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Direct observation for the cyclization of a diarylcarbonyl oxide

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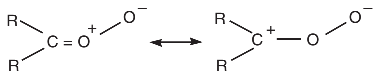
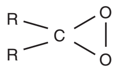
Abstract—Trapping and laser flash spectroscopic experiments showed that the cyclization of diphenylcarbonyl oxide is turned into a very facile process by introducing *p*-methoxyl substituent, the lifetime of which is as short as 10^{-8} s. The trapping with diphenylsulfide and -sulfoxide suggested the intervention of a dioxirane intermediate.

Carbonyl oxides (**1**) are the key intermediate in the ozonolysis of olefins[1] and have attracted interest in the various fields of synthetic, mechanistic, biological and atmospheric chemistry.[2] On the other hand, the cyclic isomers, dioxiranes (**2**), can be prepared by the peroxysulfate oxidation of ketones[3] and are employed as a versatile oxygen transfer agent.[4]



1a **1b**



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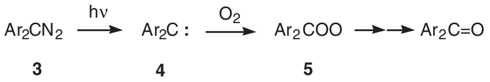
The structural and chemical property of these peroxidic species are significantly dependent on their substituents.[5] Carbonyl oxides (CO) are characterized as a nucleophilic O-transfer agent,[2b,6] and usually do not isomerize to the more stable dioxiranes (DO) because of the C–O double bond nature as shown in **1a**. While the cyclization of CO's to DO's is known to proceed photochemically,[7] the thermal reaction has been suggested only for the exceptional case of oxides with α-methoxyl[8] or α-amino substituent.[9] Herein, we report on the first direct observation of the facile cyclization of a diaryl CO.

Diaryl CO's (**1**, R = Ar) are known to decay slowly according to the second-order kinetics yielding the corresponding ketones.[10,11] As a special case, dimesityl CO is reported to be stable in solutions because of the presence of bulky mesityl group.[7a] In the course of the study on the reaction of carbenes and oxygen[9,12] we have surveyed various types of CO's by trapping and laser-flash spectroscopic experiments. The oxides were produced by the laser-flash at 308 nm for the corresponding diazomethanes in the presence of oxygen in acetonitrile (Eq. 1, Ar = Ph and X–C_6H_4).[13]



$$\underset{\mathbf{3}}{Ar_2CN_2} \xrightarrow{h\nu} \underset{\mathbf{4}}{Ar_2C:} \xrightarrow{O_2} \underset{\mathbf{5}}{Ar_2COO} \longrightarrow\!\!\!\!\rightarrow Ar_2C{=}O \qquad (1)$$

Aryl CO's are reported to possess the strong absorption at 410 ± 20 nm.[2a] A typical case of diaryl CO is shown in Figure 1. When diphenyldiazomethane (**3a**, Ar = Ph) was irradiated in the presence of oxygen, diphenyl CO (**5a**) could be detected as its absorption spectra with $\lambda_{max} = 410$ nm as shown in Figure 1A. The reaction course of Eq. 1 could be followed by monitoring the decay of carbene **4a** at 340 nm or by the formation of CO **5a** at 410 nm. The resulting rate constant for the reaction of **4a** with O_2 was $3.2 \times 10^9\ M^{-1}\ s^{-1}$, which is close to the reported value of $5.0 \times 10^9\ M^{-1}\ s^{-1}$.[11c] Time course of the absorbance of **5a** is shown in Figure 1B; its formation, which was faster under oxygen (a) than that under air (b),[14] was almost completed within 1 μs and its decay was slow and below 5% after 10 μs. The same was true for the cases of *p*-chlorophenyl or *p*-methylphenyl CO. The weak absorption for the flash under argon (c) is probably due to the formation of azine derivative by the reaction of **4a** with starting **3a**.

Keywords: Carbonyl oxides; Cyclizations; Dioxiranes; Peroxides; Oxidation; Mechanism.

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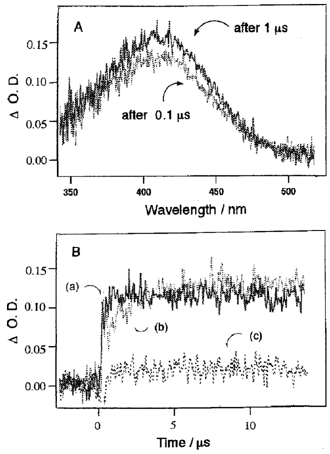


Figure 1. Formation and decay of diphenyl CO (**5a**) by the laser flash (308 nm) for **3a** in acetonitrile. A: Spectra of **5a** at 0.1 and 1.0 µs after the flash under air. B: Time-course of the 410 nm absorbance under oxygen (a), air (b) and argon (c).

Table 1. Trapping of active oxygen species during the photooxidation of Ar_2CN_2 in acetonitrile[a]

Ar	Additive	Products[b] (%)	Rel. reactivity SO/S[c]
Ph	Ph_2S, 50 mM	Ph_2SO, 2.2	
	Ph_2SO, 50 mM	Ph_2SO_2, 19	8.6
	MeOH, 1.3 M	ROOH[d], 51[e]	
Anis[f]	Ph_2S, 50 mM	Ph_2SO, 37	
	Ph_2SO, 50 mM	Ph_2SO_2, 42	1.1
	Ph_2S, 8 mM	Ph_2SO, 29	
	Ph_2SO, 8 mM	Ph_2SO_2, 18	0.62
	MeOH, 2.5 M	ROOH,[d] 35	

[a] Solutions of Ar_2CN_2 (4–20 mM), Rose Bengal (0.3 mM) and the additive were irradiated at >400 nm with a 300 W Hg lamp (1.5 h, ca. 20 °C).

[b] Products from additives were determined by GLC and % yields are based on the starting Ar_2CN_2.

[c] Relative reactivity of Ph_2SO/Ph_2S.

[d] ROOH: $Ar_2C(OMe)OOH$. Yields were determined by ^1H NMR.

[e] Ref. 12b.

[f] Anis = *p*-$MeOC_6H_4$.

When di(*p*-methoxyphenyl)diazomethane (**3b**, Ar = *p*-$MeOC_6H_4$)[15] was photolyzed under the same conditions, a quite different time course was obtained. As shown in Figure 2, the growth of the absorption at 410 nm is comparable to the other diaryl CO's, but its decay is very fast. It is interesting to note that the decay curve is well reproduced, as shown in the line of Figure 2, by the first-order rate constant of $k_1 = 4.5 \times 10^7\ s^{-1}$. Similar results were obtained as 3.8, 3.6. 3.8 and $3.5 \times 10^7\ s^{-1}$ with 0.04–0.20 mM **3b**, affording $k_1 = (3.9 \pm 0.4) \times 10^7\ s^{-1}$ for the decay in acetonitrile at 25 °C. The decay in benzene was similarly fast, the resulting k_1 value being $(2.1 \pm 0.4) \times 10^7\ s^{-1}$. The lifetime of transient species (i.e., 2.6×10^{-8} s) was too short for monitoring with the conventional CCD system, but its spectra could be obtained, as shown in Figure 2 (inset), by the time-resolved observation at 17.5 ns after the laser-flash. The transient species with $\lambda_{max} = 395$ nm is soundly assigned as CO **5b** since it appeared only in the presence of oxygen and aryl CO's are known to possess strong absorption at 410 ± 20 nm.[2a,11c]

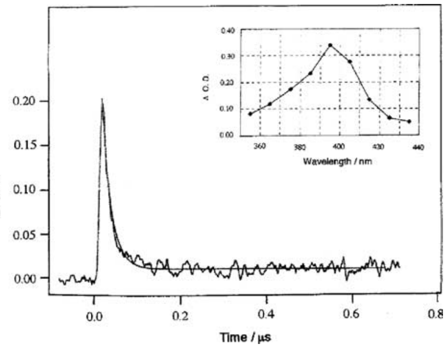
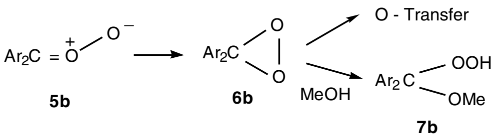


Figure 2. Formation and decay of dianisyl CO (**5b**, Ar = *p*-$MeOC_6H_4$), as monitored at 410 nm, by the laser flash (308 m) for **3b** in acetonitrile under oxygen at 25 °C. The decay line is obtained according to $k_1 = 4.5 \times 10^7\ s^{-1}$. Inset: the transient spectra obtained 17.5 ns after the flash.

In order to characterize the transient species, O-transfers to diphenylsulfide (S) and sulfoxide (SO) were examined. Here, CO's were produced by the singlet oxygen oxidation of diazomethane[11c,13a] to avoid the possible reaction of carbenes and additives. As shown in Table 1, the reaction of diphenyl CO (**5a**) with the sulfide was inefficient compared to that with the sulfoxide. Thus, the resulting relative reactivity of SO/S was 8.6, reflecting the nucleophilic nature of typical CO's.[2b,6] In contrast, the resulting SO/S ratio for intermediate(s) from *p*-anisyl diazomethane **3b** was as low as ca. 1. Now it is apparent that the transient species observed by the laser flash spectroscopy is dianisyl CO (**5b**, Ar = *p*-anisyl) but the intermediate trapped by additives is another one, that is, DO **6b**. This may be rationalized since the lifetime of 10^{-8} s is too short to be trapped intermolecularly. DO's are known to be a potent electrophilic oxidant[4,16] and hence the sulfide and sulfoxide were oxidized equally efficiently, resulting in the SO/S ratio of ca. 1.

When methanol was added in the photooxidation of **3b**, the resulting product was α-methylhydroperoxide (**7b**, $Ar_2C(OMe)OOH$).[17] The formation of **7b** seems to be evidence for the trapping of CO intermediates as reported repeatedly.[2] In the present case, however, it is not the case. This is because the reaction of diphenyl CO's with alcohols is a much slower reaction (e.g., the second-order rate constant of ca. $10^4\ M^{-1}\ s^{-1}$)[12b] and because the lifetime of CO **5b** is too short to be trapped intermolecularly. An assumption of the very fast (i.e., close to the diffusion control rate) reaction between **5b** and MeOH is not reasonable since the *p*-anisyl substituent is well known to reduce significantly the reactivity of cationic species with nucleophiles.[18] Thus, the acceptable conclusion here is such that the cyclization of **5b** to **6b** is facile ($k_1 = 3.9 \times 10^7\ s^{-1}$) and that the resulting **6b** reacts with the additives, that is, the O-transfer (Eq. 2a) and the addition of

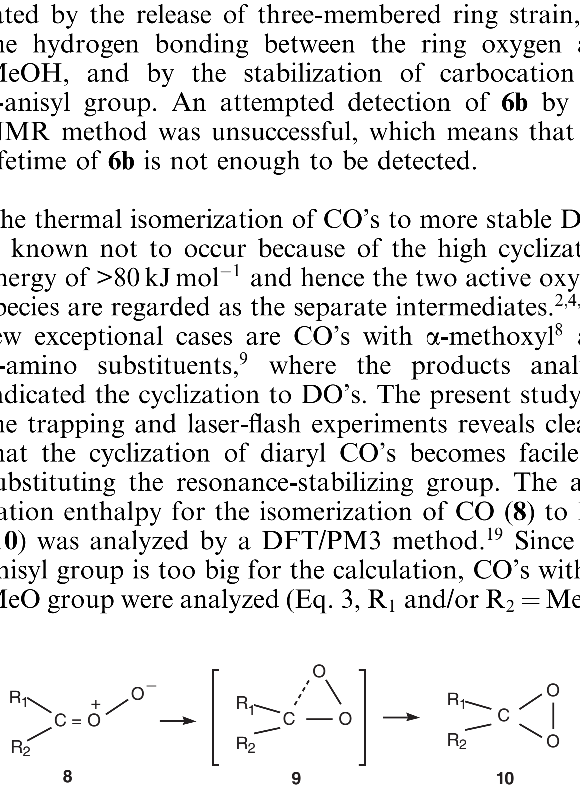


(2a)

(2b)

methanol (Eq. 2b). The latter reaction is speculated to be facile since the ring-opening reaction of **6b** is facilitated by the release of three-membered ring strain, by the hydrogen bonding between the ring oxygen and MeOH, and by the stabilization of carbocation by *p*-anisyl group. An attempted detection of **6b** by ^{13}C NMR method was unsuccessful, which means that the lifetime of **6b** is not enough to be detected.

The thermal isomerization of CO's to more stable DO's is known not to occur because of the high cyclization energy of >80 kJ mol^{-1} and hence the two active oxygen species are regarded as the separate intermediates.[2,4,5] A few exceptional cases are CO's with α-methoxyl[8] and α-amino substituents,[9] where the products analysis indicated the cyclization to DO's. The present study on the trapping and laser-flash experiments reveals clearly that the cyclization of diaryl CO's becomes facile by substituting the resonance-stabilizing group. The activation enthalpy for the isomerization of CO (**8**) to DO (**10**) was analyzed by a DFT/PM3 method.[19] Since the anisyl group is too big for the calculation, CO's with α-MeO group were analyzed (Eq. 3, R_1 and/or $R_2 = MeO$).



(3)

The activation enthalpy ($\Delta H^{\#}$) of 64.8 kJ mol^{-1} for the parent CO (**8a**, $R_1 = R_2 = H$) was decreased down to 48.5 for *anti*-MeO (**8b**, $R_1 = H$, $R_2 = MeO$) and to only 8.0 kJ mol^{-1} for dimethoxyl CO (**8c**, $R_1 = R_2 = MeO$). A small decrease in $\Delta H^{\#}$ (i.e., 31.8 kJ mol^{-1}) was obtained for the CO with $R_1 = MeO$ and $R_2 = F$, but not for other cases of dichloro- or difluoro CO (55.6 kJ mol^{-1}). These results indicate that the corporative interaction of two resonance-stabilizing groups is important to reduce the relative enthalpy of transition state **9**, that is, the activation energy for the cyclization. In other words, the introduction of two MeO groups is to increase the importance of **1b** with C–O single bond leading to the facile cyclization to DO's.

In conclusion, it is shown that the reactivity of CO intermediates is controlled and turned by the resonance-stabilizing donor substituent.

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