (**1c** and **1d**, respectively) gave benzene, Th, the corresponding alkyl phenyl sulfide and DBT, and small amounts of 2-(alkylthio)-2′-phenyldiphenyl sulfide (**2c–e**). Formation of benzene in these reactions is attributed to deprotonation of the alkyl group in **1c–e** and concomitant formation of an ylide (**6–8**). Ylide **6**, from reaction of PhLi with **1c**, was trapped by reactions with subsequently added water and phenol (reconverting **6** to **1c**) and with added benzophenone, leading to Th and 1,1-diphenyloxirane (**9**). Diphenylmercury did not react with **1a** in acetonitrile solution. The apparent complexity of reactions of Th$^{\bullet+}$ClO$_4^-$ with PhMgCl and PhLi is better understood in the light of knowledge about reactions of **1a–e**. The comparative simplicity of reaction of Th$^{\bullet+}$ClO$_4^-$ with Ph$_2$Hg is also made clearer.

Introduction

Some years ago it was found that thianthrene cation radical perchlorate (Th$^{\bullet+}$ClO$_4^-$) reacted with diorgano mercurials (R$_2$Hg) to give 5-substituted thianthreniumyl perchlorates (1) in excellent yield (eq 1).[2] A question arose as to whether or not the reaction involved electron transfer and formation of radicals, which, being trapped by Th$^{\bullet+}$, gave products 1. Later, evidence for these steps was, in

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0022-3263/89/1954-1616$01.50/0 © 1989 American Chemical Society