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Chemiluminescence from arylcarbene oxidation: phenylchlorocarbene and (2-chlorophenyl)carbene

WOLFRAM W. SANDER
Organisch-Chemisches Institut der Universität, 6900 Heidelberg, F.R.G.

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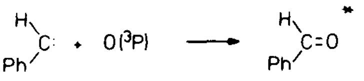
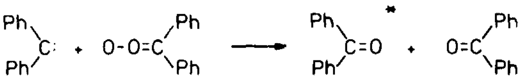
Abstract—Chemiluminescence is observed in the thermal reaction of phenylchlorocarbene or (2-chlorophenyl)carbene and O_2, matrix-isolated in Ar. The chemiluminescence spectra closely match the phosphorescence of the corresponding carbonyl compounds. The reactivity of both carbenes towards O_2 is very different. Singlet carbene phenylchlorocarbene reacts thermally only slowly with O_2 up to 60 K. The oxidation products phenylchloroformate, benzoyl chloride and $O(^3P)$ are mainly formed photochemically on irradiation of the diazirine precursor. Triplet carbene (2-chlorophenyl)carbene reacts readily with O_2 at cryogenic temperatures to give mostly 2-chlorobenzaldehyde-*O*-oxide. The carbonyl-*O*-oxide is photochemically easily cleaved to give 2-chlorobenzaldehyde and $O(^3P)$. The reaction step leading to carbonyl compounds in their excited states is in both carbene oxidations the recombination of the free carbene and $O(^3P)$.

INTRODUCTION

Although it has been known for almost 30 years that carbenes are readily trapped by molecular oxygen [1], details of this reaction and the subsequent formation of oxygen containing products are still not well understood. In some cases, a chemiluminescence was observed during the oxidation of carbenes which closely matched the phosphorescence of the corresponding carbonyl compounds [2, 3]. Turro suggested the intermediacy of both carbonyl oxides and ozone in the primary reactions producing chemiluminescence, but could not detect any of these compounds in his experimental set-up [3].

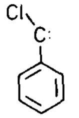
Recently, we reported on the mechanism of the oxidation of phenylcarbene [4] and diphenylcarbene [5]. By using the matrix isolation technique in combination with luminescence spectroscopy, it was possible to observe chemiluminescence and changes in the i.r.- or u.v.-spectra during the same experiment. In both carbene oxidations, the chemiluminescence is induced by oxygen transfer to the free carbenes.



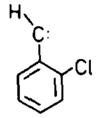


This is accomplished by an oxygen atom ($O(^3P)$) in the oxidation of phenylcarbene [4] or by benzophenone-*O*-oxide in the oxidation of diphenylcarbene [5]. While benzophenone-*O*-oxide was detected and characterized spectroscopically, no carbonyl oxide was observed in the oxidation of phenylcarbene. The source of $O(^3P)$ is the very efficient decomposition of benzaldehyde-*O*-oxide immediately after its formation [4].

In order to verify the proposed chemiluminescence mechanism and to see the influence of substituents on carbene reactivity with O_2, we have carried out matrix isolation studies on phenylchlorocarbene (**1**) and (2-chlorophenyl) carbene (**2**).



1



2

ESR experiments have shown that **1** has a singlet ground state [6] while **2** is expected to have a triplet ground state. Therefore **2** should easily react with (triplet) O_2 while **1** should not. Nevertheless a chemiluminescence was observed when **1** was generated in the presence of O_2 in Freon at 77 K [3]. On the other hand the lifetime of **1**, measured in a laser photolysis study at room temperature, did not depend on the O_2 concentration of the solution [6b].

In this paper a consistent mechanism is presented, which explains both the inertness of **1** and the chemiluminescence in the reaction of **1** and O_2. The mechanism, which was proposed for the oxidation of triplet carbenes [4, 5], was confirmed in the oxidation of **2**.

EXPERIMENTAL

Materials

3-Chloro-3-phenyldiazirin (**3**) was synthesized according to a published procedure [7]. 2-Chlorobenzoic acid (**10**), 2-chlorobenzaldehyde (**11**), phenyl chloroformate (**8**) and benzoyl chloride (**9**) were reagent grade substances (Aldrich) purified by sublimation or distillation prior to use as reference compounds. Sodium 2-chlorobenzaldehyde tosylhydrazide was prepared by treating the tosylhydrazone, dissolved in dry CH_2Cl_2, with NaH (50% suspension in mineral oil) and washing the precipitate with pentane. The sodium salt could be stored at −40°C for months but decomposed at room temperature within several days. Gently heating the sodium salt to 35–40°C in a high vacuum system gave (2-chlorophenyl)diazomethane (**6**) in a clean reaction and at a rate sufficient for matrix isolation. I.R. (Ar, 10 K): 3218 (w), 3188 (w), 3110 (m), 2066 (vs), 1596 (s), 1592 (s), 1488 (s), 1374 (s), 1283 (m), 1039 (s), 745 (s), 715 (s), 629 (m) cm^{-1}.

Matrix isolation experiments

Matrices were prepared by standard techniques (see Ref. [8] for a description of similar apparatus) using an Air Products CSW-202 Displex closed cycle helium cryostat. A CsI cold window and KBr outer windows were used in the i.r. experiments, a saphire cold window and quartz outer windows in the u.v. experiments. Argon (Messer Griesheim, 99.9995 %) was doped with various amounts (0.1–20 %) of O_2 (Messer Griesheim 99.998 %) or $^{18}O–O_2$ (Ventron, 99.8 % isotopic purity). The diffusion of O_2 was controlled by the temperature of the cold window (10–50 K). A resistance heater and a GRT or gold vs chromel thermocouple were used for temperature control. The sensors were connected to the cold tip of the refrigerator close to the window holder. Matrices were deposited at a window temperature of 28 K to obtain them optically clear. Deposition at lower temperatures gave highly scattering matrices but otherwise similar results. After deposition the matrix was cooled to 10 K. The degree of matrix-isolation was monitored by observing the line width of the i.r. bands as a function of the Ar/compound ratio. Irradiation of the matrix was achieved by using xenon or mercury high pressure arc lamps (Osram XBO 150 W or HBO 200 W/2 in an Oriel lamp housing). Cutoff filters (Schott) were used for broad band irradiation, interference filters (Schott or Oriel) for narrow band irradiation. I.R. spectra were recorded on a Perkin–Elmer 580 spectrometer, u.v. spectra on a Varian Cary 17D spectrometer. Both instruments were interfaced to a Hewlett Packard 86 microcomputer for data processing.

Luminescence spectra

To record glow curves and chemiluminescence spectra, a photomultiplier (PM) and an optical multichannel analyzer (OMA) were connected to the outer spectroscopic windows of the cryostat (Fig. 1). The current generated by the PM (Hamamatsu R446) and the temperature of the cold window were read by a data aquisition unit (Hewlett Packard 3421A). After switching off the displex system at 10 K, the temperature of the cold window rose approximately by 1 K/min. MICHL and coworkers have shown that by using polyethylene as window material the temperature gradient during a "free" warm up was less than 4 K [23]. With the higher conducting KBr or saphire the gradient is expected being smaller. Similar warm-up experiments were also used by other authors (For other thermoluminescence experiments in Ar matrices see Ref. [29]). At various temperatures, chemiluminescence spectra were recorded by the OMA. The OMA system consisted of a Princeton Applied research OMA II system and Jobin Yvonne HR320 polychromator with a 150 1/mm grating (slit width 50–500 μm). The OMA was able to record a 250 nm range between 200 and 800 nm (0.5 nm/channel), not disturbed by the temporal fluctuation of the chemiluminescence intensity. The spectra were uncorrected and calibrated by using a low pressure mercury lamp. Before and after warming the matrix, i.r. spectra were taken and changes in the spectra correlated with chemiluminescence phenomena. In some experiments, scans over regions of interest in the i.r. spectra were repeated in short intervals during the whole warm up process. From these data, rates of conversion of compounds in the matrix as a function of temperature were deduced.

Phosphorescence and fluorescence spectra of matrix isolated species were taken by using the OMA system and additionally irradiating the matrix with a monochromatic light source (Spex Minimate monochromator and a high pressure mercury arc lamp).

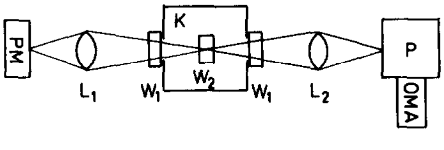


Fig. 1. Experimental set up for recording glow curves and luminescence spectra simultaneously. K = kryostat, L_1,L_2 = quartz lenses, OMA = optical multichannel analyzer, P = polychromator, PM = photomultiplier, W_1 = outer windows, W_2 = cold window.

RESULTS AND DISCUSSION

Characterization of phenylchlorocarbene (1).

The carbene 1 is generated by irradiation of matrix isolated 3-chloro-3-phenyldiazirine (3) and characterized by its i.r. and u.v. spectra. During the course of this work GANZER *et al.* [21] have reported some results on the reaction of 1 and O_2 which are in good agreement with ours. Only results differing from theirs or exceeding the scope of their work are therefore discussed in depth.

Broad band irradiation ($\lambda > 375$ nm) of 3 in Ar at 10 K results in the rapid decrease of the u.v. bands of 3 and appearance of new bands with maxima at 298 and 276 nm (Fig. 2). The spectrum is similar to a spectrum published for 1 generated in a 3-methylpentane glass at 77 K (maxima at 307 and 282 nm) [6b]. The blue shift in Ar might be due to a solvent effect or due to the rigid environment in solid Ar, which does not allow the carbene to adopt its equilibrium geometry after generation from 3 (in Ref. [9] structural changes in several carbenes have been observed by ESR spectroscopy).

The conversion of 3 to 1 is also observed spectroscopically in the i.r. Irradiation at 405 ± 10 nm gives 1 in a very clean, but slow reaction. Irradiation at 365 ± 10 nm leads to a rapid conversion, but traces of phenylchlorodiazomethane (4, weak band at 2060 cm^{-1}) are also formed [21]. This is due to the fact that diazomethanes have a low absorption coefficient at this wavelength and therefore can accumulate, even if they are formed only in low yields [22]. Subsequently broad band irradiation ($\lambda > 375$ nm)

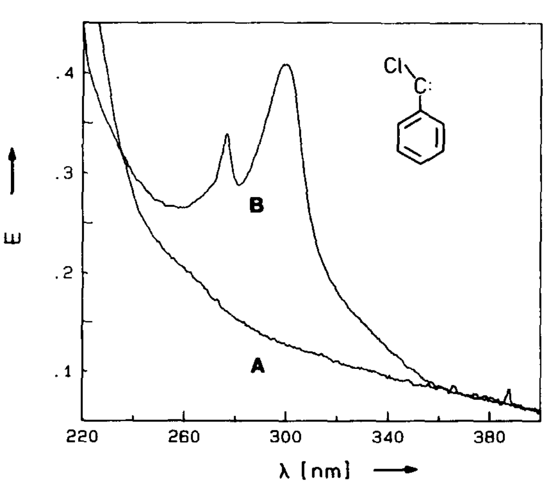
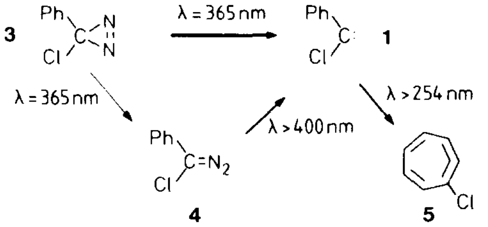


Fig. 2. (*A*) U.V. spectrum of diazirine 3 matrix isolated in Ar at 10 K. (*B*) U.V. spectrum of carbene 1 obtained after 16 min irradiation ($\lambda > 375$ nm) of 3.

gives exclusively **1** in a fast reaction (Scheme 1). The observed i.r. bands are in good agreement with those reported by GANZER *et al.* [21].

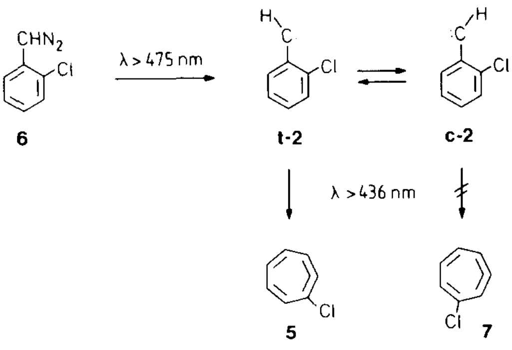


Scheme 1.

Short wavelength irradiation ($\lambda > 254$ nm) completely converts **1** to 1-chlorocyclohepta-1,2,4,6-tetraene **5** (Scheme 1, Fig. 3). The cycloheptatetraene **5** was characterized by i.r. bands at 1817 (w), 1808 (w), 1387 (m), 801 (s), 728 (s), 718 (vs) cm^{-1} (Fig. 3) which closely match the corresponding bands of unsubstituted cycloheptatetraene at 1824 (w), 1816 (w), 1380 (s), 773 (vs), 690 (s), 678 (vs) cm^{-1}, [10]. An additional intense band at 1063 cm^{-1} is assigned to a C–Cl stretching mode. Noticeable is the doublet structure of several i.r. bands (Fig. 3), which is probably due to matrix site effects. Although the possibility of isomerization under short wavelength irradiation cannot be completely excluded, a mixture of isomeric chlorocycloheptatetraenes should exhibit larger shifts in the i.r. bands. This is supported by the fact that **5** is generated independently by long wavelength irradiation ($\lambda > 435$ nm) of **2** (*vide infra*) and under these conditions an isomerization is not expected.

Characterization of (*2-chlorophenyl*)*carbene* (**2**)

Irradiation ($\lambda > 475$ nm) of (2-chlorophenyl) diazomethane (**6**) in Ar at 10 K resulted in a slow decrease of the u.v. and i.r. bands of **6** and in the appearance of bands assigned to **2** (Scheme 2). The photolysis of **6** at this wavelength is very inefficient; even after several days of irradiation some starting material is detectable in the i.r. spectra. Irradiation at a shorter wavelength caused a rapid photodecomposition of **2** (*vide infra*). Because small amounts of **6** remaining in the matrix did not interfere with the experiments, irradiation was stopped after sufficient **2** had built up.



Scheme 2.

The u.v. spectrum of **2** shows bands at 239.5 (0.75), 245.5 (1), 308 (0.35) and 456 (0.03) nm (relative intensities). The sharp band at 456 nm has its maximum close to similar bands in diphenylcarbene (455 nm) [2b] and phenylcarbene (430 nm) [10].

The i.r. spectrum of **2** is, as expected, not very characteristic, but similar to the reported spectrum of phenylcarbene [10]. The most intense bands are found at 1058 (s), 739 (s) and 680 (m) cm^{-1}. The band at 739 cm^{-1} is probably due to a C–H bending mode of the phenyl ring, corresponding to bands at 742 (s) and 669 (s) cm^{-1} in phenylcarbene. The band at 1058 cm^{-1}, not found in phenylcarbene, is assigned to a C–Cl stretching mode. Other bands of **2** are weak.

In analogy to phenylcarbene [10], **2** proved to be photolabile on irradiation with $\lambda > 436$ nm. The only photoproduct observed was **5**, identical to the compound generated by short wavelength irradiation from **1** (Scheme 2).

The identity of photoproducts generated from different precursors under different conditions of irradi-

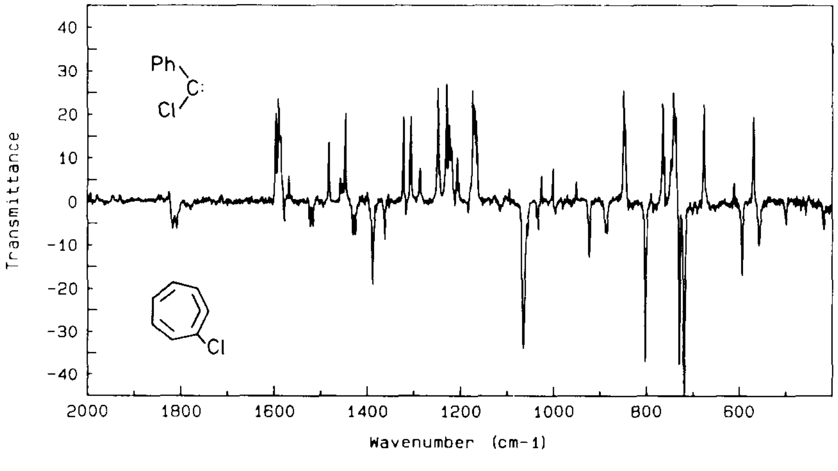
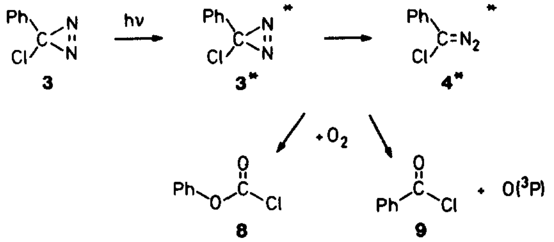


Fig. 3. I.R. difference spectrum of an Ar matrix at 10 K. Top part: bands assigned to **1**. Bottom part: same sample after 2 h irradiation ($\lambda > 254$ nm), bands assigned to **5**.

ation tempted us to assign structure **5**, and not **7**, to the photoproduct. A reason why **5**, and not **7**, is formed, might be the higher thermal stability of **t-2** as compared to **c-2** formed on irradiation of **6** (Scheme 2).

I.R. investigation of the oxidation of 1

If **3** is irradiated ($\lambda > 375$ nm, 10 K) in matrices doped with O_2, **1** and the oxidation products phenyl chloroformate (**8**) and benzoylchloride (**9**) are formed (Scheme 3). The oxidation products were identified by comparison with authentic matrix isolated **8** and **9** and furthermore are identical to those reported by other workers [21]. The relative amount of these compounds is dependent on the O_2 content of the matrix. Two medium intensity bands at 1814 and 1016 cm^{-1} and some weak bands in the complex i.r. spectrum of the reaction products could not be assigned to known compounds (Table 1). Surprisingly, even at high O_2 concentrations (4%), much free carbene **1** remains in the matrix. Under similar conditions, triplet carbenes like **2**, phenylcarbene [4] or diphenylcarbene [5] are completely oxidized and cannot be detected by i.r. spectroscopy. At 1% O_2 content, which is sufficient to oxidize a large fraction of **2** (*vide infra*), only small amounts of **8** and **9** are formed. At this O_2 concentration, the 1799 cm^{-1} peak of **8** is larger than the 1780 cm^{-1} peak of **9**. This ratio is reversed at 4% O_2 content and additionally small amounts of CO_2 (2340 cm^{-1}), CO (2044 cm^{-1}) and ozone (1038 cm^{-1}) are observed in the i.r. spectra (Table 1). Only traces of N_2O are formed under the conditions described here.



Scheme 3.

When the matrix containing **1** and excess (1–4%) O_2 is allowed to warm from 10 to 45 K (1 K/min) and recool to 10 K again, the difference spectrum shows only minor changes. In typical experiments, less than 5% of **1** was oxidized to mainly **9** on annealing. This inertness against reaction with O_2 was also observed in laser photolysis experiments [6b]; it is different from the reactivity of triplet carbenes, which readily form carbonyl oxides [5, 12–14] or carbonyl compounds and oxygen atoms [4]. Under our standardized reaction conditions, which allow us to compare the reactivity of different carbenes, no detectable amount of a carbonyl-*O*-oxide is formed. GANZER *et al.* have shown that on prolonged warming of **1** to temperatures where the diffusion of O_2 is rapid (6h at 35 K), the carbonyl-oxide is formed slowly. In our experiments **1** is kept at $T > 35$ K only for less than 10 min. The oxidation products are formed on the initial irradiation of **3**, leading primarily to the carbonyl-oxide which is photochemically not stable [21] and readily decomposes to **9** and O(^{3}P) or rearranges to **8**. The thermal oxidation of a small fraction of **1–9** mentioned above is due to the oxidation by O(^{3}P) and not by O_2. This is confirmed by the fact that after annealing all O(^{3}P) is consumed and a second annealing does not lead to more oxidation products. At high O_2 concentrations (> 4%), O_2 competes with **1** as a trap for O(^{3}P) and some O_3 is formed.

Table 1. IR spectroscopic data of the products of the photooxidation of 3. The matrix was generated by irradiating ($\lambda > 375$ nm) 3 in Ar containing 4% O_2. 8 and 9 were obtained by matrix-isolation of authentic compounds, 1 was generated by irradiation ($\lambda > 375$ nm) of matrix-isolated 3

$3+O_2$	8	9	1	
2340 (s)				CO_2
2040 (m)				CO
1814 (m)				X*
1799 (s)	1796 (s)			
1780 (vs)		1783 (vs)		
1743 (m)		1743 (s)		
1594 (s)			1595 (s)	
1588 (vs)			1588 (s)	
1494 (m)	1494 (m)			
1480 (m)			1480 (m)	
1453 (m)		1453 (s)		
1445 (s)			1445 (s)	
1321 (m)			1321 (m)	
1305 (m)			1305 (m)	
1245 (s)			1246 (s)	
1225 (vs)			1226 (vs)	
1208 (m)		1210 (s)		
1194 (m)	1194 (s)			
1171 (s)		1176 (s)	1172 (s)	
1121 (s)	1122 (s)			
1038 (m)				O_3
1016 (m)				X*
879 (s)		879 (s)		
846 (vs)			847 (vs)	
763 (s)			764 (s)	
739 (vs)			738 (vs)	
685 (m)		685 (m)		
675 (s)			675 (s)	
568 (m)			569 (m)	

*Unknown photoproduct.

The question of which intermediate is responsible for the formation of **8** and **9** can not be answered from the present data. Photoexcited **3**, **4** or **1** are possible candidates (Scheme 3). If one of these species is converted to its triplet state to some extent, the reaction with a neighbouring O_2 molecule should be facile.

Chemiluminescence from the oxidation of 1

During the annealing of a matrix containing both **1** and 0.5–4% O_2, a blue chemiluminescence is observed. A similar luminescence was observed in Freon at 77 K [3]. If the matrix does not contain O_2, or if the O_2 content is higher than 4%, the chemiluminescence intensity is suppressed by at least three orders of magnitude.

The chemiluminescence spectrum, obtained at 35 K, closely matches the phosphorescence of **9**, matrix-isolated in Ar at 10 K (Fig. 4). The peak maxima and relative peak intensities are almost identical, while the resolution is worse in the chemiluminescence spectrum. The band broadening is also observed in the phosphorescence, if the spectrum is recorded at 40 K.

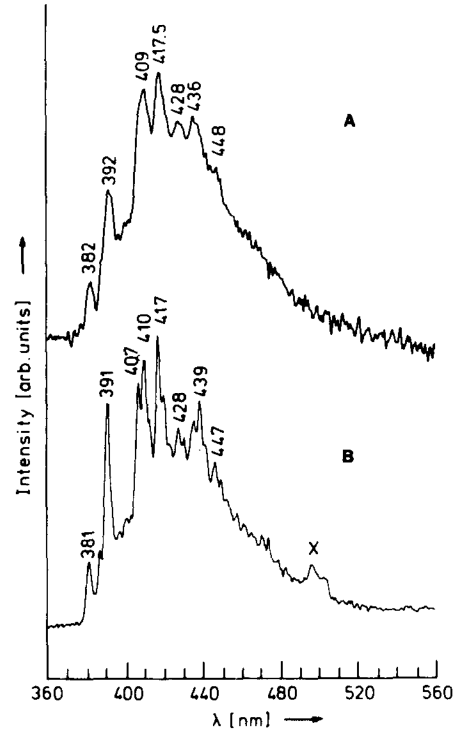
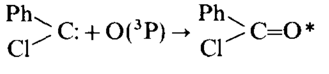


Fig. 4. (*A*) Chemiluminescence spectrum obtained by first irradiating ($\lambda > 375$ nm, Ar, 10 K) a matrix containing diazirine **3** and 1 % O_2 and then warming the matrix to 43 K. (*B*) Phosphorescence spectrum of matrix isolated **9** (Ar, 10 K), excitation wavelength 243 nm.

The glow curve (Fig. 5) shows a maximum around 45 K. Compared to triplet carbenes **2** (*vide infra*) and phenylcarbene [4] the maximum is at a higher temperature and less dependent on the O_2 content of the matrix. Noticeable is the lack of chemiluminescence in experiments when the matrix does not contain O_2, but an O_2 layer is deposited on top of the matrix and the matrix is warmed to 50–60 K. Under these conditions the matrix evaporates rapidly and an extensive mixing of the materials in the matrix takes place, causing a bright luminescence in triplet carbene reactions. The absence of chemiluminescence in the oxidation of **1** under these experimental conditions shows again the low reactivity of **1** with O_2.

From these observations we conclude that the chemiluminescence is solely produced by the recombination of **1** and $O(^3P)$. This reaction has a nonzero activation barrier, giving a strong chemiluminescence around 45 K, although the diffusion of $O(^3P)$ is already rapid at $T < 15$ K [15].* A large fraction of $O(^3P)$ is probably lost by recombination to O_2, therefore the yield of **9**, as observed spectroscopically with i.r., is low.



$$\underset{\mathbf{1}}{\overset{Ph}{\underset{Cl}{>}}C:} + O(^3P) \rightarrow \underset{\mathbf{9^*}}{\overset{Ph}{\underset{Cl}{>}}C{=}O^*}$$

1 **9***

When the matrix has a high content of O_2 (> 4 %), $O(^3P)$ is efficiently trapped by O_2 and additionally the triplet of **9** is quenched. Both processes lead to a decrease of the chemiluminescence intensity.

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*The exact rate of diffusion of $O(^3P)$ in solid Ar is not known and probably depends much on the deposition conditions of the matrix. For some examples of chemiluminescence, induced by the diffusion of $O(^3P)$ in Ar see Ref. [15].

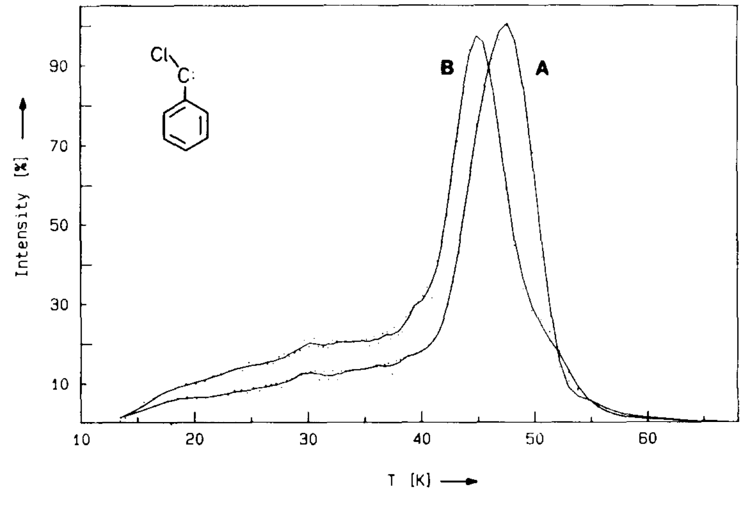
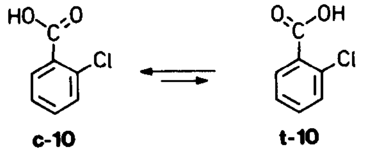


Fig. 5. Glow curves obtained from matrices (Ar) by warming from 10 to 65 K. (*A*) Matrix containing **1**, generated by irradiation ($\lambda > 375$ nm) of **3**, O_2 content 1 %. (*B*) Same conditions as (*A*), but O_2 content 2 %.

I.R. and u.v. investigation of the oxidation of **2**

Photolysis ($\lambda > 475$ nm, 10 K) of diazomethane **6** in Ar, doped with 0.5–4 % O_2, results in the formation of carbene **2** and the oxidation products 2-chlorobenzoic acid (**10**) and 2-chlorobenzaldehyde (**11**). The oxidation products were identified by comparison with authentic matrix-isolated compounds.

If the acid **10** is deposited from the vapour phase (room temperature) in Ar at 10 K, two i.r. bands in the C=O stretching region (1766 and 1744 cm^{-1}) and four bands in the O–H stretching region (3571, 3562, 3548 and 3531 cm^{-1}) are found (Fig. 6) [16].* On annealing at 40 K, the bands at 3548 and 1744 cm^{-1} disappeared almost completely. This is explained by two rotamers of **10**, which are similar in energy and separated by a small activation barrier.



The room temperature equilibrium is frozen out if the matrix is deposited at $T < 30$ K. At $T > 40$ K, a rapid isomerization takes place and the low temperature equilibrium, which is far on the side of one rotamer, is established. By comparison with 2-chloroacetic acid [17], the rotamer with i.r. bands at 1766, 3571 and 3562 cm^{-1} was tentatively assigned to **c-10** (Cl and carbonyl *O* are *cis*) and the less stable rotamer with i.r. bands at 1744, 3548 and 3531 cm^{-1} **t-10** (Cl and carbonyl *O* are *trans*). The higher frequency bands are thus assigned to the more stable and more polar rotamer [17]. Hydrogen bonds probably do not contribute much to the stability of either isomer; otherwise a larger shift of the O–H stretching modes would be expected. Short wavelength irradiation ($\lambda > 254$ nm) again leads to the formation of the less stable isomer **t-10** in approximately the same ratio as in the room temperature equilibrium. The photo process–thermal process can be cycled several times.

The aldehyde **11**, deposited under similar conditions as **10**, also shows two bands in the C=O stretching region (1711, 1706 cm^{-1}), as expected from gas phase investigations [18]. These bands were not well resolved; therefore the thermal behavior was not investigated.

The acid **10**, formed on irradiation ($\lambda > 475$ nm, 10 K) of **6** in Ar doped with O_2, showed almost the same intensity for both carbonyl vibrations. This shows that the rotamers **c-10** and **t-10** are formed rather statistically and not in their thermal equilibrium at 10 K.

If the matrix containing carbene **2**, oxidation products **10** and **11**, and excess O_2 is allowed to warm to 45 K (ca 1 K/min) and recool to 10 K, several changes occur:

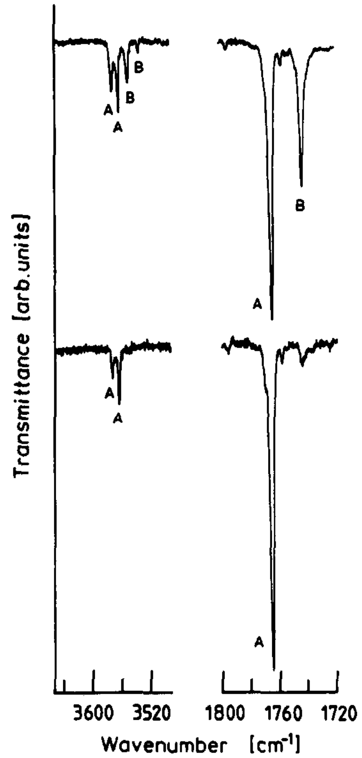


Fig. 6. Parts of the i.r. spectra of **10**, matrix-isolated in Ar at 10 K. Upper spectrum: obtained after depositing the matrix at 26 K and cooling to 10 K. Lower spectrum: same sample as above, spectrum taken after annealing at 45 K. A = **c-10** (3571, 3562, 1766 cm^{-1}), B = **t-10** (3548, 3531, 1744 cm^{-1}).

- —a complete isomerization of **t-10** to **c-10** takes place.
- —a fraction of aldehyde **11** is oxidized to **10**.
- —all i.r. bands assigned to **2** vanish and new bands (Table 2) appear with the most intense band at 901 cm^{-1}.

Table 2. I.R. spectroscopic data of **12** and ^{18}O-**12**

12	^{18}O-12	Δ*
1582 (m)	1585	0
1432 (m)	1428	4
1296 (m)	1287	9
1268 (w)	1268	0
1194 (w)	1189	5
1123 (w)	1122	1
1054 (w)		
1034 (w)		
931 (m)	890	41
901 (s)	871	30
841 (m)	826	15
710 (w)	710	0
668 (w)		
507 (w)	500	7

*Difference.

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*Spectra in Nujol show bands at 3080 (m), 3060 (m), 1693 (vs) cm^{-1}, probably due to dimers.

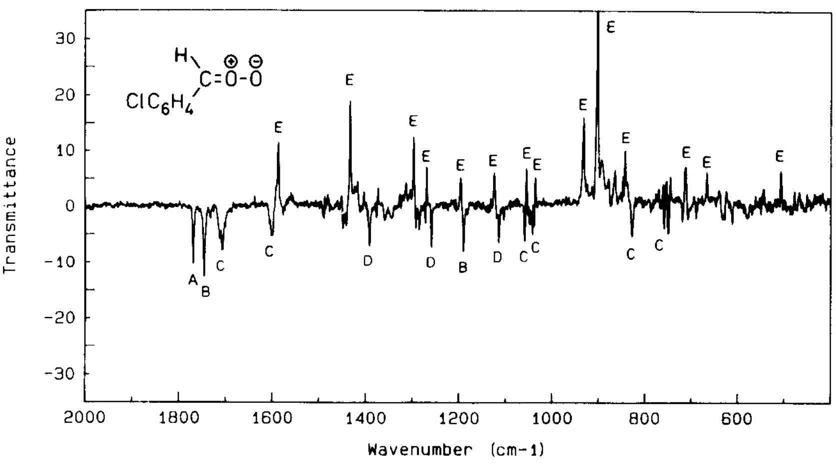


Fig. 7. I.R. difference spectrum of an Ar matrix at 10 K. Top part: bands assigned to **12**. Bottom part: same sample after 2 min irradiation ($\lambda > 475$ nm). *A* = **c-10**, *B* = **t-10**, *C* = **11**, *D* = tentatively assigned to **13**, *E* = **12**.

The intense band at 901 cm^{-1} is almost indicative for the O–O stretching mode of a carbonyl oxide [5, 12, 13]. If the annealing experiment is repeated by using $^{18}O_2$, the band is shifted 30 cm^{-1} to 871 cm^{-1}. This large shift can only be explained by an O–O stretching mode; the maximum, calculated for a diatomic C–O oscillator (for examples of ^{18}O isotopic shifts see Ref. [19]) at 901 cm^{-1} is 22 cm^{-1}. The medium intensity band at 931 cm^{-1}, which exhibits an isotopic shift of 41 cm^{-1} (Table 2), is possibly due to a rotamer of **12**. The band at 1296 cm^{-1} is shifted 9 cm^{-1} to lower frequencies, which is considerably less than the calculated 31 cm^{-1} for the diatomic C–O oscillator. The corresponding band in benzophenone-*O*-oxide was found at 1377 cm^{-1} (8 cm^{-1} isotopic shift) [5].

The formation of **12** is also observed by u.v. spectroscopy (Fig. 8, Table 3). The broad u.v. band with a maximum at 405.7 nm is characteristic for carbonyl oxides [5, 14, 20]. On the low frequency side, the band shows a fine structure corresponding to a 790 ± 25 cm^{-1} vibration in the excited state. After repeating the reaction with $^{18}O_2$, the vibration is shifted 40 cm^{-1} (average from Table 3) to lower frequencies. These data allow us to assign the vibration to the O–O stretching mode of the first excited state of **12** and clearly show that this state is a bound state. The excitation of higher vibrational levels should finally lead to the rupture of the O–O bond, as it is observed experimentally.

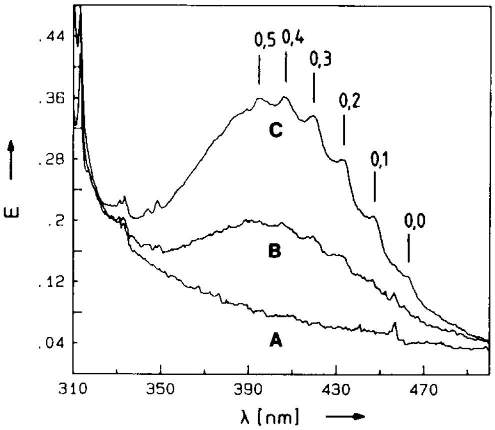


Fig. 8. U.V./vis spectrum of an Ar matrix at 10 K. (*A*) Bands assigned to carbene **2**, generated by irradiation ($\lambda > 475$ nm) of **6**. (*B*) Same sample as (*A*) after warming the matrix to 38 K and recooling to 10 K. (*C*) Same sample as (*A*) and (*B*) after warming the matrix to 45 K and recooling to 10 K. **2** has completely reacted to mainly **11**. Spectrum (*C*) was taken with a higher *S*/*N* ratio (slower scan) than (*A*) and (*B*).

The carbonyl oxide **12** is very sensitive to irradiation and completely destroyed after 2 min photolysis at

Table 3. U.V./vis spectroscopic data of **12** and ^{18}O-**12**

	12			^{18}O-**12**		
	λ[nm]	I_R^*	$\Delta\nu[cm^{-1}]$†	λ[nm]	I_R^*	$\Delta\nu[cm^{-1}]$†
0–0	462.5	0.36	790	462.5	0.32	730
0–1	446.2	0.56	750	447.4	0.52	750
0–2	431.7	0.76	740	432.9	0.73	720
0–3	418.4	0.92	750	419.9	0.89	700
0–4	405.7	1.0	700	407.8	0.98	620
0–5	394.5	0.98		397.7	1.0	

*Relative intensities.
† ± 25 cm^{-1}.

> 475 nm. The main photoproducts are **11**, **c-10** and **t-10**. The peak intensities of the rotamers of **10** are about 1:1 (Fig. 7). Medium intensity bands at 1390, 1257 and 1113 cm^{-1} cannot be assigned to any of these compounds. Although it is tempting to assign these bands to (2-chlorophenyl)dioxirane (**13**, Scheme 4), there is not enough evidence to confirm this hypothesis. On short wavelength irradiation ($\lambda > 254$ nm), **10** and **11** are the only products. In contrast to the photochemistry of **12**, benzophenone-*O*-oxide rearranges photochemically exclusively to diphenyldioxirane; no carbonyl compounds are formed on irradiation with > 475 nm [5].

Chemiluminescence from the oxidation of **2**

Matrices containing **2** and O_2 give a blue chemiluminescence on warming to $T > 20$ K. The chemiluminescence spectrum [Fig. 9(*A*)] closely matches the phosphorescence spectrum of **11** taken in Ar at 10 K [Fig. 9(*B*)]. The main difference is the larger band width in the luminescence spectrum, while band intensities and peak maxima are almost identical. The glow curves (Fig. 10) are strongly dependent on the O_2 content of the matrix. A matrix not doped with O_2 [Fig. 10(*A*)] shows a maximum of the luminescence intensity at 53 K. At this temperature the matrix evaporates quickly and **2** is able to react with an air layer (surface contamination from small leaks in the vacuum system) on top of the Ar matrix. If the matrix is doped with 2% O_2, the maximum is at 35 K with a strong chemiluminescence starting below 20 K [Fig. 10(*C*)].

The shape of the glow curves are explained best by assuming that the largest contribution to the luminescence comes from the recombination of **2** and $O(^3P)$. The diffusion of $O(^3P)$ in solid Ar at $T > 20$ K is high enough to give a complete reaction within minutes [15]. The source of $O(^3P)$ is the photochemical cleavage of **12** and to a lesser extent the thermal

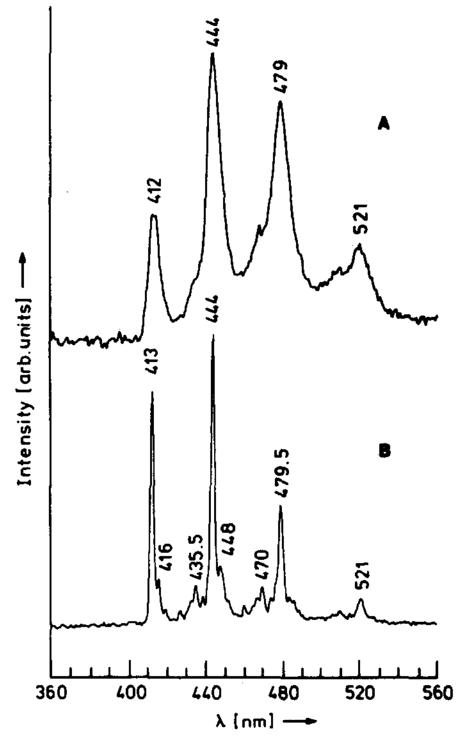


Fig. 9. (*A*) Chemiluminescence spectrum obtained by first irradiating ($\lambda > 375$ nm, 10 K) a matrix containing diazomethane **6** and 0.9% O_2 and then warming the matrix to 44 K. (*B*) Phosphorescence spectrum of matrix isolated **11** (Ar, 10 K), excitation wavelength 303 nm.

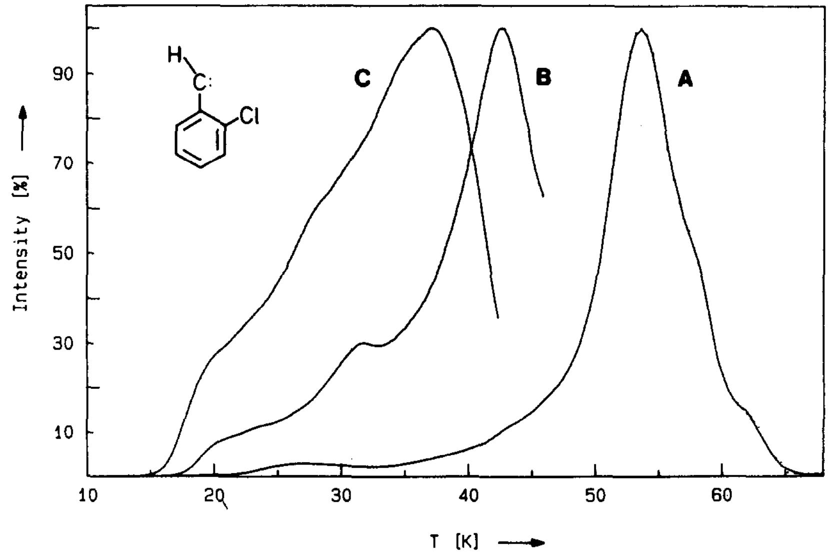
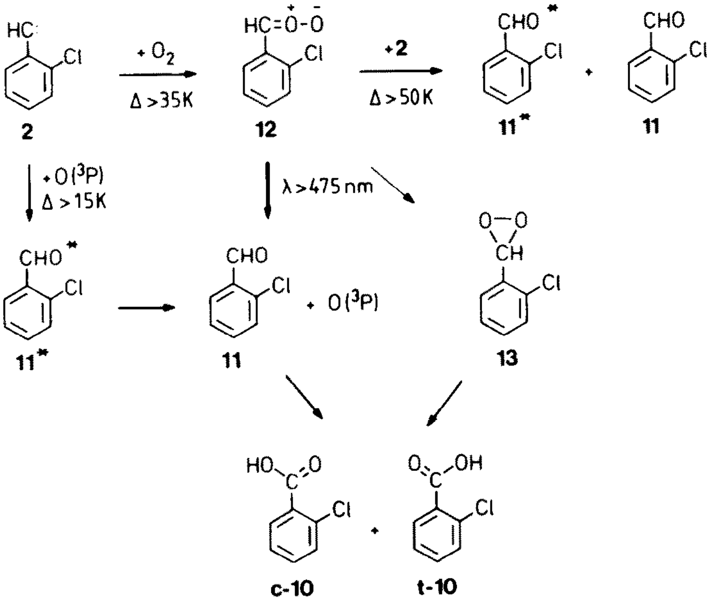


Fig. 10. Glow curves obtained from matrices (Ar) by warming from 10 to 65 K. (*A*) Matrix containing **2**, generated by irradiation ($\lambda > 475$ nm) of **6**, and no O_2. The chemiluminescence was induced by the reaction of **2** with an air layer on top of the matrix. (*B*) Same conditions as in (*A*), but O_2 content 0.9%. (*C*) Same conditions as in (*A*), but O_2 content 1.7%.

decomposition of vibrationally excited **12** immediately after its formation. At $T > 30$ K, the diffusion of O_2 becomes rapid, leading to the formation of **12** and more $O(^3P)$. At $T > 50$ K the matrix becomes soft and larger molecules (**2** and **12**) start to diffuse rapidly. At this temperature the direct transfer of oxygen from **12** to **2**, as it was proposed for the oxidation of diphenylcarbene [5], might become important. At very high O_2 concentrations (> 4%) the emission from the matrix is almost completely quenched. As in the case of the oxidation of **1**, this is explained by the efficient quenching of triplet **11** and by the trapping of $O(^3P)$ to form O_3 by excess O_2. Additionally **2** is also trapped by O_2 to give **12** (Scheme 4).



Scheme 4.

CONCLUSIONS

This work demonstrates the usefulness of combining the matrix isolation technique and luminescence spectroscopy for exploring primary carbene reactions. One advantage of the low temperature experiments is that carbenes react from their electronic ground state, even if the *S–T* gap is small. Thus the population of excited states, which caused some confusion in room temperature experiments [28], is negligible.

In contrast to earlier suggestions [3], O_3 is not, and carbonyl oxides are not necessarily, involved in the primary reactions leading to chemiluminescence in carbene oxidations. The reaction steps leading to carbonyl compounds in their excited states are oxygen transfer reactions to free carbenes. Remarkable is the high selectivity of carbenes towards O_2. While triplet carbene **2** reacts fast (probably diffusion controlled *), singlet carbene **1** reacts only slowly up to 60 K, as is expected from the SKELL–WOODWORTH rules [24, 25]. The reaction of carbenes and $O(^3P)$ shows also some selectivity. Again **2** reacts fast while the reaction of **1** has a nonzero reaction barrier, although the latter reaction is exothermic by about 150 kcal/mol (thermochemical estimate: for calculations of the thermochemistry of carbene reactions see Ref. [26]). From the data presented here it is not clear if the carbonyl compounds are initially formed in their S_1 or T_1 state. The intersystem crossing in these compounds is very efficient [27]† and only the phosphorescence is expected to be observed. If we assume that the reaction proceeds on a singlet surface to S_1 of the carbonyl compound, the reaction barrier can be explained by the necessity of a surface jump in the reaction of **1** and $O(^3P)$. In the reaction of **2** and $O(^3P)$ the chance of getting a singlet encounter complex is statistically 1:9. If we assume that the quintet state (5:9 chance) is repulsive and the triplet state (3:9 chance) has a nonvanishing activation barrier as in **1**, the reaction can proceed fast and completely on the singlet surface.

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*The absolute rate of the reaction of diphenylcarbene and O_2 in acetonitrile at room temperature was determined to $5 \times 10^9\ M^{-1} s^{-1}$ [14].

†Most aromatic carbonyl containing molecules show solely phosphorescence.

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