Mechanistic Study on the Reaction of Phenyldiazomethanes with Singlet Oxygen: Formation and Cycloreversion of 1,2,3,4-Dioxadiazole Intermediates

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The formation of carbonyl oxides in the singlet oxygen ($^1O_2$) oxidation of phenyldiazomethanes **1** has been investigated mechanistically. Product ratios of N_2/N_2O, which are indicative of the selectivity in the carbonyl oxide/ketone formation, were determined by gas chromatography/mass spectrometry (GC/MS). The yields of carbonyl oxides were not affected by changing solvents but were significantly increased with the increasing electron-donating ability of substituents on diazomethanes. Rate constants for the quenching of $^1O_2$ by **1** as determined by monitoring the emission of $^1O_2$ at 1270 nm were also insensitive to solvents. These results suggest the predominant formation of 1,2,3,4-dioxadiazole intermediates by the cycloaddition of $^1O_2$ to **1** followed by its cycloreversion, the selectivity of which is controlled by the relative stability of resulting carbonyl oxides. The formation of carbonyl oxides, observable from its transient absorption at ~400 nm, was in good agreement with the decay of $^1O_2$ within the experimental error, indicating that the 1,2,3,4-dioxadiazoles are a highly labile intermediate with the lifetime of less than 100 ns.

Introduction

Carbonyl oxides and related compounds have been attracting much attention as an intermediate in ozonolysis of olefins and as a chemical mimic of biological oxygen transfer systems.[1] The oxides can be generated from diazo compounds via a triplet route; i.e., the photolysis of diazo compounds yields triplet carbenes, which react with ground-state oxygen to afford the oxides.[2] Alternatively, carbonyl oxides could be generated by a singlet oxygen oxidation of diazo compounds (the singlet route), in which singlet oxygen sensitizers such as methylene blue (MB) are employed.[3] The singlet route offers a great advantage for the investigation of the behavior of carbonyl oxides in solutions, especially in reactive solvents such as alcohols,[4] since the intermediacy of highly reactive carbenes can be avoided.

The singlet route, as outlined in Scheme 1, was first proposed by Murray and co-workers,[3a] in which the addition of singlet oxygen to diazo compounds **1** formed a zwitterion (**3**), followed by its decomposition yielding nitrogen and carbonyl oxide (**2**) or by its cyclization to yield a secondary intermediate, 1,2,3,4-dioxadiazole (**4**). The five-membered heterocycle **4** might decompose to give either N_2 and **2** or N_2O and ketone **5**. The latter process was suggested by mass and infrared spectral observation of N_2O in the gaseous products. On the other hand, Bethell and co-workers[5] proposed the concerted cycloaddition of singlet oxygen to **1** affording **4** as the primary intermediate, since rate constants for quenching of singlet oxygen by **1** were not so sensitive to solvent polarity and labeled N_2O was obtained from the reaction of singlet oxygen with 9-diazofluorene labeled at the terminal nitrogen. However, the involvement of **3** or **4** and their chemistry have not so far been clarified.

In the present study, we have examined the detailed mechanism of singlet oxygenation of **1**, i.e., the formation and cycloreversion of **4**, by systematic evaluations of substituent effects on the carbonyl oxide yields as determined from the product ratios of N_2/N_2O, and more directly by comparing rates for the reaction of $^1O_2$ with **1** and the subsequent formation of **2** by the time-resolved spectroscopy.

Results and Discussion

Product Ratios of N_2/N_2O and Intermediacy of Dioxadiazole Intermediate. Photolysis of phenyldiazomethanes **1** sensitized with methylene blue (MB) in acetonitrile or with *meso*-tetraphenylporphine (TPP) in benzene under an oxygen atmosphere affords ketones in almost quantitative yields.[3a,6] Since it has been shown that ketones are formed by the self-reaction of carbonyl oxides[3b] and/or the elimination of N_2O from **4**,[3a] the selectivity of carbonyl oxides can be determined from the ratios of N_2/N_2O according to Scheme 1. Thus, the gases evolved during the photooxidation of **1** in a closed system have been analyzed by GC/MS,[7] and the results are summarized in Table 1.

The ratio of N_2/N_2O from the reaction of diphenyldiazomethane with singlet oxygen was determined to be 1.62 in acetonitrile, which means, according to Scheme 1, the formation of diphenylcarbonyl oxide in ca. 60% yield. In order to check the reliability of this analysis, the trapping

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(1) (a) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *29*, 344−354. (b) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335−362 and references cited therein.

(2) (a) Kirmse, W.; Horner, L.; Hoffmann, H. *Justus Liebigs Ann. Chem.* **1958**, *614*, 19−30. (b) Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1962**, *84*, 3408−3409. (c) Murray, R. W.; Suzui, A. *J. Am. Chem. Soc.* **1971**, *93*, 4963−4964. (d) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391−2392.

(3) (a) Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 3330−3332. (b) Casel, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623−7624.

(4) Fujiwara, Y.; Tanimoto, Y.; Itoh, M.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1987**, *109*, 1942−1946.

(5) Bethell, D.; Mckeivor, R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 327−333.

(6) Ishiguro, K.; Hirano, Y.; Sawaki, Y. *J. Org. Chem.* **1988**, *53*, 5397−5405.

(7) Preliminary results on the reaction of singlet oxygen with diazomethanes are reported: Nojima, T.; Ishiguro, K.; Sawaki, Y. *Chem. Lett.* **1995**, 545−546.

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Scheme 1

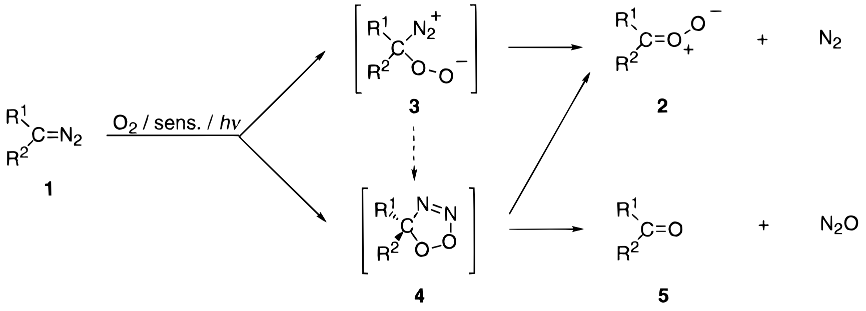

Table 1. Evolved Gases in the Photooxygenation of Diazo Compounds $R^1R^2CN_2$[a]

	diazo compounds				products[b]		
run no.	R^1	R^2	concn/mM	solvent	N_2/%	N_2O/%	N_2/N_2O
1	Ph	Ph	3.2	C_6H_6	55.2 ± 0.7	44.8 ± 0.7	1.23
2			3.0	CH_2Cl_2	59.3 ± 1.0	40.7 ± 1.0	1.46
3			3.3	CH_3OH	55.6 ± 1.0	44.4 ± 1.0	1.25
4			3.1	CH_3CN	61.8 ± 0.6	38.2 ± 0.6	1.62
5	Ph	Me	3.3	CH_3CN	78.3 ± 0.8	21.7 ± 0.8	3.61
6		Et	3.4	CH_3CN	72.0 ±1.2	28.0 ± 1.2	2.57
7		*i*-Pr	3.5	CH_3CN	64.1 ± 1.2	35.9 ± 1.2	1.79
8		*t*-Bu	3.2	CH_3CN	52.9 ± 0.5	47.1 ± 0.5	1.12
9	*p*-$MeOC_6H_4$	H	2.7	CH_3CN	84.5 ± 0.4	15.5 ± 0.4	5.45
10	*p*-MeC_6H_4		3.3	CH_3CN	72.4 ± 0.8	27.6 ± 0.8	2.62
11	Ph		3.5	CH_3CN	70.2 ± 0.9	29.8 ± 0.9	2.36
12	*p*-ClC_6H_4		2.5	CH_3CN	65.4 ± 0.3	34.6 ± 0.3	1.89
13	Ph	CF_3	5.9	CH_3CN	41.3 ± 1.7	58.7 ± 1.7	0.71

[a] Solutions of 0.15 mM MB (CH_3CN or CH_3OH) or 0.10 mM TPP (C_6H_6) and ~3 mM of diazoalkane were irradiated at >400 nm under oxygen for 30 min at ca. 20 °C. [b] The gaseous products, N_2 and N_2O, determined by GC/MS.

experiments were carried out using diphenyl sulfoxide (Ph_2SO), since it is known that carbonyl oxides are quite efficiently trapped by Ph_2SO yielding the corresponding sulfone Ph_2SO_2.[8] As shown in Figure 1A, the reciprocal plot of the yields of Ph_2SO_2 against the concentration of Ph_2SO were linear, where the intercept (i.e., 1.7 ± 0.1) indicated the (58.8 ± 3.5)% yield of Ph_2SO_2 at $[Ph_2SO] = \infty$. This value was in good agreement with the 60% selectivity of carbonyl oxide estimated from the ratio of N_2/N_2O. Thus, it was shown that the selectivity for carbonyl oxides formation can be conveniently determined from the ratios of N_2/N_2O.

As shown in Table 1, ratios of carbonyl oxide and ketone ($\equiv N_2/N_2O$) were insensitive to solvent properties, e.g., polarities. It is worth noting that the product ratios in methanol, a protic solvent, were almost identical to those in benzene. If zwitterion **3** was involved in the $^1O_2$ oxidation of **1**, a dramatic change in the ratios of N_2/N_2O would be expected in methanol. This is because zwitterion intermediate **3** would be significantly stabilized by hydrogen bonding with methanol. But this was not the case. No effect of methanol clearly indicates that the carbonyl oxide formation via **3** is not operative. Moreover, *ab initio* calculations support the concerted cycloaddition of diazomethane to singlet oxygen as discussed in detail later. Thus, the predominant reaction of **1** and singlet oxygen proceeds via the direct formation of dioxadiazole **4** without involving zwitterionic intermediate **3**.

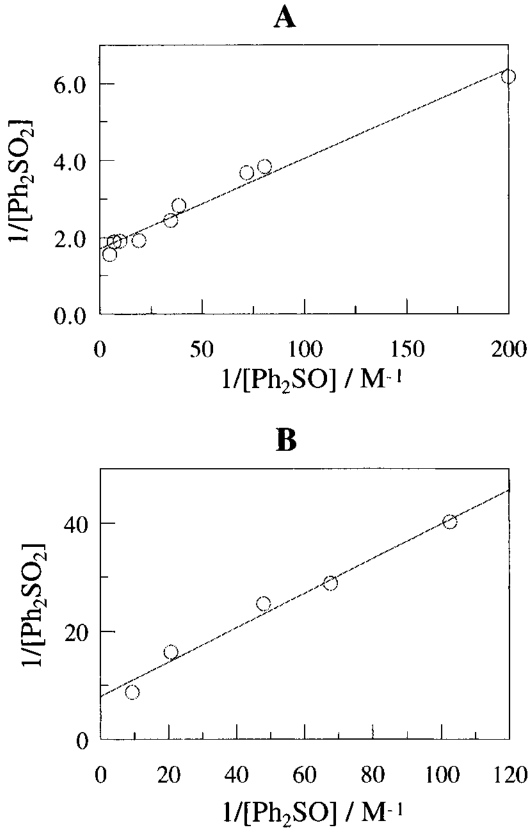

Figure 1. Reciprocal plot of the yields of Ph_2SO_2 against Ph_2SO on the photooxidation of diphenyldiazomethane (3 mM) in the presence of MB (0.1 mM) in $CH_3CN:CH_2Cl_2 = 2:3$ at ca. 20 °C (A) and at ca. −75 °C (B) under oxygen.

The substituent effects on N_2/N_2O ratios for substituted phenyldiazomethanes were examined in order to clarify the factor governing the selectivity for carbonyl oxides. For alkyl(phenyl)diazomethanes ($Ph(R)C{=}N_2$), N_2/N_2O ratios decreased from 3.6 (R = Me) to 1.1 (R = *t*-Bu) as the bulkiness of alkyl groups increased (runs 5−8). The results obtained for *p*-substituted phenyldiazomethanes

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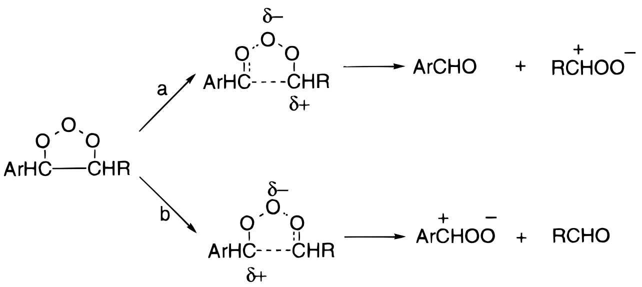
[8] Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832−3837.

Scheme 2



($X\text{-}C_6H_4(H)C{=}N_2$) show that N_2/N_2O ratios increased from 1.9 (X = Cl) up to 5.5 (X = MeO) with the increasing electron-donating ability of substituents (see runs 9−12). The resulting Hammett ρ-value was −0.83 (vs σ, $r = 0.86$) for the carbonyl oxide formation. In addition, for the case of phenyl(trifluoromethyl)diazoethane having the potent electron-withdrawing trifluoromethyl group, the ratio of N_2/N_2O reduced down to 0.7, in which the formation of ketones and N_2O exceeded that of carbonyl oxides and N_2 (run 13).

These effects of substituents could be explained in relation to the stability of carbonyl oxides as discussed in the following. In the present cycloreversion of dioxadiazole **4**, the reaction selectivity is governed by the relative stability of carbonyl oxides; i.e., electron-donating substituents favor the oxide formation, the maximum selectivity of 85% being obtained for *p*-methoxy substituent. The least amount of formation of carbonyl oxide for the case of R^2 = *t*-Bu is also explainable by the steric effect destabilizing the oxides, i.e., the steric repulsion between phenyl and bulky *t*-Bu group results in a reduction of the coplanarity of **2**. It is interesting to note that a similar substituent effect was reported for the cleavage of primary ozonides affording ketones and carbonyl oxides. Fliszár and co-workers[9] reported that in the cleavage of the primary ozonides of unsymmetrical olefins, ArCH=CHR (Scheme 2), the cleavage proportions to yield ArCHOO were 0.18, 0.43, 0.59, and 0.79 for *p*-NO_2, *p*-Cl, H, *p*-Me, and *p*-MeO substituents, respectively. That is, path b became predominant with increasing electron-donating ability of substituents. It was concluded that the zwitterion (carbonyl oxide) was preferentially formed when the positive charge on the α-carbon in the carbonyl oxide was stabilized by inductive and mesomeric effects.

For the present case of cycloreversion of **4**, similar effects would be expected in determining the reaction selectivity as shown in Scheme 3. For example, the relative order of CF_3 < *t*-Bu < *i*-Pr < Et < Me for the carbonyl oxide formation from alkylphenyldiazomethanes reflects the cation-stabilizing ability of each substituent; i.e., the cationic carbons are stabilized by the hyperconjugation of C−H bonds and are destabilized by the bulky *tert*-butyl and the strongly electron-withdrawing CF_3 groups.

Another interpretation of the steric effect may be possible. According to the Woodward−Hoffmann rule, the cycloreversion of **4** to **2**, $[_{\pi}4_s + _{\pi}2_s]$ cycloreversion, is allowed in the disrotatory mode, in which 1,3-dipolar unit is forced to twist out of the five-membered-ring plane. Thus, the cycloreversion of **4** to **2** with more bulky substituents (path a in Scheme 3) would be less favorable than that of **4** to **5** without substituent on the 1,3-dipolar molecule formed, N_2O (path b in Scheme 3).

Scheme 3

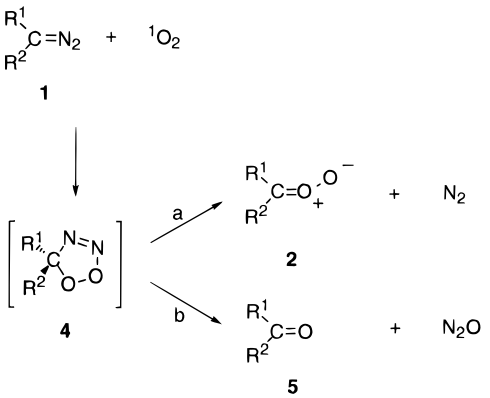


Table 2. Effect of Temperature on the $^1O_2$ Oxidation of Ph_2CN_2 in $CH_3CN:CH_2Cl_2$ = 2:3[a]

		products[b]		
run no.	temp/°C	N_2/%	N_2O/%	N_2/N_2O
1	60 ± 1[c]	64.7 ± 1.6	35.3 ± 1.6	1.83
2	21 ± 1	59.8 ± 0.7	40.2 ± 0.7	1.49
3	−30 ± 3[d]	36.0 ± 1.7	64.0 ± 1.7	0.56
4	−75 ± 2[e]	9.3 ± 0.4	90.7 ± 0.4	0.10

[a] Solutions of 0.1 mM MB and 2.4 mM of Ph_2CN_2 were irradiated at >400 nm under oxygen. [b] The relative yields of N_2 and N_2O as determined by GC/MS. [c] Heated by a pipe heater. [d] Cooled by dry ice and bromobenzene. [e] Cooled by dry ice and ethanol.

Next, the influence of temperature on the cycloreversion of diphenyldioxadiazole (**4**, $R^1 = R^2$ = Ph) was examined, and results are summarized in Table 2. The ratio of N_2/N_2O at −75 °C was 0.1, i.e., only 10% yield of carbonyl oxide, while the ratios increased up to 1.8 at 60 °C. The trapping experiment with Ph_2SO at low temperature resulted in the similar reaction selectivity; that is, the reciprocal plot of yields of Ph_2SO_2 against [Ph_2SO] at −75(± 2) °C was linear, where the intercept (8.0 ± 1.6) indicated the (12.4 ± 2.4)% yield of Ph_2SO_2 at [Ph_2SO] = ∞ (Figure 1B). This examination shows that the N_2/N_2O ratios really reflects the selectivity for the carbonyl oxide formation.

The activation enthalpy difference between transition states corresponding to paths of cleavages a and b in Scheme 3 was estimated using the relative ratios of N_2/N_2O in Table 2. Let X be the proportion of cleavage following path a, with the rate constant k_a, $1 - X$ is the proportion of cleavage following path b, with the rate constant k_b. It follows that

$$\ln \frac{X}{1 - X} = \ln \frac{k_a}{k_b} = \ln \frac{A^a}{A^b} - \frac{E^a - E^b}{RT} \qquad (1)$$

where A^a and A^b represent the frequency factors and E^a and E^b represent the activation energies corresponding to the two types of cleavages a and b, respectively. The plot of $\ln k_a/k_b$ (= $\ln N_2/N_2O$) against $1/T$ was linear, and from its slope (= $-(E^a - E^b)/R$), the activation energy difference was calculated to be 2.9 kcal/mol.

Lifetime of Dioxadiazole. The mechanism in Scheme 3 involves $[_{\pi}4_s + _{\pi}2_s]$-cycloaddition−cycloreversion of different 1,3-dipole−dipolarophile couples. Thus, the stability of dioxadiazole intermediate **4** in the 1,3-dipolarmetathesis[10] is quite interesting, the lifetime of

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[9] Fliszár, S.; Granger, M. *J. Am. Chem. Soc.* **1969**, *91*, 3330−3337.

[10] Burger, K.; Schickaneder, H.; Zettl, C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 54−55.

Table 3. Rate Constants (k_q) for the Quenching of Singlet Oxygen by Diazomethanes in Solutions[a]

run no.	diazomethanes R^1	R^2	solvent	k_q/M^{-1} s^{-1}
1	Ph	Ph	MeOH:CH$_2$Cl$_2$ = 1:3[b]	$(3.7 \pm 0.2) \times 10^8$
2			CH$_3$COCH$_3$	$(3.5 \pm 0.1) \times 10^8$
3			CH$_3$CN:CH$_2$Cl$_2$ = 5:3	$(3.6 \pm 0.1) \times 10^8$
4			C$_6$H$_6$	$(3.1 \pm 0.1) \times 10^8$
5		H	C$_6$H$_6$	$(2.9 \pm 0.1) \times 10^8$
6		Me	C$_6$H$_6$	$(7.5 \pm 0.2) \times 10^8$
7		*t*-Bu	C$_6$H$_6$	$(8.3 \pm 0.3) \times 10^8$
8		CF$_3$	CH$_3$CN:CH$_2$Cl$_2$ = 5:3	$(2.2 \pm 0.2) \times 10^6$

[a] Solutions of ~5 mM diazomethane and 0.2 mM *meso*-tetraphenylporphine were irradiated by a Nd:YAG laser, and the quenching rates of singlet oxygen were monitored by following its phosphorescence decay. See Experimental Section for details. [b] 0.2 mM mesoporphyrin IX dimethyl ester.

which may be estimated from the apparent rate constant (k_{ap}) for the formation of carbonyl oxides as compared with that (k_q) for the quenching of singlet oxygen by diazomethanes. If dioxadiazole **4** has a sufficient lifetime, an induction period would appear for the formation of carbonyl oxides. Thus, the two rate constants were determined by using a laser flash photolysis technique as stated below.

The quenching rate constants, k_q, were determined by monitoring the $^1O_2$ emission at 1270 nm, and the results are summarized in Table 3. The k_q values were practically unaffected by solvents (runs 1−4), which was consistent with results by Bethell et al.[5] where the rate constant were obtained indirectly by competitive quenching experiments under steady-state irradiation conditions. Observed insensitivity to solvents in the quenching rates, as well as the ratios of N_2/N_2O as mentioned above, again indicates no intervention of polar zwitterion **3** in the present $^1O_2$ oxidation of diazomethanes.

Next we examined the substituent effect of alkyl groups on the quenching rates of alkylphenyldiazomethanes. In spite of its bulkiness of substituents, Ph(*t*-Bu)CN$_2$ quenched singlet oxygen about three times faster than PhHCN$_2$ (*cf.* runs 5 and 7 in Table 3). In contrast, the k_q value for Ph(CF$_3$)CN$_2$ having potent electron-withdrawing trifluoromethyl group reduced down to 2.2×10^6 M^{-1} s^{-1}, which is about 2 orders of magnitude lower than that of PhHCN$_2$ (2.9×10^8 M^{-1} s^{-1}) (runs 5 and 8). These results showed that the quenching of $^1O_2$ by diazoalkanes is sensitive to electronic effects of substituents rather than steric effects, where Me and *t*-Bu groups work as a similar electron-donating one in the present reaction. The decreased reactivity of diazomethanes toward $^1O_2$ with increasing the electron-withdrawing ability of substituents is reasonable in terms of the electrophilic nature of singlet oxygen.[11] The insensitivity of k_q's to the steric hindrance of substituents might be due to the small size of oxygen molecule, compared with carbon analogues with four substituents.[12]

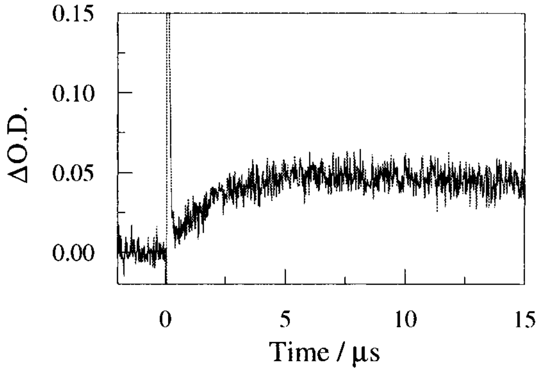

Figure 2. Growth of benzophenone oxide monitored at 410 nm in a benzene solution of 1.8 mM diphenyldiazomethane and 0.1 mM TPP under oxygen. The initial fast decay arose from the T−T absorption of TPP as quenched by molecular oxygen.

Table 4. Apparent Rate Constants (k_{ap}) for the Formation of Carbonyl Oxides in Benzene[a]

run no.	R^{1}R^{2}C=O$^+$−O$^-$ R^1	R^2	λ_{max}/nm	k_{ap}/M^{-1} s^{-1}
1	Ph	H	390	$(3.4 \pm 0.6) \times 10^8$
2		Ph	410	$(3.5 \pm 0.2) \times 10^8$
3		*t*-Bu	360	$(8.7 \pm 0.8) \times 10^8$

[a] The rate constants (k_{ap}) were determined by following the growth of carbonyl oxides. See Figure 2 for conditions and Experimental Section for details.

The k_{ap} values in benzene were determined by the growth of absorption of carbonyl oxides at around 400 nm. A typical growth of benzophenone oxide **6** as monitored at 410 nm in the $^1O_2$ oxidation of Ph$_2$CN$_2$ is shown in Figure 2. The very strong absorption of ^{3}TPP* was first observed, but its decay curve was so fast that it did not disturb the analysis of the growth of carbonyl oxide. The buildup of the absorption for the carbonyl oxide was best fitted, without any induction period, to the pseudo-first-order kinetics as a function of diazomethane concentrations under present experimental conditions. This indicates that the rate-determining step for the carbonyl oxide formation is the cycloaddition of $^1O_2$ to diazomethanes. The results obtained in this way for some of diazomethanes are given in Table 4. The k_{ap} value of $(3.5 \pm 0.2) \times 10^8$ M^{-1} s^{-1} for the formation of **6** from Ph$_2$CN$_2$ is in good agreement with that measured by Scaiano[13] using the same technique. The observed k_{ap}'s for other diazomethanes agreed well with the k_q's within experimental errors, from which lifetimes of dioxadiazole intermediates **4** could be estimated to be less than ~100 ns.[14]

Determination of Carbonyl Oxide from Its Absorption Spectra. Above results suggested that dioxadiazole intermediates are quite short lived species. This result is particularly surprising in view of the fact that the "1,3-dipole metathesis" of **4** occurred so fast. Thus, the formation of carbonyl oxides during the time scale of laser experiments in the $^1O_2$ oxidation of diazomethanes were examined from a quantitative point of view.

According to Scheme 3, the yields of carbonyl oxides ([CO]) against those of $^1O_2$ ([$^1O_2$]) should be consistent with the ratios of $N_2/(N_2O+N_2)$, i.e.,

$$\frac{[CO]}{[^1O_2]} = \frac{[N_2]}{[N_2 + N_2O]} \qquad (2)$$

The relative yield of benzophenone oxide **6** vs [$^1O_2$] is critical to confirm that the cycloreversion is completed

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[11] Wilkinson, F. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663−1021.

[12] Regits, M.; Heydt, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; 1984; Vol. 1, Chapter 4.

[13] Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612−1616.

[14] Although the induction period might be observable at much higher concentration of diazomethanes, 2 mM concentration was an upper limit under the present conditions, because of the problem of the absorption of the second harmonic (532 nm) of Nd:YAG laser by diazomethanes and of undesirable side reactions.[6]

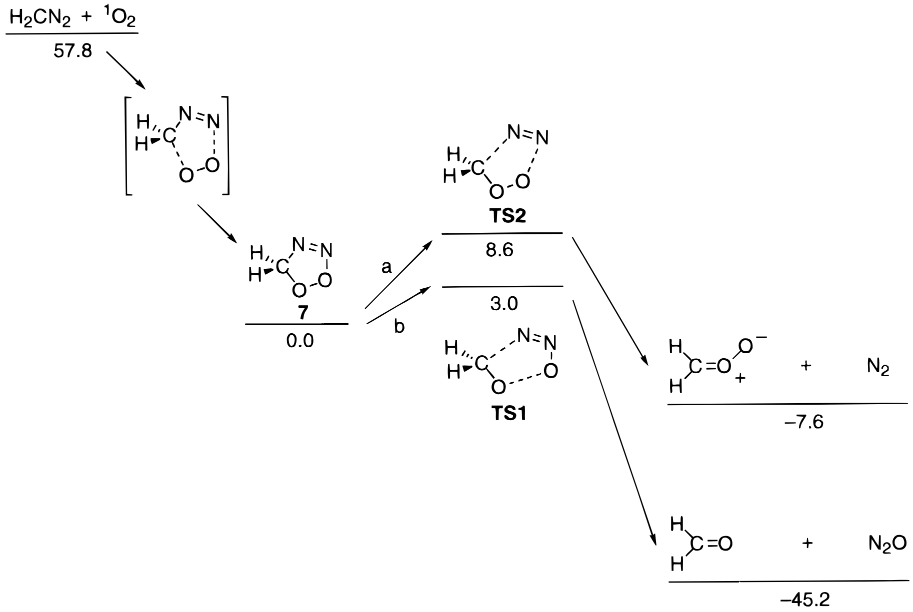

Figure 3. Reaction enthalpies (kcal/mol) for the reaction of $^1O_2$ and parent diazomethane to yield the corresponding carbonyl oxide and ketone.

within the observed time scale of experiments. The $[^1O_2]$ formed was obtained from the quantum yield of the $^1O_2$ formation and the concentration of triplet TPP in the laser photolysis, which was determined from the T−T absorption of TPP with the absorption coefficient of ^{3}TPP (ϵ = 6000 M^{-1} cm^{-1}).[15] The concentration of **6** was obtained from its absorption intensity by using the absorption coefficient of dimesitylketone oxide (ϵ = 4400 M^{-1} cm^{-1}).[16] The value of $[\mathbf{6}]/[^1O_2]$ in benzene determined from above procedure was 0.49, which showed a good agreement with the value of 0.55 obtained from the ratio of N_2/N_2O. This examination supports that the $^1O_2$ oxidation of diazomethanes yields carbonyl oxides quite rapidly by the cycloaddition−reversion as illustrated in Scheme 3.

Theoretical Calculation of Dioxadiazole. In order to evaluate the thermal stability of 1,2,3,4-dioxadiazole intermediates, theoretical calculations have been carried out. Electron correlations were required in the calculation of a highly correlated 1,3-dipolar system such as carbonyl oxides. Thus, we used the density functional B3LYP[17]/6-31G* method, since the optimized geometry of parent carbonyl oxide (H_2COO) at this level of theory was in good agreement with that obtained with more elaborate CCSD(T)/TZ+2P calculations as reported by Cremer.[18]

The calculated geometries and total atomic charges for the parent dioxadiazole are available as Supporting Information, and the calculated enthalpy diagram is shown in Figure 3. When singlet oxygen were gradually enforced close to the diazocarbon, the potential energy surface became rather flat in the range from R(C−O) = 3 to 2 Å, where the N−O distances were close to those of C−O, indicating that the diazomethane interacts with singlet oxygen in a concerted manner (*cf.* Figure 3). No local minimum corresponding to charge-transfer complex was obtained, and at closer distance between diazomethane and singlet oxygen, dioxadiazole **7** was formed with no activation energy. This result strongly supports the concerted cycloaddition of diazomethane to singlet oxygen.

The parent dioxadiazole **7** thus calculated possesses a true local minimum with a planar five-membered ring.[19] The barrier of cycloreversion of **7** yielding carbonyl oxide and N_2 was calculated to be 8.6 kcal/mol, while that yielding ketone and N_2O was 3.0 kcal/mol; i.e., the activation enthalpy difference between cleavages a and b in Figure 3 was ca. 5 kcal/mol. Although the effect of the phenyl group is unknown, this value is close to that estimated from the experimental data on the $^1O_2$ oxidation of Ph_2CN_2 (*vide supra*).

Thus, it is revealed that the formation of carbonyl compounds and N_2O (path b in Scheme 3) is enthalpically more favorable than that of carbonyl oxide and N_2 (path

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[15] Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407−2411.

[16] The $[^1O_2]$ formed was determined to be 2.34 × 10^{-5} M from the quantum yield of the $^1O_2$ formation and the concentration of triplet TPP. The molar absorptivity (ϵ) of benzophenone oxide (**6**) was reported to be (1850 ± 450) M^{-1} cm^{-1} by Griller et al. using optical modulation technique (Girard, M.; Griller, D. *J. Phys. Chem.* **1986**, *90*, 6801−6804). The concentration of **6** was calculated by using ϵ = 1850 M^{-1} cm^{-1} to be 2.70 × 10^{-5} M, which is beyond the $[^1O_2]$ value of 2.34 × 10^{-5} M and the ratio of $[\mathbf{6}]/[^1O_2]$ = 1.15 is inconsistent with the experimental value of 0.55 obtained from the ratio of N_2/N_2O. On the other hand, the concentration of **6** was calculated to be 1.14 × 10^{-5} M using the ϵ value of dimesityl ketone oxide (ϵ = 4400 M^{-1} cm^{-1}) as determined from the UV absorption in low temperature (Sander, W.; Kirschfeld, A.; Kappert, W.; Muthusamy, S.; Kiselewsky, M. *J. Am. Chem. Soc.* **1996**, *118*, 6508−6509). This value is acceptable, since the ratio of $[\mathbf{6}]/[^1O_2]$ is calculated to be 0.49, which is good agreement with the product ratios of 0.55.

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[19] Other notable results of calculations were the dipole moment and charge distribution of the parent dioxadiazole, which may explain the minor solvent effect on the cycloreversion of **4**. The calculated dipole moment for parent dioxadiazole, TS1, and TS2 (*cf.* Figure 3) were 2.03, 1.43, and 3.41, respectively. Since TS2 has the largest dipolar moment, it is more stabilized than TS1 in polar solvent. This difference may explain the fact that the ratios of N_2/N_2O slightly increase in polar solvents more than those in nonpolar ones (runs 1, 2, 4 in Table 1). The charge distribution of parent dioxadiazole revealed that the oxygen adjacent to the carbon of five-membered ring had the largest negative charge (see Supporting Information for details). It could therefore be presumed that a hydrogen bonding between this oxygen with solvent alcohol is formed, resulting in facile cleavage of the O−O bond. This may explain the preferable formation of N_2O in MeOH than in CH_3CN (*cf.* runs 3 and 4 in Table 1).

a) on the cycloreversion of dioxadiazole. Such a case where the formation of **5** and N_2O is predominant was observed for the low-temperature reaction (e.g., −75 °C), while that of **2** and N_2 became comparable or faster at ambient temperature as shown in Table 2. These experimental results indicates that the cycloreversion of **4** is governed by the activation enthalpy at low temperature and by the entropy factor at ambient or higher temperatures. It is interesting to recall the contrasted result that there was only a minor temperature effect on the direction of cleavage of primary ozonides;[20] this case may be explained by no significant difference of reaction enthalpies between the two paths of cleavage of primary ozonide (*cf.* Scheme 2).

One possible scenario for the origin of the entropy factor is a concerted nonsynchronous nature of the cycloreversion of **4** to **5** (*cf.* path b in Scheme 3) involving weak O−O bond fission, which would be more facile than that of the N−O bond. Such nonsynchronous cycloreversion tends to have a small activation entropy as reported for 1,3-dipolar cycloreversions of tetrazoles.[21] Therefore, path b in Scheme 3 would be, although enthalpically favored, entropically less favorable than path a. Thus, the temperature dependence of the cycloreversion of **4** would be caused by such opposite directions between enthalpy and entropy factors controlling pathways a and b.

Conclusions

The singlet oxygen oxidation of diazomethanes has been clarified by substituent effects on the carbonyl oxide yields as determined from the product ratios of N_2/N_2O, and more directly by kinetics of the reaction of $^1O_2$ with **1** and the formation of carbonyl oxides by the time-resolved spectroscopy. Results are summarized as follows: (a) The predominant formation of dioxadiazole **4** in the $^1O_2$ oxygenation of **1** was suggested, since the product ratios of N_2/N_2O were not affected by protic solvents. (b) Product selectivities in the cycloreversion of **4** were controlled by the relative stability of resulting carbonyl oxides, as supported by the effects of substituents on diazomethanes. (c) The lifetime of 1,2,3,4-dioxadiazole **4** was too short ($\tau < 100$ ns) to be observable with the time-resolved spectroscopy under the present conditions.

Experimental Section

GC/MS analyses were carried out with a Shimadzu QP-5000 mass spectrometer using a 0.2 mm × 25 m capillary column of CBP1-M50−025 (Shimadzu). GLC analyses were performed with a Shimadzu GC-14A gas chromatograph, using a 2.5 mm × 1 m column of Carbowax 300M, 2% on Chromosorb WAW (GL Sciences).

Materials. Phenyldiazomethane,[22] 4-substituted phenyldiazomethanes,[22] 1-phenyldiazoethane,[22] 1-phenyldiazopropane,[22] diphenyldiazomethane,[23] 2-methyl-1-phenyldiazopropane,[23] 2,2-dimethyl-1-phenyldiazopropane,[23] and 1-phenyl-2,2,2-trifluorodiazoethane[24] were prepared by the reported procedures.

Acetonitrile, benzene, and dichrolomethane (Tokyo Kasei) were distilled over calcium hydride prior to use. Acetone and methanol of spectrophotometric grade (Nacalai) were used without further purification.

Determination of Gaseous Products Evolved during the Photooxidation of 1. The relative sensitivity of N_2/N_2O on the GC/MS spectroscopy at the ionizing voltage of 70 eV was determined to be 0.91 ± 0.02 from a mixture of authentic N_2 and N_2O gases of known ratio. A 1.65-mL solution of 0.15 mM MB or TPP (0.10 mM) and ~3 mM of diazoalkane in a 1.7-mL Pyrex tube capped with a rubber septum (Aldrich) was purged with N_2-free O_2 gas for 15 min. The solution was irradiated with a 300 W medium pressure Hg lamp through a 5% KNO_2 filter solution (i.e., >400 nm) for 30 min at 21 °C at which diazoalkane was completely converted to ketones. In the low-temperature experiment, the solution was purged with N_2-free O_2 for 10 min at −30(±3) °C or −75(± 2) °C to prevent the contamination of air and was irradiated in the same way but the irradiation time was 90 min.

After irradiation, the contents of N_2 and N_2O in solution were analyzed by GC/MS spectroscopy from relative peak areas at m/e 28 (N_2) and 44 (N_2O), respectively. Small amounts of N_2 and CO_2 (m/e 44) leaked at the injection (less than 5% of evolved gases) were corrected and the analyses were repeated for 3−5 times.

Laser Flash Photolysis Study. Laser flash photolysis experiments were carried out on O_2-saturated solution of diazo compound (~10^{-3} M) including sensitizer (~10^{-4} M). All experiments were carried out by flowing the solutions through a 10 × 5 mm^2 cell made of quartz in order to ensure that each laser pulse irradiated a fresh volume of solution.

O_2 ($^1\Delta_g$) phosphorescence (1270 nm) decay curves were measured by the time-resolved single-photon counting method as summarized in the followings. A Continuum Surelight I Nd-YAG laser (532 nm, ~10 ns, ~3 mJ/pulse) was used as the excitation source. The unfocussed 8-mm laser beam was attenuated by being passed through a pinhole and neutral density filters, and the total energy incident at the cuvette was ca. 0.1 mJ/pulse. A sample cell was held in a specially designed holder placed just ahead of a lens adapter, which was used to focus the signal light onto the detector. A custom interference filter (centered at 1270 nm, fwhm = ca. 40 nm, obtained from ASAHI SPECTRA Co. Ltd) and some cutoff filters were placed between the lens adapter and the sample holder to cut off unwanted scattered laser light. In this way, the phosphorescence of O_2 ($^1\Delta_g$) isolated from the signal light was detected by a photomultiplier tube (R5509-41, HAMAMATSU), which was located in the vidicon chamber (C6544, HAMAMATSU) cooled at -80 °C utilizing liquid nitrogen as the coolant medium. Signals from the photomultiplier were amplified with a fast preamplifier (SR445, Stanford Research Systems, Inc.) and stored in a multichannel scaler/averager (SR430, Stanford Research Systems, Inc.) which counted incoming pulses in successive time bins (5 ns). The counts of O_2 ($^1\Delta_g$) phosphorescence were prevented not to exceed 3% of maximum counts (32 767) in order to maintain the single-photon counting conditions.

The system to determine the rate constants of carbonyl oxide formation is summarized as follows. A Spectron SL284G Nd-YAG laser (266 nm, ~6 ns, ~25 mJ/pulse) was used as the excitation source. The decay kinetics were observed by the photomultiplier tube (PMT) monitoring system. This system consisted of a 150 W Xe flash lamp (XF-80, Tokyo Instruments), a SPEX 270M monochromator, and a HAMAMATSU R-1221HA photomultiplier tube. The system was controlled by a PC-9801 RA computer which was interfaced (GPIB) to a GOULD 4072 digital oscilloscope for data acquisition. The transient spectra were observed with a CCD monitoring system. The CCD detector (ICCD-1024-MLDG-E, Princeton Instruments) was controlled by a detector controller (ST-135, Princeton Instruments) and a pulse generator (PG-200, Princeton Instruments). The system was controlled by a PC-9801 BA2 computer which was interfaced (GPIB) to the detector controller.

All delay time of systems was controlled by a digital delay/pulse generator (DG-535, Stanford Research system).

Ab Initio Calculations. Ab initio calculations were carried

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out on a DEC VENTURIS 5100 computer using Gaussian 94.[25] Density functional theory (DFT) calculations with 6-31G* basis set[26] employed the B3LYP[17] exchange correlation functionals.

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Supporting Information Available: A table of geometries and total atomic charges for the parent dioxadiazole (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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