

interactions. More precisely this can be summarized in the following way:

(4) Methanol differs in this respect from the heavier alcohols. The bandshape for betaine-26 in methanol is only well reproduced if two, rather than a single, molecular modes are introduced into the bandshape expressions and combined with Gaussian solvent-broadened sub-bands. If one of the two modes is associated with the same degree of freedom as emerged for the aprotic solvents, then the vibrational frequency and displacement values of the second one, i.e., 2400 cm^{-1} and 0.84, respectively, are indicative that O-H stretching and bending are involved in the reorganization of this mode. This is, however, only partly borne out by the deuterium isotope effect investigations. Although the appropriate frequency is smaller and the displacement larger for the deuterated methanol, as expected when O-H reorganizations are involved, the emerging frequency ratio is smaller than the ratio between pure O-H frequencies. This suggests that the second molecular mode for methanol contains elements of librational motion which are much less isotope sensitive.

The remaining solvent band broadening, Δ_s , does not fit the $\epsilon_0^{-1} - \epsilon_s^{-1}$ correlation for the polar solvents but is larger by 10-15%. This observation is also indicative of some additional, either vibrational or spatial, solvent dispersion, but so far it is elusive of more precise identification.

(5) Solvent vibrational dispersion appears even more pronounced for the heavier alcohols, for which the two-mode Gaussian approximation is also inadequate. Accurate band representation is, however, obtained if the additional asymmetry parameter ξ_3 is introduced. The parameters for the two molecular modes which

emerge for the heavier alcohols then coincide approximately with the ones for methanol, while the asymmetry of the sub-bands and the relatively large values of Δ_s must reflect additional high-frequency solvent dispersion which is not well incorporated by a discrete single-mode approximation.

We can conclude that rigorous bandshape analysis for betaine-26 has provided physically plausible and quite precise criteria for the adequacy or failure of the simplest approach to solute-solvent interactions as bulk electrostatic coupling to a structureless dielectric. It has also provided a disclosure of the nature of the solute intramolecular reorganization which accompanies the electronic transition. Such achievements furthermore have to rely on bandshape rather than band maximum analysis. A clue to the more composite behavior of protic solvents has finally emerged. Specific interactions, the nature of which can be traced to hydrogen bonding, perhaps solvent librational motion, and dispersion in the solvent vibrational frequency spectrum, can thus account for nearly all the observed band features for these solvents. Further details of this could be substantiated by suitable molecular models for the solvent and the solute-solvent interactions. As disclosed by our present analysis, the formalism applied here has the merit of incorporating such solvent structural details in the form of vibrational frequency and spatial dispersion of the solvent susceptibility functions, thus going far beyond structureless continuum models. Such a requirement is also needed in the elucidation of real solute-solvent interactions.

Acknowledgment. We acknowledge financial support from the Danish Natural Science Research Council.

Laser Flash Photolysis Studies of Methoxycarbonyl Phenyl Carbene and Its Derived Carbonyl Oxide at Room Temperature

Yoshihisa Fujiwara,^{1a} Yoshifumi Tanimoto,^{1a} Michiya Itoh,^{*1a} Katsuyuki Hirai,^{1b} and Hideo Tomioka^{1b}

Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan, and the Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan. Received August 25, 1986

Abstract: Laser flash photolysis of methyl α -diazophenylacetate gives triplet methoxycarbonyl phenyl carbene (³MPC) exhibiting a transient absorption spectrum (<270 nm), which shows a pseudo-first-order decay with lifetime of 461 ns in deaerated Freon 113. The triplet carbene readily reacts with an oxygen molecule to afford a corresponding carbonyl oxide in aerated solvents at room temperature. The formation of carbonyl oxide was demonstrated by the buildup of the transient absorption spectrum ($\lambda_{\text{max}} \sim 410$ nm) at the expense of the absorption band of the carbene. Quenching rate constants of this triplet carbene by 2-methyl-2-butene and methyl alcohol were obtained to be $7.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively, by means of monitoring the decay of the triplet carbene. The difference of the reactivity between the triplet carbene and the carbonyl oxide toward methyl alcohol has been investigated. The carbonyl oxide is much more stable with methanol than the parent triplet carbene (³MPC). Kinetic data reported in this paper demonstrate that the stability of this carbene (³MPC) is regarded as an intermediate between reported diphenylcarbene and fluorenylidene.

It is well-known that an oxygen molecule scavenges a triplet carbene²⁻⁵ to afford an intermediate, carbonyl oxide, which is ultimately led to the formation of a corresponding ketonic compound. Recently, aromatic carbonyl oxides, which are frequently referred to as Criegee intermediates,⁶ have been studied by means

of laser flash photolysis in organic solvents at room temperature.⁷⁻¹⁰ Scaiano and his co-workers^{8,9} have reported a transient absorption spectrum of a carbonyl oxide formed from triplet diphenylcarbene and oxygen, and also they¹¹ have presented information about the

(1) (a) Kanazawa University. (b) Mie University.

(2) Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1962**, *84*, 3408.

(3) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

(4) Murray, R. W.; Suzui, A. *J. Am. Chem. Soc.* **1971**, *93*, 4963.

(5) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(6) (a) Criegee, R. *Rec. Chem. Prog.* **1957**, *18*, 111. (b) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

(7) Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* **1983**, 1261.

(8) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391.

(9) Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623.

(10) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

structure of the oxide by measuring the dipole moment. They have proposed that the oxide is a highly dipolar species sharing some of properties expected for a biradical, which probably shows some zwitterionic character. Casal et al.¹⁰ have observed transient absorption spectra of fluorenone oxide and obtained kinetic and mechanistic data on the oxide and triplet fluorenylidene as a precursor by means of the effect of the carbene or singlet oxygen quenchers on the yield of the carbonyl oxide. To the best of our knowledge, little has been reported on the time-resolved spectroscopic studies both on the aromatic carbene and its carbonyl oxide at room temperature except diphenylcarbene^{8,9} and fluorenylidene,¹⁰ though several studies on the oxide have been carried out by infrared spectroscopy in the low-temperature matrices¹²⁻¹⁴ and by product analysis. On the other hand, Tomioka et al.¹⁵ have reported extensive studies on the reactivity of arylcarbenes such as olefin cyclopropanation and C-H and/or O-H insertion reactions which dramatically change in rigid matrix at low temperature. They have suggested that the reaction of the singlet carbene may be predominant at room temperature, while the reaction of the triplet carbene becomes more important in the rigid matrix at low temperature. This paper describes the laser flash photolysis studies of methyl α -diazophenylacetate leading to the formation of the triplet methoxycarbonyl phenyl carbene (³MPC) at room temperature. The triplet ³MPC readily reacts with oxygen to afford transient carbonyl oxide. The kinetic studies on the reaction with 2-methyl-2-butene and methyl alcohol are also presented. The reaction mechanism and dynamics of ³MPC and corresponding carbonyl oxide are discussed in comparison with other carbenes mentioned above.

Experimental Section

Materials. Methyl α -diazophenylacetate (MDP) was prepared¹⁶ by the formylation of methyl phenylacetate, followed by diazidation with tosyl azide reported by Tomioka et al.^{15c} Spectrograde acetonitrile, benzene, chloroform, carbon tetrachloride, *n*-hexane, and *n*-heptane were obtained from Nakarai Chemical Co. and used without further purification. 3-Methylpentane (Aldrich Chemical Co.), 2-methyltetrahydrofuran (MTHF) (Nakarai Chemical Co.), and hexafluorobenzene (Tokyo Kasei Co.) were refluxed over LiAlH₄ (Nakarai Chemical Co.) for several hours and rendered free of impurities by distillation. 1,1,2-Trichlorotrifluoroethane (Freon 113) from Nakarai Chemical Co. was treated in basic alumina (Merk Chemical Co.) column before use. 2-Methyl-2-butene (MB) (Tokyo Kasei Chemical Co.) and 1,4-cyclohexadiene (Nakarai Chemical Co.) were distilled before use. Spectrograde methyl alcohol was used without further purification.

Deaerated samples were prepared by repeated freeze-pump-thaw cycles. The quenching experiments of carbonyl oxide in a variety of oxygen concentrations in Freon 113 was performed by means of sufficiently bubbling nitrogen and oxygen gas mixtures of known composition, where the concentration of oxygen was calculated from the reported solubility value (5.23×10^{-3} M)¹⁷ in Freon 113 at room temperature.

Transient absorption spectra were determined by using an excimer laser (Lambda Physik, EMG-50E, 308 nm) and a monitoring steady Xe arc lamp with a synchronously operated shutter (COPAL). The electric signals obtained from a photomultiplier tube (HTV, R-666) were stored into a storage scope (IWATSU, TS-8123) and analyzed by means of a microcomputer (FUJITSU, FM-11BS).

Steady-state, high-pressure mercury lamp (USHIO, USH-500D, 500 W) equipped with a band-pass filter (UV-D36B, TOSHIBA) was employed on photolysis of low-temperature matrices. The absorption spectra were measured on a spectrophotometer (HITACHI, U-3200).

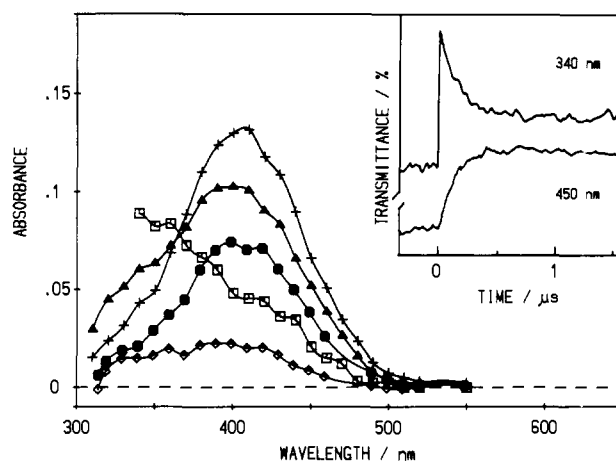


Figure 1. Time-resolved absorption spectra obtained upon 308-nm excitation of methyl α -diazophenylacetate in air-saturated Freon 113 at room temperature: \square , 70-ns delay; \blacktriangle , 210-ns delay; $+$, 490-ns delay; \bullet , 2.5- μ s delay; \diamond , 55- μ s delay from 308-nm laser pulsing. Insets are oscillogram traces monitored at 340 and 450 nm.

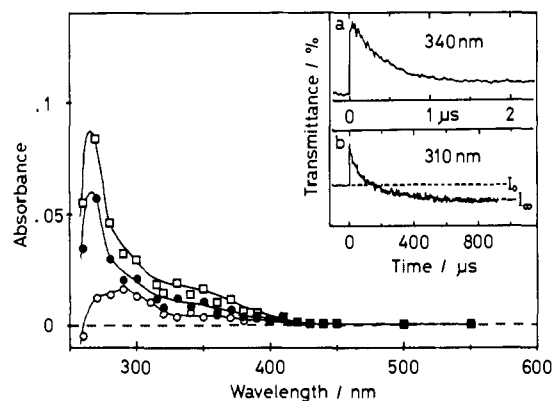


Figure 2. Time-resolved absorption spectra obtained upon 308-nm excitation of methyl α -diazophenylacetate in deaerated Freon 113 at room temperature: \square , 170-ns delay; \bullet , 420-ns delay; \circ , 23.5- μ s delay from 308-nm laser pulsing. Insets are oscillogram traces: (a) at 340 nm and (b) at 310 nm. Since the intensity of transmitted light (I_{∞}) at a very long delay time after laser excitation was larger than that of incident light (I_0) at a shorter wavelength region (<320 nm) because of the bleaching of the original absorption band of MDP, the optical density ($\log(I_{\infty}/I_0)$) was calculated by using I_{∞} in place of I_0 .

Results and Discussion

Laser flash photolysis of methyl α -diazophenylacetate (MDP) in air-saturated 1,1,2-trichlorotrifluoroethane (Freon 113) at room temperature gives the transient absorption spectrum as shown in Figure 1. This spectrum shows two absorption bands at $\lambda_{\max} < 340$ and 410 nm, though a distinct absorption maximum of the former band cannot be detected because of the bleaching of the original absorption band of MDP. Two oscillogram traces of the transient absorptions monitored at 340 and 450 nm are shown in an inset of Figure 1. The former band ($\lambda_{\max} < 340$ nm) exhibits a fast single exponential decay ($\tau = 161$ ns), while the latter band ($\lambda_{\max} 410$ nm) with a very long decay is generated by the first-order kinetics with a risetime of 145 ns. Taking account of the agreement of the fast decay time of the former band with the buildup time of the latter and also of the appearance of an isosbestic point at 365 nm between these two transient absorption bands, it seems that the metastable species exhibiting the former transient absorption band ($\lambda_{\max} < 340$ nm) is ascribed to a carbene as a precursor of the relatively stable species exhibiting the latter absorption band ($\lambda_{\max} 410$ nm). Further, the latter transient species was tentatively ascribed to the carbonyl oxide generated from the carbene and oxygen, as will be mentioned later.

In the deaerated Freon 113 solution of MDP, however, only the former band was obtained as shown in Figure 2, while a 290-nm absorption band characteristic of the benzyl-type radical

- (11) Fessenden, R. W.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *117*, 103.
 (12) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213.
 (13) Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1842.
 (14) Dunkin, I. R.; Bell, G. A. *Tetrahedron* **1985**, *41*, 339.
 (15) (a) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128. (b) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *J. Am. Chem. Soc.* **1979**, *101*, 6009. (c) Tomioka, H.; Okuno, H.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1636. (d) Tomioka, H.; Mijwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753. (e) Tomioka, H.; Suzuki, S.; Izawa, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3156. (f) Tomioka, H.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 492. (g) Tomioka, H.; Izawa, Y. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 344.
 (16) Regitz, M.; Menz, F. *Chem. Ber.* **1968**, *101*, 2622.
 (17) Battino, R. *IUPAC Solubility Data Series: Oxygen and Ozone*; Pergamon Press: Oxford, 1981; Vol. 7.

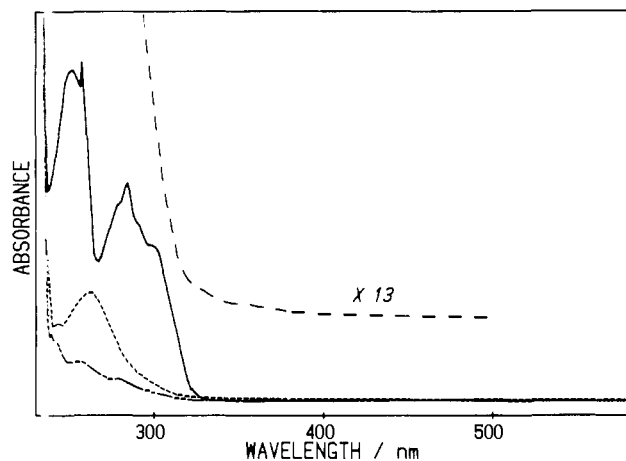


Figure 3. Photolysis of methyl α -diazophenylacetate in 2-methyltetrahydrofuran at 77 K: —, before photolysis; ---, —, after 2 min of irradiation; - · - ·, after warming and refreezing.

was observed at the long delay time. The shorter wavelength transient absorption band due to carbene (λ_{\max} 270 nm) is also observed on a steady photolysis experiment in frozen media. Figure 3 shows the absorption spectral change on irradiation of the deaerated solution of MDP in a 2-methyltetrahydrofuran (MTHF) glass at 77 K. The spectrum obtained after irradiation at 360 ± 50 nm for 2 min exhibits a maximum at 260 nm and a red-edge at 400 nm. The glassy solution does not exhibit any spectral change for several hours if kept at 77 K. However, warming it up to room temperature and refreezing at 77 K lead to disappearance of this absorption band (Figure 3). In these circumstances, the absorption spectrum at 240–400 nm may be attributable to the carbene generated by the photodissociation of MDP. The low-temperature absorption spectrum (240–400 nm) of photolyzed solution is compatible with transient absorption spectrum at room temperature (Figure 1 and 2) which was tentatively ascribed to the carbene as mentioned above.

The ESR spectroscopy is very useful for the identification of carbene in frozen media. Irradiation of MDP in a MTHF glass at 3.6 K gives paramagnetic species easily identified as triplet methoxycarbonyl phenyl carbene (^3MPC) from ESR spectroscopy. The triplet ESR signals are also obtained at 77 K and stable for several hours at this temperature, though ESR parameters E and D due to the triplet cannot be obtained at the present stage.¹⁸ The observation of ESR signals indicates the triplet multiplicity of this carbene in the ground state. On the other side, ESR spectrum of a doublet species, presumably due to a benzyl-type radical, was obtained. This ESR spectrum was almost identical with that of a benzyl-type radical generated by irradiation of methyl α -bromophenylacetate (MBP) in MTHF at 77 K, which gives an absorption spectrum with a maximum at 290 nm. Therefore, these results demonstrate that two metastable species, triplet carbene and benzyl-type radical are generated in the MTHF glass on the irradiation at 77 K. From these results at room temperature and at 77 K, it was suggested that the triplet carbene and the benzyl-type radical are generated on the irradiation of the deaerated solution of MDP, while the triplet carbene and the carbonyl oxide exhibiting 410-nm absorption are formed in the aerated solution.

The decay rate constants for this triplet carbene were measured in several deaerated solvents, whose results are summarized in Table I. In the toluene, cyclohexane, and MTHF solutions, however, no transient absorption signal of the carbene was observed at room temperature, which seems to suggest that chemical reactions such as hydrogen abstraction take place very effectively. In the other solvents, the decay of this carbene was observed to follow pseudo-first-order kinetics. Taking account of a singlet-triplet equilibrium and reactions from these states, the decay rate constant is expected to be a composite of reaction rate constants

Table I. Lifetimes of Triplet Carbene ($\text{Ph}-\dot{\text{C}}-\text{COOMe}$) in Several Solvents at 293 K

solvent	lifetime ^a ns	lifetime ^b ns
Freon 113	461	161
hexafluorobenzene	433	232
benzene	137	80.7
3-methylpentane	126	^c
carbon tetrachloride	139	79.2
chloroform	35.1	27.7
acetonitrile	85.6	57.9

^a Monitored at 350 nm; deaerated solution. ^b Monitored at 350 nm; aerated solution. ^c No signal of ^3MPC was observed.

of both singlet and triplet carbene. Assuming that the singlet (S) and triplet (T) levels are equilibrated more rapidly than reactions of their respective levels and moreover that a rate constant (k_{TS}) of $\text{T} \rightarrow \text{S}$ is much smaller than that (k_{ST}) of $\text{S} \rightarrow \text{T}$, the observed rate constant k_{obsd} is expressed as follows

$$k_{\text{obsd}} = k_{\text{T}} + k_{\text{S}}/K_{\text{eq}}$$

where k_{T} and k_{S} are rate constants for a reaction from these levels, respectively, and K_{eq} is an equilibrium constant equal to $k_{\text{ST}}/k_{\text{TS}}$. Although any information about K_{eq} was not obtained in this system, it seems to be interpreted that the second term in the above equation is more responsible for the observed kinetic parameter, k_{obsd} , being similar to the reported examples with respect to aromatic triplet carbenes.

As mentioned in the introductory section, the formation of carbonyl oxides so-called Criegee intermediate was suggested in the reaction of an aromatic carbene with oxygen. Werstiuk et al.⁸ have reported a reaction rate constant ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) of diphenylcarbene with oxygen and a transient absorption spectrum (λ_{\max} 410 nm) due to carbonyl oxide in an acetonitrile solution at 300 K. Further, Casal et al.¹⁰ have reported a transient absorption spectrum (λ_{\max} 450 nm) due to a carbonyl oxide from diazofluorene in Freon 113. They have obtained a reaction rate constant of fluorenylidene with oxygen, $(1.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 300 K, from the rise of this transient absorption band.

The lifetime of the transient absorption spectrum attributable to the triplet carbene (^3MPC) is appreciably quenched by oxygen. The lifetime of ^3MPC in the aerated condition was obtained to be 161 ns in comparison with that (461 ns) in the deaerated. In addition to the absorption spectrum due to the triplet carbene, ^3MPC , another transient absorption band at 410 nm appeared and increased at the expense of the former in the aerated Freon 113 solution as shown in Figure 1. However, the latter spectrum cannot be observed in the deaerated solution (see Figure 2). Therefore, these experimental results indicate that its transient species may be carbonyl oxide generated by the reaction of ^3MPC and oxygen molecule. Since similar transient absorption spectra are obtained in solvents, the 410-nm band cannot be attributable to the result from reactions involving the solvent. However, little or no fluorescent emission of this carbonyl oxide is obtained even by two-step laser excitation fluorescence technique.¹⁹⁻²¹

The kinetics of the carbonyl oxide formation via ^3MPC were studied by monitoring transient absorption band at 420 nm in the laser excitation of MDP solutions containing various concentrations of oxygen. The buildup of the transient absorption and also the decay of ^3MPC were analyzed by pseudo-first-order kinetics. The apparent buildup rate constant, k_{obsd} , of the carbonyl oxide should be identical with that of the decay of ^3MPC , if the carbonyl oxide is generated from ^3MPC , and k_{obsd} is expressed as follows

$$k_{\text{obsd}} = \tau_0^{-1} + k_{\text{O}_2}[\text{O}_2]$$

where τ_0 is a lifetime of ^3MPC without oxygen and k_{O_2} is a quenching rate constant of ^3MPC by oxygen. A plot of k_{obsd} vs.

(19) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1984**, *106*, 850.

(20) Itoh, M.; Fujiwara, Y. *J. Phys. Chem.* **1985**, *87*, 4558.

(21) Itoh, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1561.

(18) The detailed data will be reported together with those of triplet carbenes from other related compounds in the near future.

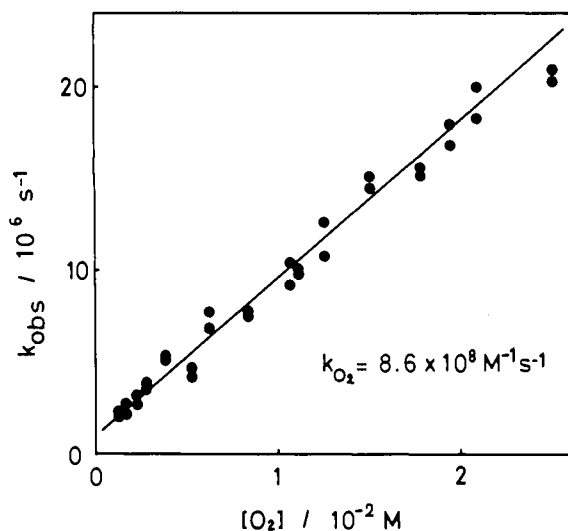


Figure 4. Plots of the growth rate of the carbonyl oxide vs. each oxygen concentration in Freon 113 solution at room temperature.

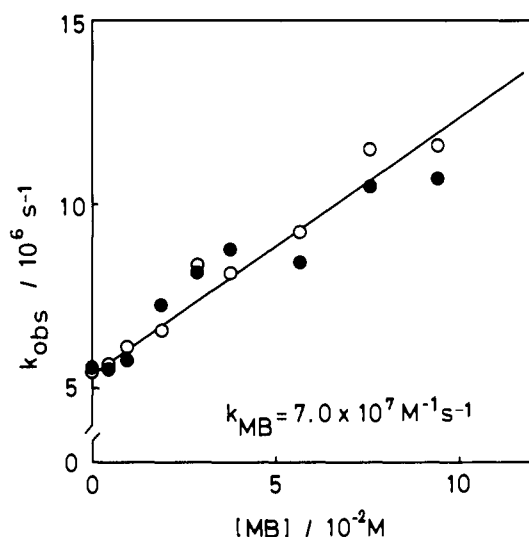


Figure 5. Plots of the decay rate of the carbene (O, measured at 340 nm) and the growth rate of the carbonyl oxide (●, measured at 410 nm) in air-saturated Freon 113 solution containing each concentration of 2-methyl-2-butene at 293 K.

the oxygen concentration affords $k_{O_2} = 8.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $\tau_0 = 1 \mu\text{s}$ (Figure 4), based on the concentration of oxygen of $5.23 \times 10^{-3} \text{ M}$ in air-saturated Freon 113.¹⁷ The obtained value of k_{O_2} is comparable to those reported for diphenylcarbene ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and fluorenylidene ($(1.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). These experimental results support our assignments of transient absorption spectra of carbene and carbonyl oxide and their reaction scheme.

On the other hand, the reactions of triplet diphenylcarbene and fluorenylidene with alkyl olefins and alcohols are known to afford corresponding cyclopropane and ether. Further, the hydrogen abstraction reaction has been reported to take place from 1,4-cyclohexadiene. Therefore, the triplet carbene (³MPC) reactivity toward olefin (2-methyl-2-butene, MB) and alcohol (methyl alcohol, ME) was examined by assuming competitive reaction of these molecules with oxygen. The formation kinetics of carbonyl oxide is given by following equation

$$k_{\text{obsd}} = \tau_0^{-1} + k_{O_2}[O_2] + k_{MB}[MB]$$

where k_{MB} is a quenching rate constant of ³MPC by MB. A plot of k_{obsd} vs. the olefin concentration gives $k_{MB} = 7.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in air-saturated Freon 113 at 293 K (see Figure 5). In the same way, the quenching rate constant, $k_{ME} = 2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for ME, was obtained (see Figure 6a). These values are almost

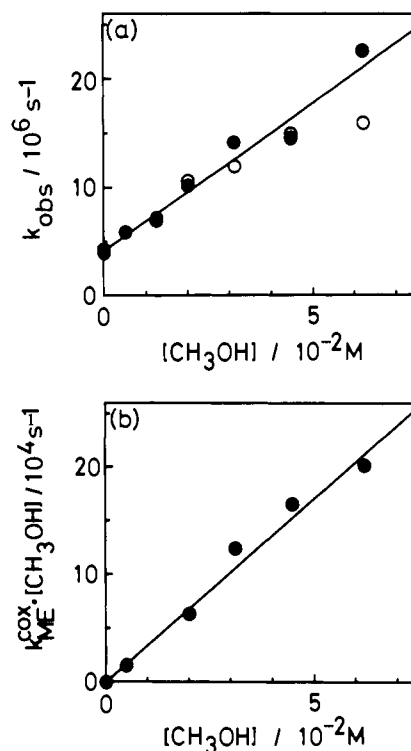


Figure 6. (a) Plots of the decay rate of the carbene (O, measured at 340 nm) and the growth rate of the carbonyl oxide (●, measured at 410 nm) in air-saturated Freon 113 solution containing each concentration of methyl alcohol at 293 K. (b) Plots of $k_{ME}^{COX}[CH_3OH]$ as a function of added methyl alcohol in air-saturated Freon 113 solution at 293 K.

Table II. Growth Rate Constants (k_{obsd}) and Bimolecular Rate Constants (k^{COX}/ϵ) of the Carbonyl Oxide in Several Solvents at 293 K

solvent	$k_{\text{obsd}}^a \text{ s}^{-1}$	$k^{COX}/\epsilon^a \text{ s}^{-1} \text{ cm}$
Freon 113	6.9×10^6	6.6×10^5
hexafluorobenzene	5.0×10^6	1.6×10^5 ^b
benzene	1.5×10^7	4.5×10^6
3-methylpentane	1.5×10^7	2.6×10^5
carbon tetrachloride	1.2×10^7	1.2×10^5 ^b
n-hexane	2.2×10^7	1.6×10^5
n-heptane	2.2×10^7	2.2×10^5

^a Monitored at 420 nm; aerated solution. ^b The inverse of the half-life was listed because of the incomplete second-order decay.

identical with those obtained by direct analysis of the decay of ³MPC as shown in Figure 5 and 6a. Furthermore, by means of the direct analysis of the decay of ³MPC in deaerated Freon 113 solution with several concentrations of 1,4-cyclohexadiene, the reaction rate constant (k_{HA}) for the hydrogen abstraction reaction of ³MPC was obtained to be $2.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Several investigations on the typical quenching experiments of carbenes have been reported; $k_{ME} = (6.30 \pm 1.23) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for fluorenylidene in hexafluorobenzene at 300 K;²² $k_{HA} = (1.0 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for diphenylcarbene in cyclohexane at 300 K.²³ Comparing our experimental data included in Table I with those reported, the reactivity of ³MPC toward these substrates seems to be intermediate between diphenylcarbene and fluorenylidene.

Further, in order to investigate the reactivity of carbonyl oxide from ³MPC, lifetime of the oxide was examined in several air-saturated solvents at 293 K. In most solvents, the decay is not expressed by the pseudo-first-order kinetics but by the second-order kinetics. This means that the carbonyl oxide may react each other to form a final product such as a ketone, methyl benzoylformate, as pointed out by Bartlett and Traylor.² The second-order pa-

(22) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

(23) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283.

rameters, k^{COX}/ϵ , were obtained in the several solvents as summarized in Table II. Assuming that the deactivation process of the carbonyl oxide is diffusion-controlled, the molar extinction coefficient (ϵ) of carbonyl oxide at 410 nm was estimated to be $<19\,400$ ($\log \epsilon < 5.29$) by using the diffusion coefficient ($3.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) at 293 K in *n*-hexane.²⁴ Since the occurrence of the coupling reaction of the carbonyl oxide is not expected from a dioxirane type structure in the usual chemical sense, it is likely that the structure of carbonyl oxide from ³MPC is a biradical or zwitterionic type rather than dioxirane.

Carbonyl oxides are known to have an appreciable reactivity with a wide range of organic compounds. Methyl alcohol quenches effectively not only ³MPC but also carbonyl oxide.²⁵ The decay of the transient absorption of the carbonyl oxide follows via second-order kinetics without methyl alcohol, which suggests a coupling reaction of carbonyl oxide, as mentioned above. When methanol concentration increases in the methanol/Freon 113 mixed solvent system, decay kinetics of the transient absorption band due to carbonyl oxide goes from second-order-kinetics to pseudo-first-order kinetics. The fact reflects scavenging of carbonyl oxide by methyl alcohol. Therefore, these complex reactions are expressed by the following differential equation

$$\frac{d[\text{COX}]}{dt} = k_{\text{O}_2}[\text{O}_2][^3\text{MPC}] - k^{\text{COX}}[\text{COX}]^2 - k_{\text{ME}}^{\text{COX}}[\text{CH}_3\text{OH}][\text{COX}]$$

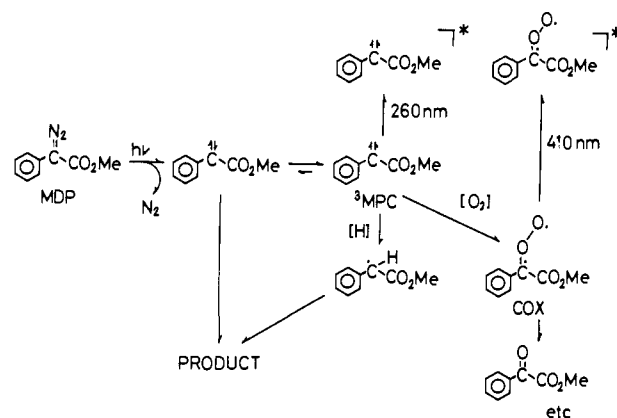
where $[\text{COX}]$ is a concentration of the carbonyl oxide, and k^{COX} and $k_{\text{ME}}^{\text{COX}}$ are the second-order and first-order rate constants of carbonyl oxide, respectively. Since the time profile of transient absorption exhibits the fast rise compared with the slow decay (Figure 4, Tables I and II), the magnitude of the first term in the above equation was estimated approximately 100 times greater than those of the other terms. If it is the case, the first term can be time-independent compared with the second and third terms. Therefore, if we integrate the above differential equation, we finally obtain the following equation

$$[\text{COX}] = \frac{k_{\text{ME}}^{\text{COX}}[\text{CH}_3\text{OH}]}{k^{\text{COX}}} \left[\left(1 + \frac{k_{\text{ME}}^{\text{COX}}[\text{CH}_3\text{OH}]}{k^{\text{COX}}} \frac{1}{[\text{COX}]_0} \right) \exp(k_{\text{ME}}^{\text{COX}}[\text{CH}_3\text{OH}]t) - 1 \right]^{-1}$$

(24) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973.

(25) Bartlett and Traylor reported the formation of Creigee carbonyl oxide in the photooxidation of diphenyldiazomethane. In the quenching of the carbonyl oxide by methanol, they proposed the formation of germinal methoxyhydroperoxide. Therefore, a similar methoxyhydroperoxide may be the best candidate as an oxidation product of the carbonyl oxide (see ref 2).

Scheme I



We obtained the reaction rate and rate constant, $k_{\text{ME}}^{\text{COX}}$, $[\text{CH}_3\text{OH}]$ and k^{COX} , in several concentrations of methyl alcohol in Freon 113 at 293 K by means of computerized-fitting²⁶ this equation to time profiles of transient absorption of carbonyl oxide. Further, by plotting obtained values, $k_{\text{ME}}^{\text{COX}}[\text{CH}_3\text{OH}]$ vs. each concentration of methyl alcohol as shown in Figure 6b, the rate constant was found to be $k_{\text{ME}}^{\text{COX}} = 3.44 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, while the value k^{COX}/ϵ was almost constant ($5.2 \times 10^5 \text{ s}^{-1} \text{ cm}$) throughout used concentrations of methyl alcohol. And if this value, $k_{\text{ME}}^{\text{COX}}$, is compared with the quenching rate constant ($k_{\text{ME}} = 2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) of ³MPC, this carbonyl oxide is suggested to be much more stable in nearly two orders than ³MPC.

Summary

Quenching rate constants of ³MPC suggested that the stability of triplet methoxycarbonyl phenyl carbene (³MPC) is regarded as an intermediate between diphenylcarbene and fluorenylidene. In this system, on the other hand, ³MPC reacted with oxygen by a pseudo-first-order kinetics to afford a corresponding carbonyl oxide exhibiting a transient absorption spectrum ($\lambda_{\text{max}} \sim 410 \text{ nm}$). However, the carbonyl oxide was much more stable toward methyl alcohol in nearly two orders than ³MPC. The reaction is shown in scheme I.

Acknowledgment. We are grateful to Professor Hirota and Dr. Yamauchi of Kyoto University for their giving us the opportunity to perform the ESR spectroscopy measurements and for valuable discussions. The present work was supported by a Grant-in-Aid for Scientific Research (No. 58470125) from the Ministry of Education, Science and Culture of Japan.

(26) We analyzed the data by using non-linear least-squares computer programs (NONLIN74).