Formation and Cycloreversion of Dioxadiazole Intermediates in the Reaction of Diazo Compounds with Singlet Oxygen

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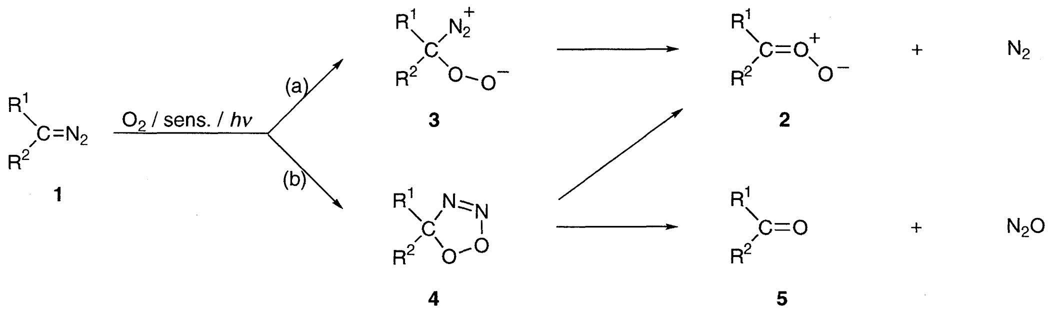
Product ratios of N_2/N_2O as an indicator for carbonyl oxide formation in the $^1O_2$ oxygenation of phenyl diazomethanes were not affected by protic solvents but were significantly increased by electron-donating substituents. A mechanism is suggested in which 1,2,3,4-dioxadiazole intermediates are formed by the cycloaddition of $^1O_2$ and diazomethanes and its cycloreversion is controlled by the relative stability of resulting carbonyl oxides.

Carbonyl oxides and related compounds have been attracting much attention as an intermediate in alkene ozonolysis and as a chemical mimic of biological oxygen transfer systems.[1] The oxides **2** can be generated from diazo compounds **1** either by photolysis in the presence of oxygen (carbene-oxygen reaction) or by sensitized irradiation (singlet oxygenation of **1**).[2] In solution, the singlet route offers a great advantage since the intermediacy of highly reactive carbenes can be avoided.[3] The singlet oxygen reaction may proceed by a direct substitution via a zwitterion **3** (Eq. 1, path a) and/or by an 1,3-dipolar cycloaddition of $^1O_2$ to **1** generating an 1,2,3,4-dioxadiazole **4** followed by its cycloreversion (path b). The intermediacy of **4** and its cycloreversion yielding ketones **5** have been evidenced by the formation of N_2O,[4] but the involvement of **3** or **4** and their chemistry are not clarified. We wish to report here the sole involvement of **4** and the interesting behavior of its cycloreversion.

Photolysis of phenyldiazomethanes **1** sensitized with Methylene Blue (MB) in MeCN or with *meso*-tetraphenylporphine (TPP) in benzene under oxygen atmosphere affords ketones in almost quantitative yields.[2a,5] Since all the ketones are formed by the self-reaction of carbonyl oxide[6] and/or the elimination of N_2O from **4**, the selectivity of carbonyl oxide can be determined from the ratios of N_2/N_2O. Thus, the gasses evolved during the photochemical oxidation in a closed system have been analyzed by GC-MS[7] and the results are summarized in Table 1. The ratios of carbonyl oxides vs ketones ($\equiv N_2/N_2O$) have been shown to be slightly higher in acetonitrile (runs 2 and 5) than those in benzene (runs 1 and 4).[8] In contrast, practically no effect was shown by methanol, a protic solvent (runs 3 and 6). This fact eliminates clearly an intervention of zwitterion **3** (Eq. 1, path a) since **3** would be stabilized by hydrogen bonding with MeOH. Thus, it may be concluded that the predominant reaction of diazomethanes and



(1)

Table 1. Evolved gasses in the photo-oxygenation of diazomethanes[a]

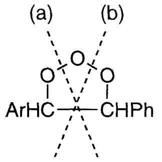
Run No.	Diazo compounds R^1	R^2	conc.(mM)	Solvent	Products[b] N_2 / %	N_2O / %	N_2/N_2O
1	Ph	Ph	3.2	C_6H_6	55.2 ± 0.7	44.8 ± 0.7	1.23
2			3.1	CH_3CN	61.8 ± 0.6	38.2 ± 0.6	1.62
3			3.3	CH_3OH	55.6 ± 1.0	44.4 ± 1.0	1.25
4	Ph	Et	3.8	C_6H_6	59.8 ± 0.4	40.2 ± 0.4	1.49
5			3.4	CH_3CN	72.0 ± 1.2	28.0 ± 1.2	2.57
6			3.4	CH_3OH	58.0 ± 0.3	42.0 ± 0.3	1.38
7	Ph	Me	3.3	CH_3CN	78.3 ± 0.8	21.7 ± 0.8	3.61
8		*i*- Pr	3.5	CH_3CN	64.1 ± 1.2	35.9 ± 1.2	1.79
9		*t*- Bu	3.2	CH_3CN	52.9 ± 0.5	47.1 ± 0.5	1.12
10	4-MeO-C_6H_4-	H	2.7	CH_3CN	84.5 ± 0.4	15.5 ± 0.4	5.45
11	4-Me-C_6H_4-	H	3.3	CH_3CN	72.4 ± 0.8	27.6 ± 0.8	2.62
12	Ph	H	3.5	CH_3CN	70.2 ± 0.9	29.8 ± 0.9	2.36
13	4-Cl-C_6H_4-	H	2.5	CH_3CN	65.4 ± 0.3	34.6 ± 0.3	1.89

[a] A solution of 0.15 mM MB (CH_3CN or CH_3OH) or 0.10 mM TPP (C_6H_6) and ~3 mM of diazoalkane was irradiated at > 400 nm under oxygen for 30 min at ca. 20℃. (1M = 1 mol dm^{-3}) [b] The productions of N_2 and N_2O determined by GC-MS.

singlet oxygen is the direct formation of dioxadiazole **4**, i.e., the concerted 1,3-dipolar cycloaddition of singlet oxygen to **1** (Eq. 1, path b).

For alkyl(phenyl)diazomethanes ($Ph(R)C=N_2$), the N_2/N_2O ratios decreased from 3.6 (R = Me) to 1.1 (R = *t*-Bu) as increasing the bulkiness of alkyl groups (*cf.* runs 7, 5, 8, and 9). The results obtained for *p*-substituted phenyldiazomethanes (runs 10-13) show that the N_2/N_2O ratios increased from 1.9 (*p*-Cl) up to 5.5 (*p*-MeO) with increasing the electron-donating ability of substituents. The resulting Hammett ρ value was -0.83 (vs σ , $r = 0.86$) for the carbonyl oxide formation.

The substituent effects may be discussed in relation to the stability of carbonyl oxides. The present cycloreversion of dioxadiazole **4** is governed by the relative stability of carbonyl oxides; i.e., electron-donating substituents favor the oxide formation. A similar effect of substituents has been reported for the cleavage (b) of primary ozonides **6**.[9,10]



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The least amount formation of carbonyl oxide for the case of *t*-butyl group (run 9) is well explained by the steric effect in stabilizing the oxides. Here again, a similar trend of bulky substituents is reported in the cycloreversion of primary ozonides of trans-dialkyl etylenes.[11]

Thus, major process in the oxygenation of diazomethanes is the cycloaddition of $^1O_2$ yielding dioxadiazole **4** and its cycloreversion is affected by the relative stability of carbonyl oxides. It is interesting to note that the predominant formation of carbonyl oxides (i.e., >50%) is controlled kinetically, since a preliminary PM3-CI calculation[12] indicated that the cycloreversion of **4** (R^1 = Ph, R^2 = H) to **2** and N_2 is almost thermoneutral ($\Delta H = -6.7$ kJ/mol), the decomposition affording benzaldehyde and N_2O being highly exothermic ($\Delta H = -259$ kJ/mol). This may indicate that the cycloreversion yielding a linear N_2O proceeds via a significantly distorted transition state and hence is kinetically less favorable. Further studies on the reactive intermediates in the oxygenation of diazomethanes are in progress.

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References and Notes

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7 Typically, a 1.65-mL solution of MB (0.15 mM) 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 ca. 20℃ at which the diazoalkane was completely converted to ketones. The solution was injected to a Shimadzu QP-5000 GC-MS spectroanalyzer using a 0.2 mm × 25 m capillary column of CBP1-M50. The concentrations of N_2 and N_2O dissolved in the solution were obtained by integrating mass peaks at *m/e* 28 and 44, respectively, at the ionizing voltage of 70 eV. The relative sensitivity of N_2O/N_2 was determined to be 0.91 ± 0.02 from a mixture of authentic N_2 and N_2O gasses of a known ratio. Small amounts of N_2 and CO_2 (*m/e* 44) leaked at the injection (less than 5% of evolved gasses) were corrected and the analysis was repeated for several times.

8 a) Since the dipole moments of carbonyl oxides are greater those of ketones,[8b] the slightly higher ratios of N_2/N_2O may indicate the more favorable formation of carbonyl oxides in polar solvents. But a more systematic examination of various solvents is to be carried out in order to reach a safe conclusion.; b) R. W. Fessenden and J. C. Scaiano, *Chem. Phys. Lett.*, **117**, 103 (1985).

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