

Reaction of Diphenylmethylene and Phenylmethylene with Oxygen. A Matrix Isolation Study

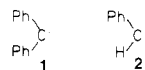
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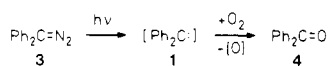
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The thermal and photochemical reactions of phenylcarbene and diphenylcarbene in oxygen-doped matrices have been investigated. The primary thermal adducts of free carbenes and O₂ are carbonyl O-oxides, which are characterized by IR and UV spectroscopy. Most characteristic are intense O-O stretching modes in the IR ($\nu \approx 900 \text{ cm}^{-1}$) and $\pi \rightarrow \pi^*$ transitions in the UV ($\lambda \approx 400 \text{ nm}$) spectra. The carbonyl O-oxides are very photolabile toward long-wavelength irradiation (500-630 nm) and either rearrange to dioxiranes or split off oxygen atoms. The distribution of photoproducts is determined by substituents: benzophenone O-oxide mainly gives diphenyldioxirane while benzaldehyde O-oxide gives the aldehyde and oxygen atoms. The strong chemiluminescence observed during the thermal reaction is explained by the reaction of free carbenes and oxygen atoms forming a C=O bond in situ. This reaction is highly exothermic and produces carbonyl compounds in their triplet states.

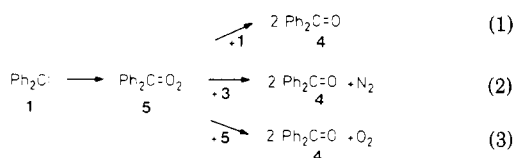
Numerous papers on the chemistry and spectroscopy of diphenylmethylene (1) and phenylmethylene (2) have appeared in the literature.¹ From these studies it is clear that both carbenes have triplet ground states. Thus the reaction between 1 or 2 and triplet O₂ to give stable singlet products is "spin-allowed" and expected to be very rapid.



The reaction of 1 and O₂ was studied by several authors, but not much has been reported about the reaction of 2 and O₂. Kirmse et al. found benzophenone (4) as the sole photooxidation product of diphenyldiazomethane (3) in up to 73% yield.²

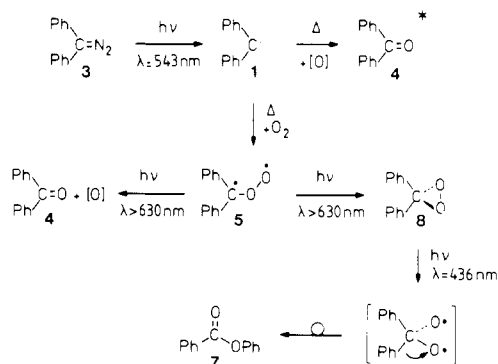


A mechanism involving oxygen transfer from benzophenone O-oxide (5) to carbene 1 (reaction 1) or diazo compound 3 (reaction 2) was proposed.



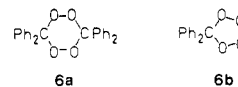
Several years later Bartlett and Traylor were able to isolate low yields of tetroxane 6a, and thus the formation of 5 as a reactive intermediate was confirmed.³ By using ¹⁸O₂ in the photooxidation experiments they could also exclude reaction 3 as a source of 4. In the same year Trozzolo reported the observation of a blue emission during warm up of an organic glass containing 1 and O₂.⁴ The spectrum of the emission was shown to correspond to the phosphorescence spectrum of benzophenone. Several mechanisms explaining the chemiluminescence appeared in literature. Turro et al. showed that chemiluminescence is a general phenomenon in carbene oxidations as long as the corresponding ketones exhibit phosphorescence.⁵ In all cases the chemiluminescence spectrum was

Scheme I



similar to the phosphorescence spectrum of the corresponding ketones, although in some cases a perturbation of the vibrational fine structure was observed. The transfer of oxygen atoms from carbonyl O-oxides to O₂ to give ozone was suggested to be the chemiluminescent step in these reactions (reaction 7).⁵

An alternative mechanism was published by Ishiguro et al.⁶ They observed a complete scrambling of oxygen atoms in esters formed as oxidation products when a mixture of ¹⁸O₂ and ¹⁶O₂ was used in the photooxidation of diazomethanes. This was explained by the formation of the cyclic tetroxide 6b. The decomposition of 6b was proposed as being the origin of the chemiluminescence.



More insight into the mechanism of carbene oxidations has been obtained by the direct spectroscopic characterization of free carbenes and carbonyl O-oxides. The most important techniques for this purpose have been matrix isolation spectroscopy⁷⁻¹⁰ and time-resolved laser flash

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Table I. IR Spectroscopic Data of Four Isotopomers of Benzophenone (4a-d), Matrix Isolated in Ar at 10 K (Wavenumbers in cm^{-1})

$\text{Ph}_2^{12}\text{C}^{16}\text{O}$ 4a	$\text{Ph}_2^{12}\text{C}^{18}\text{O}$ 4b	$\text{Ph}_2^{13}\text{C}^{16}\text{O}$ 4c	$\text{Ph}_2^{13}\text{C}^{18}\text{O}$ 4d	assignment ^a
1674 (vs)	1644	1637 (vs)	1573	ν C=O
1669 (s)		1633 (s)		
1605 (m)		1604 (m)	1604	ν C-C (8a)
1602 (m)	1602	1601 (m)	1598	
1581 (m)	1579	1579 (m)		ν C-C (8b)
1450 (s)	1451	1449 (m)	1450	ν C-C (19b)
1319 (s)	1320	1317 (m)	1318	ν C-C (14)
1308 (s)	1309	1305 (m)	1305	β C-H (3)
1280 (vs)	1280	1268 (vs)	1267	ν_{as} C-C(O)-C
1275 (s)	1275		1254	
1176 (m)	1178	1175 (m)	1177	β C-H (9a)
942 (s)	942	936 (m)	937	ν_{sy} C-C(O)-C
920 (s)	920	911 (s)	910	γ C-H (17b)
762 (m)	760	761 (m)	760	γ C-H (11)
700 (s)	700	697 (vs)	697	ϕ C-C (4)
639 (s)	636	637 (s)	634	β C=O

^a Approximate description, Wilson notation for vibrations of phenyl rings in parentheses. Assignment on the basis of isotopic shifts and by comparison with gas phase spectra (ref 32).

spectroscopy.¹¹ Several carbonyl *O*-oxides were identified by their intense absorptions in the visible region of the spectrum. Matrix isolation spectroscopy in addition allowed to obtain highly resolved IR spectra.

In this paper we report the matrix isolation and spectroscopic characterization of carbenes 1 and 2 as well as their reaction products with molecular oxygen.¹² The assignment of spectra of reactive intermediates is confirmed by isotopic labeling studies. A mechanism that explains the chemiluminescence is proposed.

Results

Oxidation of Diphenylmethylene (1). Irradiation ($\lambda = 543$ nm) of diphenyldiazomethane (3), matrix isolated in Ar at 10 K, gave carbene 1 in a clean reaction (Scheme I). The visible spectrum of 1 has a maximum at 454 nm and shows vibrational fine structure. Band position and shape are similar to the data reported for 1 in solid 2-methyltetrahydrofuran at 77 K ($\pi \rightarrow \pi^*$ transition).^{4b}

IR bands assigned to 1 and $[1-^{13}\text{C}]-1$ are summarized in Table II.¹³ Criteria for the assignment are (1) the bands appear on irradiation of 3 and $[1-^{13}\text{C}]-3$, respectively; (2) the bands disappear on annealing a matrix containing 1 (or $[1-^{13}\text{C}]-1$) and CO or O_2 (vide infra).

As most IR bands of 1 are associated with vibrations of the phenyl groups they exhibit only minor isotopic shifts on ^{13}C substitution. The largest shift was observed for a very weak band at 1282 cm^{-1} (isotopic shift 24 cm^{-1}), which is assigned to the asymmetric C-C(1)-C stretching vibration (Table II). Carbene 1 proved to be remarkable photostable. Visible light irradiation (4 h, $\lambda = 435$ nm) gave rise to a small increase in the intensity of the band at 700 cm^{-1} and a decrease of the band at 743 cm^{-1} . Prolonged UV irradiation (13 h, $\lambda > 310$ nm) did not lead to any further changes in the spectra. The initial perturbation in the band intensities can be explained by the photoannealing of the matrix. Beside carbene 1 no other photoproduct, and particularly no diphenyldiazirine, was ob-

Table II. IR Spectroscopic Data of 1 and $[1-^{13}\text{C}]-1$, Matrix Isolated in Ar at 10 K (Wavenumbers in cm^{-1})

Ph_2^{12}C :	Ph_2^{13}C :	Δ^a	assignment ^b
3072 (m)	3072 (m)	0	ν C-H
1539 (w)	1538 (w)	-1	
1479 (m)	1472 (m)	-7	
1465 (w)	1467 (w)	2	ν C-C (19a)
1432 (w)	1432 (w)	0	ν C-C (19b)
1282 (vw)	1258 (vw)	-24	ν_{as} C-C(1)-C
1089 (w)	1089 (w)	0	β C-H (18b)
1060 (w)	1059 (w)	-1	β C-H (18a)
1020 (m)	1019 (m)	-1	ring (12)
891 (w)	887 (w)	-4	γ C-H (17b)
759 (m)	755 (m)	-4	
743 (s)	742 (s)	-1	γ C-H (11)
733 (w)			
700 (m)	699 (m)	-1	
673 (s)	676 (s)	+3	ϕ C-C (4)
	672 (s)		
662 (w)	650 (w)	-12	
565 (w)	561 (m)	-4	
496 (m)	491 (m)	-5	
456 (w)	457 (w)	+1	

^a Isotopic shifts. ^b Approximate description, Wilson notation for vibrations of phenyl rings in parentheses. Tentative assignment on the basis of isotopic shifts and by comparison with spectra of benzophenone 4.

served during photolysis of 3.

If 3 was irradiated ($\lambda = 543$ nm) in oxygen-doped matrices (0.5–15% O_2 in Ar, 10 K), carbene 1 and several oxidation products were formed (Scheme I). The ratio of 1 and oxidation products was strongly dependent on the O_2 content of the matrix. In 0.5% O_2 -doped matrices 1 was the main product whereas at high O_2 concentrations (>5%) the oxidation was almost complete and 1 could not be detected by IR spectroscopy. At 1–2% O_2 content both 1 and oxidation products could easily be observed, and therefore this concentration was used in most experiments. Although under these conditions excess O_2 is present in the matrix, no thermal reaction between O_2 and 1 was observed, as long as the matrix was kept at 10 K. This shows that the diffusion of O_2 in solid Ar is very slow at this temperature. The formation of oxidation products during irradiation is caused by the direct photooxidation of 3 with (statistically distributed) O_2 in the same matrix cage.

The photooxidation products were identified as benzophenone (4), phenyl benzoate (7), and diphenyldioxirane (8). The main products were ketone 4 and dioxirane 8; ester 7 was formed only in small amounts after long irradiation times. The carbonyl compounds were identified by comparison with authentic matrix isolated material. Dioxirane 8 was identified by its subsequent photochemistry (Scheme I) and characterized by IR spectroscopy (vide infra). Ozone was only a minor product formed at high O_2 contents (>4%).

To investigate the thermal reaction of 1 and excess O_2 , the matrix was warmed above 10 K to allow diffusion of O_2 . In "free warm up" experiments the matrix was warmed to 42 K at a rate of 1–2 deg/min and then rapidly cooled back to 10 K. If the matrix was doped with 2% O_2 , carbene 1 was completely oxidized after one "free warm up" cycle, at 1% O_2 content several cycles were necessary.

Only traces of 4 and no detectable amount of 7 or 8 were formed in the thermal reaction of 1 and O_2 . In the visible spectra the formation of a new product was monitored by the disappearance of the medium intensity carbene band at 454 nm and the growth of a very intense band at 422 nm. Simultaneously the matrix turned yellow. Band shape and position are similar to the band assigned to

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(12) Preliminary communications describing some aspects of this work have appeared. See ref 10a and 10b.

(13) Some IR data of 1 but no vibrational assignment have been published: see ref 8b.

Table III. IR Spectroscopic Data of Four Isotopomers of Benzophenone *O*-Oxide (5a-d), Matrix Isolated in Ar at 10 K (Wavenumbers in cm⁻¹)

Ph ₂ ¹² C ¹⁶ O ₂ , 5a	Ph ₂ ¹² C ¹⁸ O ₂ , 5b	Ph ₂ ¹³ C ¹⁶ O ₂ , 5c	Ph ₂ ¹³ C ¹⁸ O ₂ , 5d	assignment ^a
1375 (s)	1368 (s)	1354 (s)	1351 (s)	ν_{as} C-C(O)-C
1346 (w)		1339 (w)	1338 (w)	
1184 (w)	1178 (w)	1184 (w)	1182 (w)	β C-H (9a)
1157 (w)	1150 (w)	1157 (w)	1148 (w)	β C-H (15)
981 (m)	976 (w)	976 (m)	962 (m)	ν_{sy} C-C(O)-C
896 (vs)	861 (s)	892 (vs)	858 (vs)	ν O-O
777 (w)	776 (w)	773 (w)	772 (w)	
760 (w)	759 (m)	760 (w)	758 (m)	γ C-H (11)
689 (s)	688 (s)	688 (s)	689 (s)	ϕ C-C (4)
658 (m)	653 (m)	656 (m)	651 (m)	
646 (m)	645 (w)	637 (m)	634 (w)	δ C(O)-C
550 (w)	543 (w)	547 (w)	541 (w)	δ O-O

^a Approximate description, Wilson notation for vibrations of phenyl rings in parentheses. Tentative assignment on the basis of isotopic shifts and by comparison with spectra of 4.

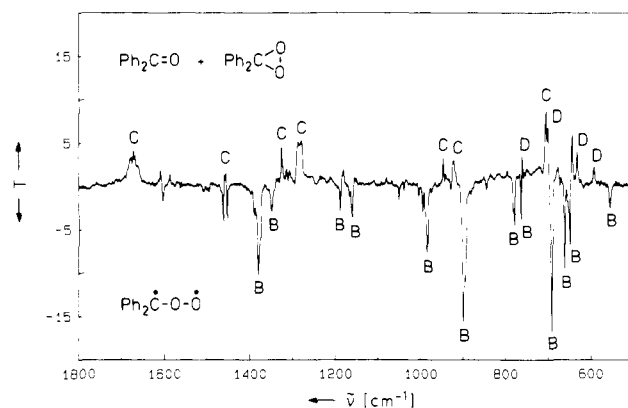


Figure 1. Difference IR spectrum showing the photochemistry of carbonyl *O*-oxide 5 in a 1% O₂-doped Ar matrix at 10 K: bottom, bands disappearing; top, bands appearing on irradiation ($\lambda > 630$ nm) of 5. B: bands assigned to 5. C: bands assigned to 4. D: bands assigned to 8.

benzophenone *O*-oxide 5 in laser flash photolysis experiments.

A more definitive proof for the formation of 5 came from IR spectra and isotopic labeling experiments. The reaction of 1 or [1-¹³C]-1 with ¹⁸O₂ or ¹⁸O₂ produced four isotopomers (5a-d) (Table III). The most intense band in the spectrum of 5a is found at 896 cm⁻¹. This band shows an isotopic shift of 35 cm⁻¹ (3.9%) in the doubly ¹⁸O-labeled isotopomer 5b and is assigned to the O-O stretching mode. The large isotopic shift can only be explained by a major contribution of an O-O vibration, as the maximum shift possible for a C-O oscillator is 2.4%. ¹³C labeling has only a small effect on the position of this band (Table III). The strong band at 1375 cm⁻¹ in 5a shows a shift of 21 cm⁻¹ on ¹³C labeling and a shift of 7 cm⁻¹ on ¹⁸O labeling. This band is assigned to the asymmetric C-C(1)-C stretching mode with some contribution of the C(1)-O(1) vibration. The corresponding symmetric mode is tentatively assigned to a band at 981 cm⁻¹. In 4 the symmetric and asymmetric vibrations are found at 1276 and 939 cm⁻¹, respectively.

To study the kinetics of the formation of 5 a matrix containing 1 and 0.5% O₂ was rapidly warmed to 30 K and kept at this temperature. The formation of the 896-cm⁻¹ band of 5a was monitored by IR spectroscopy. A pseudo-first-order rate constant $k = (2.0 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$ was observed for the formation of 5a.

Carbonyl *O*-oxide 5 is very photolabile. Long-wavelength irradiation with the filtered light of a mercury high-pressure arc lamp ($\lambda = 575$ nm or $\lambda > 630$ nm) rapidly

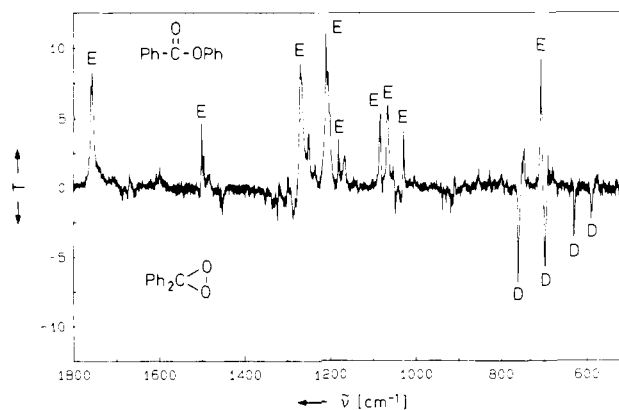


Figure 2. Difference IR spectrum showing the photochemistry of dioxirane 8 in a 1% O₂-doped Ar matrix at 10 K: bottom, bands disappearing; top, bands appearing on irradiation ($\lambda = 436$ nm) of 8. D: bands assigned to 8. E: bands assigned to 7.

Table IV. IR Spectroscopic Data of Four Isotopomers of Diphenyl Dioxirane (8a-d), Matrix Isolated in Ar at 10 K (Wavenumbers in cm⁻¹)

Ph ₂ ¹² C ¹⁶ O ₂	Ph ₂ ¹² C ¹⁸ O ₂	Ph ₂ ¹³ C ¹⁶ O ₂	Ph ₂ ¹³ C ¹⁸ O ₂	assignment ^a
1450 (w)	1451 (w)	1450 (w)	1450 (w)	ν C-C (19b)
	1457 (w)			
1285 (w)	1285 (w)	1276 (m)	1275 (m)	ν_{as} C-C(1)-C
916 (vw)	915 (w)	905 (m)	905 (m)	ν_{sy} C-C(1)-C
	772 (m)		771 (m)	
759 (m)	754 (m)	758 (ms)	753 (ms)	ϕ C-C (4)
693 (m)	694 (m)	695 (m)	695 (m)	γ C-H (11)
628 (w)	627 (m)	625 (m)	624 (m)	
588 (w)	575 (w)	586 (w)	573 (w)	δ O-O

^a Approximate description. Tentative assignment on the basis of isotopic shifts and by comparison with spectra of 4.

produced ketone 4 and dioxirane 8 (Figure 1).

Dioxirane 8 was identified by its subsequent photochemistry. Irradiation with blue light ($\lambda = 436$ nm) produced phenyl benzoate (7) in a clean reaction while ketone 4 was not formed (Figure 2). The cleavage of the O-O bond followed by migration of one substituent to give esters (Scheme I) is a characteristic photoreaction of dioxiranes.⁷⁻¹⁰

The structure of 8 was further confirmed by IR spectroscopy in combination with isotopic labeling. The IR data of the four isotopomers 8a-d are summarized in Table IV. The largest isotopic shift on ¹⁸O labeling is observed for a weak band at 588 cm⁻¹ (13 cm⁻¹ or 2.2%), ¹³C labeling leads only to a minor shift of 2 cm⁻¹. This is explained by a large contribution of the O-O stretching mode of the dioxirane moiety to this vibration.

The bands at 1285 and 916 cm⁻¹ (8a, Table IV) exhibit ¹³C isotopic shifts of ≈ 10 cm⁻¹ and are not effected by ¹⁸O labeling. These bands are assigned to the asymmetric and symmetric C-C(1)-C stretching mode, respectively. In benzophenone (4a, Table I) the corresponding bands are found at 1280 and 942 cm⁻¹. Several other bands, not showing any pronounced isotopic shifts on ¹³C or ¹⁸O labeling, were assigned to vibrations of the phenyl rings (Table IV).

Chemiluminescence from the Oxidation of 1. During annealing matrices containing 1, the photooxidation products of 1, and O₂, a bright blue chemiluminescence was observed. Chemiluminescence spectra were recorded during "free warm up" experiments in 5-deg intervals between 15 K (λ_{max} 418, 449, 485, 528 nm) and 55 K (λ_{max} 425, 457, 491, 531 nm). Below 15 K the intensity was too low to obtain spectra. The spectra closely match the phosphorescence spectrum of 4, matrix isolated in Ar at

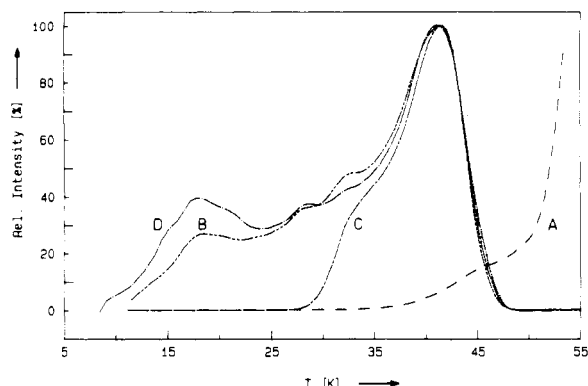


Figure 3. Luminescence intensities as function of temperature obtained from Ar matrices by warming ("free warm up", rate 1–2 deg/min) from 10 to 55 K. A: matrix containing 1, generated by irradiation ($\lambda = 543$ nm) of 3 and no O_2 . B: same conditions as in A, but 1% O_2 -doped matrix. C: same conditions as in B, but 15 min warming to 27 K prior to recording the luminescence intensity. D: same conditions as in A, but 2% O_2 -doped matrix.

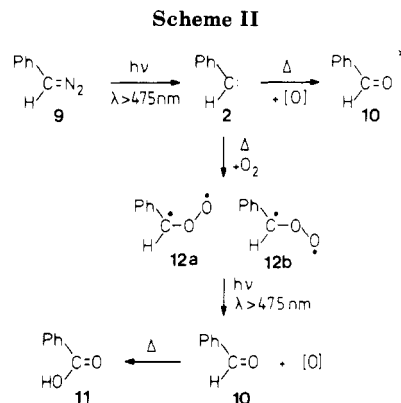
10 K (λ_{\max} 417, 448, 484, 525 nm). The major difference is broadening and perturbation of the relative intensities of the bands (vibrational fine structure corresponding to the C=O stretching vibration of triplet 4) in the chemiluminescence spectra. Raising the temperature causes red shift and further broadening of the bands. A possible explanation for this is the thermal relaxation of the phosphorescent state of 4 in soft matrices at higher temperatures.

The luminescence intensity depends on the O_2 content and the temperature of the matrix. Figure 3 shows the luminescence intensity in "free warm up" experiments (warm up rate 1–2 deg/min) for matrices containing 0%, 1%, and 2% O_2 . The luminescence intensities are normalized to 100% for the highest intensity measured in each experiment. The maximum absolute intensities (PM Voltage) in the 0%, 1%, and 2% experiments are 8, 0.05, and 0.009 V, respectively. At 5% O_2 content no luminescence was observed. At higher O_2 contents the phosphorescent state of 4 is quenched effectively and thus the luminescence intensity is reduced.

Matrices containing 1 and no O_2 exhibit a very intense luminescence at temperatures above 50 K. At this temperature the matrix evaporates rapidly and free carbene 1 reacts with the surface contamination of the matrix (air layer from small leaks in the vacuum system).

In O_2 -doped Ar matrices the luminescence starts as soon as the temperature rises above 10 K (Figure 3). A rapid increase of the luminescence intensity is followed by a maximum (or plateau, depending on the O_2 concentration) around 20 K. At $T > 30$ K the luminescence intensity starts to increase again, and at 41 K the highest luminescence intensity (independent of O_2 concentration, Figure 3) is measured. Remarkable is the "memory effect" found in the luminescence intensities as a function of temperature. If the matrix is annealed for several minutes at a temperature between 20 and 30 K prior to recording the luminescence intensity, the luminescence starts at temperatures slightly higher than the annealing temperature. This effect was also observed in other carbene oxidations.^{10b,c}

The kinetics of the luminescence decay was monitored by rapidly warming the matrix to 27 or 30 K and measuring the luminescence intensity at these temperatures as a function of time. The statistical analysis of the decay curves showed systematic deviation if single exponential decay was assumed. A biexponential curve gave an excellent fit with statistically distributed residuals. At 30



K the initial fast decay is described by a rate constant $k_1 = (8.5 \pm 1) \times 10^{-3} \text{ s}^{-1}$, for the slow component a rate constant $k_2 = (2.5 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$ was calculated. If the experiment was repeated at 27 K, k_1 and k_2 were lowered to $(7.8 \pm 1) \times 10^{-3} \text{ s}^{-1}$ and $(1.8 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$, respectively. The rate constants depend strongly on the exact experimental conditions (O_2 content, irradiation wavelength and frequency, matrix deposition) but were repeatable within the error limits given above.

Oxidation of Phenylmethylene 2. The photochemistry of phenyldiazomethane (9) has been reported by Chapman and co-workers.¹⁴ The formation of carbene 2 by irradiation of 9 is less effective than the formation of 1 from 3 described above. At $\lambda = 475$ nm irradiation the photolysis of 9 is still slow, but shorter wavelength irradiation ($\lambda = 435$ nm) gives cycloheptatetraene exclusively and no 2.

Irradiation ($\lambda > 475$ nm) of 9 in oxygen-doped matrices (0.5–5% O_2 in Ar, 10 K) produced carbene 2 and the oxidation products benzaldehyde (10) and benzoic acid (11). At high O_2 concentrations (>5%) O_3 was formed in substantial amounts. The oxidation products were identified by comparison with authentic matrix isolated material. Matrices containing 1–2% O_2 most easily allowed the spectroscopic observation of both free carbene 2 and oxidation products 10 and 11. If a matrix containing these products and excess O_2 was warmed to 40 K ("free warm up") and recooled to 10 K, the major change in the spectra was the decrease of bands assigned to 2 and 10, increase of the bands assigned to 11, and the appearance of several weak bands assigned to benzaldehyde O-oxide (12) (Scheme II). The matrix turned slightly yellow, and a broad band, exhibiting weak vibrational fine structure, appeared in the visible absorption spectrum (λ_{\max} 492, 482, 472, 462, 454, 445, 438, 430, 423, 410, 399, 387 (max), 359 nm). On the blue side of the band the fine structure is less pronounced.

Due to the low yield of 12, only the most intense bands were observed in the IR (Ar, 10 K: 915 (m), 890 (s), 839 (s), 630 (m) cm^{-1}). With use of $^{18}O_2$ several bands were shifted to lower frequencies (Ar, 10 K: 885 (m), 869 (s), 841 (s), 813 (s), 630 (m) cm^{-1}). On the basis of the isotopic shifts the bands at 915 and 890 cm^{-1} were assigned to O–O stretching modes. Irradiation ($\lambda > 475$ nm) of 12 rapidly produced 10 as the only detectable photoproduct.

After annealing matrices containing 2 and its photooxidation products, the most obvious change in the spectra was the decrease of aldehyde 10 and the increase of acid 11.¹⁵ The oxidation of 10 was also observed at O_2 contents

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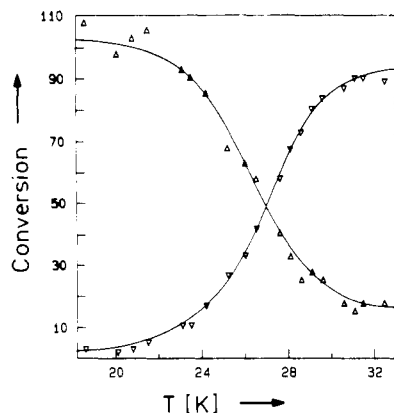


Figure 4. Oxidation of aldehyde **10** to acid **11** in a 1% O₂-doped Ar matrix as a function of temperature ("free warm up", rate 1–2 deg/min). Peak height of the carbonyl band of **10** at 1717 cm⁻¹. Peak height of the carbonyl band of **11** at 1757 cm⁻¹.

> 5%, where neither **2** nor **12** were formed in substantial amounts, and thus the oxidation of **10** to give **11** is not linked to the formation of carbonyl *O*-oxide **12**. In "free warm up" experiments the increase of **11** and the decrease of **10** followed the same kinetics (Figure 4). The conversion starts at 20 K; above 30 K no further reaction is observed. The amount of **11** formed in one "warm up" cycle was quite substantial and dependent on the exact experimental conditions (O₂ concentration, irradiation wavelength, and time). In a typical experiment (1.5% O₂, 5 h λ > 475 nm) the amount of **10** decreased by 30% and the amount of **11** increased by a factor of 3. At short irradiation times (<1 h, λ > 475 nm), with only incomplete photolysis of **9**, acid **11** was barely detectable. This shows that **11** is exclusively a thermally formed secondary product and not a primary product of the photooxidation of **9** (Scheme II).

Chemiluminescence from the Oxidation of 2. As in the case of **1**, an intense blue emission was observed when a matrix containing **2**, photooxidation products, and excess O₂ was warmed above 15 K. The chemiluminescence spectra obtained at various temperatures (0.5% O₂-doped Ar matrix, 44 K: λ_{max} 399, 428, 461, 499 nm) closely matched the phosphorescence spectrum of aldehyde **10** (methyl cyclohexane, 4.2 K: λ_{max} 399, 428, 462, 501 nm)¹⁶ if a small red shift with increasing temperature was taken into account. The temperature-dependent changes in the spectra are less pronounced than in the case of the oxidation of **1**.

The luminescence intensities as a function of temperature obtained from the oxidation of **2** (Figure 5) also showed some differences compared to the curves obtained from **1** (Figure 3). The maxima were shifted to lower temperatures with increasing O₂ content (Figure 5). At 2% O₂ content the maximum was found at 42 K, at 1% O₂ content at 44 K. Otherwise the intensity curves obtained from the oxidation of **1** and **2** are similar.

Discussion

Spectroscopic Characterization of Carbonyl *O*-Oxides. The carbonyl *O*-oxides of which spectroscopic data are available have several features in common: in the UV-vis spectra strong and broad bands with maxima between 370 and 470 nm, assigned to π → π* transitions,¹⁷

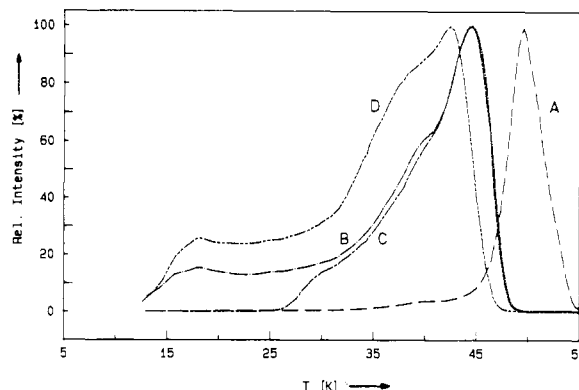


Figure 5. Luminescence intensities as function of temperature obtained from Ar matrices by warming ("free warm up", rate 1–2 deg/min) from 10 to 55 K. A: matrix containing **2**, generated by irradiation (λ > 475 nm) of **9** and no O₂. B: same conditions as in A, but 1% O₂-doped matrix. C: same conditions as in B, but 20 min warming to 25 K prior to recording the luminescence intensity. D: same conditions as in A, but 2% O₂-doped matrix.

and in the IR spectra very strong bands around 900 cm⁻¹, assigned to O–O stretching vibrations,^{7–10} are observed. These are the spectroscopic properties important for the identification of carbonyl *O*-oxides. In carbonyl compounds the C–O stretching modes form characteristic group frequencies¹⁸ and thus the question of the position of the analogous band in carbonyl *O*-oxides arises.

The most intense bands in the UV-vis spectra of **5** and **12** are π → π* transitions, found at 422 and 398 nm, respectively. The inclusion of a second phenyl group causes a small red shift in **5**. The UV-vis spectra of **5** and **12** were calculated by using semiempirical CNDO/S¹⁹ calculations on MINDO/3-UHF²⁰ optimized geometries (**5**, 455 nm, log ε = 3.84; **12a**, 423 nm, log ε = 3.98; **12b**, 427 nm, log ε = 4.09).¹⁷ The positions of the π → π* transitions and the influence of the phenyl groups are quite well reproduced. The calculated very weak n → π* transitions (**5**, 648 nm, log ε = 1.6; **12a**, 598 nm, log ε = 1.34; **12b**, 598 nm, log ε = 1.52) were not observed directly in the spectra, but some indirect evidence comes from the photochemistry of **5** (vide infra).

The fine structure in the visible spectrum of **12** is somewhat irregular and corresponds mainly to vibrational spacing of ≈450 and ≈740 cm⁻¹. In the case of *o*-chlorobenzaldehyde *O*-oxide a spacing of 790–700 cm⁻¹ was observed and assigned to the O–O stretching mode of the excited state by isotopic labeling. It is not clear if the irregular spacing in **12** is due to coupling of the visible transition with several vibrations or if it is caused by the superposition of the spectra of syn and anti isomers **12a** and **12b**. Some hint for the latter assumption comes from the CNDO/S calculations and the IR data.

In the IR spectrum of **5** the characteristic O–O stretching mode is observed at 896 cm⁻¹ (Table III). The basis for this assignment is the large ¹⁸O and the small ¹³C isotopic shift. In the IR spectrum of **12** the bands at 915 and 890 cm⁻¹ exhibit isotopic shifts of 30 and 21 cm⁻¹, respectively, and thus both have large contributions of O–O stretching vibrations. The observation of two bands is explained either by coupling of the O–O stretching mode with other

(15) Due to the low yield of **12**, it was only detected after the spectroscopic properties of other matrix isolated carbonyl *O*-oxides were known. See ref 10.

(16) Olmsied, J.; El-Sayed, M. A. *J. Mol. Spectrosc.* 1971, 40, 71.

(17) For a comparison of experimental and calculated UV-vis data, see: Cremer, D.; Schmidt, T.; Sander, W.; Bischof, P. *J. Org. Chem.*, in press.

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vibrations (Fermi resonance) or by the presence of syn and anti isomers **12a** and **12b** with slightly different O–O stretching modes.

From the frequency of the O–O stretching vibration the O–O bond order can be estimated. In H_2O_2 the O–O stretching vibration is found at 863 cm^{-1} (bond order 1), in O_3 at 1103 cm^{-1} (bond order 1.7), and in O_2 at 1580 cm^{-1} (bond order 2).²¹ Thus in carbonyl *O*-oxides a bond order of slightly more than 1 is estimated from the IR data. This is in accordance with high level ab initio calculations of formaldehyde *O*-oxide, which predict a bond length of 1.349 \AA , half way between the bond lengths of H_2O_2 (1.46 \AA) and O_3 (1.272 \AA).²²

A characteristic C–O stretching mode could not be localized in the spectra of **5** or **12**. Due to the low yield of **12**, only the most intense bands were observed, and these bands were assigned to O–O stretching or C–H deformation modes. In **5** the strong band assigned to the asymmetric C–C(O)–C stretching mode shows both a large ^{13}C and a moderate ^{18}O isotopic shift (Table III), which proves some coupling of this mode with the C–O stretching vibration. At higher frequencies, and especially in the carbonyl region, no bands were found. This indicates a bond order of substantially less than 2 and a low polarity of the C–O bond and is in accordance with the findings in other carbonyl *O*-oxides.^{10d,e}

Photochemistry of Carbonyl *O*-Oxides. Visible light irradiation of carbonyl *O*-oxides readily produces dioxiranes or carbonyl compounds and oxygen atoms (Scheme I and II). The relative amount of these photoproducts depends on the substituents. Benzophenone *O*-oxide (**5**) gives dioxirane **8** and small amounts of ketone **4** while benzaldehyde *O*-oxide (**12**) splits off oxygen atoms to give aldehyde **10**.²³ *m*-Chlorobenzaldehyde *O*-oxide also produces the corresponding aldehyde as the main product.

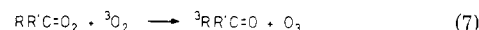
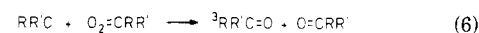
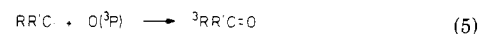
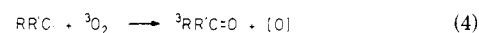
Interestingly, rapid photoreaction of carbonyl *O*-oxides is observed by irradiation far on the red side of the strong $\pi \rightarrow \pi^*$ transition. Several minutes of irradiation with red light ($\lambda > 630\text{ nm}$) completely destroyed **5** although the maximum of the $\pi \rightarrow \pi^*$ transition is at 422 nm . This long wavelength photochemistry is characteristic for carbonyl *O*-oxides and attributed to the weak $n \rightarrow \pi^*$ transition.

Shorter wavelength irradiation of dioxirane **8** causes the rupture of the O–O bond and subsequent migration of a phenyl group to give ester **7**. In contrast acid **11** is formed in two steps: (1) abstraction of an H atom from aldehyde **10** by $\text{O}(\text{^3P})$ (ground state oxygen atoms) to give a hydroxyl and a benzoyl radical and (2) matrix cage radical combination to give **11**.²⁴

Chemiluminescence. Warming matrices containing free carbenes, photooxidation products, and excess O_2 produces a strong, blue chemiluminescence, which can be observed easily in a dark room. The luminescence spectrum corresponds to the phosphorescence of a ketone or aldehyde, and thus the light emitting species is a carbonyl compound in its triplet state. Ketone **4** and aldehyde **10** both show an effective intersystem crossing (ISC) and

therefore only phosphorescence is expected, even if the carbonyl compound is initially formed in its singlet excited state. In the case of the oxidation of bis(trifluoromethyl)methylene it was shown that the ketone is indeed formed initially in its triplet state,^{10d} and thus it is reasonable (if all carbene oxidations follow the same mechanism) that **4** and **10** are also formed directly in their triplet states.

Reactions 4–7 have to be considered as chemiluminescent steps. The first three reactions are oxygen transfer reactions to a free carbene; the last reaction, suggested by Turro,⁵ is an oxygen transfer from a carbonyl *O*-oxide to an O_2 molecule. To elucidate the chemiluminescence mechanism it is necessary to observe luminescence and changes in the IR spectra from the same sample. This is complicated by the fact that very low levels of light are more easily detected than small changes in IR spectra.



The chemiluminescence is a thermal reaction, induced by raising the matrix temperature and controlled by the diffusion of particles involved in the reaction. The diffusion rate in imperfect solids, such as Ar matrices, depends on the matrix temperature, the size of diffusing particles, and on the deposition conditions of the matrix.²⁵ Under identical temperature and deposition conditions particles of different size can be discriminated. Large molecules, such as carbenes **1** and **2**, diffuse very slowly at $T < 35\text{ K}$, and therefore dimerization is not observed even after many hours. Atoms of first-row elements, on the other hand, diffuse rapidly at $T > 8\text{ K}$. The exact description of diffusion processes is complicated by the presence of different matrix sites and the possible formation of complexes between atoms and the matrix.^{26,27}

The slow diffusion of large molecules in Ar matrices at $T < 35\text{ K}$ excludes reaction 6 as the source of chemiluminescence at low temperatures. This mechanism can only be of importance at temperatures where the matrix rapidly evaporates ($T > 45\text{ K}$).

Reaction 7 leads to the formation of O_3 , which was only observed as a byproduct at very high O_2 concentrations (>5%). This reaction requires the formation of a carbonyl *O*-oxide in a first step, which is in contrast to the observation of strong chemiluminescence starting immediately after warming the matrix above 10 K (Figures 3 and 5), where no carbonyl *O*-oxide is present. On the other hand, the luminescence decreases rapidly if the matrix is kept at 30 K , although large amounts of carbonyl *O*-oxide is formed and excess O_2 is present.

If a common chemiluminescence mechanism is assumed, reaction 7 is also disfavored by the observation of the luminescence in the oxidation of chlorophenylcarbene.^{10c} This carbene has a singlet ground state, and the reaction with O_2 is slowed down by several orders of magnitude (after one "warm up" cycle no carbonyl *O*-oxide was detected by IR spectroscopy), but nevertheless a bright

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(22) Cremer, D.; Schmidt, T.; Gauss, J.; Radhakrishnan, T. P. *Angew. Chem.* 1988, 100, 431.

(23) Due to the low yield of **12** and the lack of intense and characteristic bands in the spectra of dioxiranes, small amounts of phenyl-dioxirane might not be detectable in our experiments. However, on short wavelength irradiation, phenyl-dioxirane should rearrange to acid **11**, which was only formed after the initial long wavelength irradiation and in the thermal reaction of **10** and $\text{O}(\text{^3P})$.

(24) The reaction of $\text{O}(\text{^3P})$ and acetaldehyde has been studied by molecular beam experiments: Kleinermanns, K.; Luntz, A. C. *J. Chem. Phys.* 1982, 77, 3774.

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(26) (a) Van de Bult, C. E.; Allamandola, L. J.; Baas, F.; van Ijzendoorn, L.; Greenberg, J. M. *J. Mol. Struct.* 1980, 61, 235.

(27) Fournier, J.; Lalo, C.; Deson, J.; Vermeil, C. *J. Chem. Phys.* 1977, 66, 2656.

chemiluminescence was observed during warming of the matrix.^{10c} This shows that a fast thermal reaction between carbenes and O₂ to give carbonyl *O*-oxides is not necessary to produce chemiluminescence and thus reaction 4 as well as reaction 7 cannot be the chemiluminescent steps.

Reactions 4 and 5 can be discriminated by the different speed of diffusion of O₂ and O(³P). The luminescence starts at temperatures well below 20 K, when the diffusion of O₂ is still slow, which supports reaction 5 (Figures 3 and 5). The thermal formation of benzophenone *O*-oxide (5) from 1 and O₂ at 30 K follows pseudo-first-order kinetics while the chemiluminescence is approximated best by a biexponential decay curve. This and the observation of a "memory effect" of the matrix (described above) shows that diffusion in Ar matrices is a complicated process involving several rates for different sites. The initial luminescence decay is 4 times faster than the formation of 5, which indicates again that the reaction of the free carbene and O₂ (reaction 4) is not the luminescent step.

Reaction 4 is also ruled out as chemiluminescent step by a crude thermochemical estimate for the oxidation of phenylcarbene (2). If $\Delta H_f(2) \approx 102$ kcal/mol,²⁸ $\Delta H_f(\text{triplet-10}) = 65.6$ kcal/mol²⁹ and $\Delta H_f(\text{O}^3\text{P}) = 59.5$ kcal/mol are used, reaction 4 is endothermic by 23.1 kcal/mol, while reaction 5 is exothermic by 95.9 kcal/mol. In reaction 5 a C=O double bond is formed from its components, and therefore this reaction is extremely exothermic.

In summary, the best explanation of all observations is that chemiluminescence is produced by the combination of free carbenes and oxygen atoms in their ground state (reaction 5). The multiplicity of the carbenes (singlet or triplet) has only minor influence on this reaction, and the carbonyl compounds are generated in their triplet states. Oxygen atoms are produced by the photochemical decomposition of carbonyl *O*-oxides, which are formed in the reaction of carbenes and O₂. There is some evidence that "hot" carbonyl *O*-oxides are also able to split off oxygen atoms immediately after their formation and thus are a thermal source of O(³P).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer PE580 spectrometer interfaced to a Hewlett-Packard 86 microcomputer. UV-vis spectra were obtained on a Varian Cary 17 D spectrometer connected to a Hewlett-Packard 9835 microcomputer via a Hewlett-Packard 3421 A data acquisition unit. Phosphorescence and chemiluminescence spectra were taken on a home built instrument^{10c,d} with an optical multichannel analyzer as detector.

Matrix-isolation experiments were performed by standard techniques³⁰ with an Air Products CSW-202 Displex closed cycle

helium cryostat. Argon (Messer Griesheim 99.9995%), oxygen (Messer Griesheim 99.998%), and [¹⁸O₂]oxygen (Ventron, 99.8% isotopic purity) were mixed in a gas handling system by standard manometric techniques. In "free warm up" experiments the Displex was switched off, and the matrix was allowed to warm from 10 K to 40–60 K (rate 1–2 deg/min). With this method, the temperature of the matrix increased in a highly reproducible manner. Details of the experimental conditions and instrumentation are described in previous publications.^{10c,d}

Irradiations were carried out by using Osram HBO 200 W/2 or 500 W/2 mercury high-pressure arc lamps. IR irradiation from the lamps was absorbed by a 10-cm path length of water and by a Schott KG 1 filter (if only $\lambda > 300$ nm was required). For broad-band irradiation, Schott cut-off filters were used (50% transmission at the wavelength specified); for narrow-band irradiation, interference filters (Schott or Oriel) were used to isolate mercury lines.

Materials. Benzophenone (4) and benzaldehyde (10) were obtained as commercial samples and purified by sublimation and distillation, respectively, prior to use. [¹³C]Benzophenone (99% isotopic enrichment) was purchased from ICN and used without further purification.

Diphenyldiazomethane (3). Benzophenone tosylhydrazone was prepared by a standard procedure and recrystallized from dry ethanol: mp. 184 °C (lit.³¹ mp 184 °C). The sodium salt was prepared by treating the tosylhydrazone, dissolved in dry CH₂Cl₂, with 1.1 equiv of NaH (50% suspension in mineral oil). After removing the CH₂Cl₂ in vacuo, the residue was washed three times with pentane. The slightly pink salt was stored at -40 °C. If exposed to air at room temperature it was oxidized to give 4 within several weeks. Diphenyldiazomethane (3) was generated by heating the salt gently to 40–45 °C and directly sublimed on the cold window. The IR spectrum obtained was identical with that of a sample that was isolated before matrix deposition. IR (Ar, 10 K): 3070 (m), 2046 (vs), 1598 (s), 1582 (m), 1502 (s), 1497 (s), 1457 (m), 1447 (m), 1320 (m), 1268 (m), 1262 (m), 1034 (m), 936 (m), 756 (s), 750 (s), 697 (s), 692 (s), 651 (s), 482 (m) cm⁻¹.

[¹³C]Diphenyldiazomethane (¹³C-3). IR (Ar, 10 K): 3070 (m), 2046 (vs), 1598 (s), 1582 (m), 1502 (s), 1495 (s), 1455 (m), 1446 (m), 1316 (m), 1259 (m), 1034 (m), 927 (m), 755 (s), 750 (s), 697 (s), 692 (s), 650 (s), 482 (m) cm⁻¹.

Phenyldiazomethane (9). Diazomethane 9 was obtained from benzaldehyde tosylhydrazone by a literature procedure. IR (Ar, 10 K): 3204 (w), 3034 (m), 2536 (w), 2066 (vs), 1604 (s), 1508 (m), 1499 (s), 1388 (s), 1185 (m), 1077 (m), 747 (s), 690 (s), 645 (s), 439 (m) cm⁻¹.

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Registry No. 1, 3129-17-7; [¹³C]-1, 5066-20-6; 2, 3101-08-4; 3, 883-40-9; 4b, 62861-50-1; 4c, 32488-48-5; 4d, 118017-12-2; 5a, 111351-12-3; 5b, 118017-05-3; 5c, 118017-06-4; 5d, 118017-07-5; 8a, 118017-04-2; 8b, 118017-08-6; 8c, 118017-09-7; 8d, 118017-10-0; 9, 766-91-6; 12, 118017-11-1; benzophenone tosylhydrazone, 4545-20-4.

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