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An infrared study of the formation and photochemical decomposition of tetrachlorocyclopentadienone *O*-oxide in low temperature matrices

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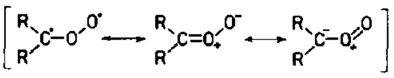
Abstract—Photolysis of tetrachlorodiazocyclopentadiene at 12 K in Ar or N_2 matrices containing O_2 yields tetrachlorocyclopentadienone and tetrachloro-2-pyrone. Matrix i.r. spectra are reported for each of these products. The reaction proceeds by the addition of O_2 to the previously identified carbene, tetrachlorocyclopentadienylidene, giving initially the highly labile carbonyl oxide, tetrachlorocyclopentadienone *O*-oxide. The identification of the carbonyl oxide was assisted by experiments using isotopically labelled O_2, and this reactive intermediate has now been characterized in low temperature matrices by both u.v.-visible and i.r. spectroscopy.

INTRODUCTION

Carbonyl oxides (**1**) have been proposed as reactive intermediates in ozonolysis [1, 2], in the oxidation of diazo compounds [3–13], and in oxygen atom transfer reactions [8–17], but until recently they had escaped direct detection by physical methods. In the past few years, however, the techniques of matrix isolation and flash photolysis have yielded vibrational and electronic absorption spectra for several of these unstable but important species. For example, there have been reports of matrix i.r. spectra of cyclopentadienone *O*-oxide [18], indenone *O*-oxide [19] and fluorenone *O*-oxide [19]; matrix u.v.-visible absorption spectra of these three and the analogous tetrachlorocyclopentadienone *O*-oxide [20] and transient electronic spectra of 10,10-dimethyl-10-silaanthracen-9[10*H*]-one *O*-oxide [21], benzophenone *O*-oxide [22, 23], and fluorenone *O*-oxide [24]. The independent matrix and flash photolysis results for the electronic absorption of fluorenone *O*-oxide (λ_{max} = 460 and 450 nm, respectively) are in good agreement [20, 24].

Matrix i.r. studies have shown that carbonyl oxides (**1**) undergo photolytic decomposition by two routes [18, 19, 25]. The first is the simple loss of an oxygen atom, giving the parent ketone (R_2CO). The second is a rearrangement which, in the cyclic molecules examined so far, yields the corresponding lactone (R.CO.OR), in which both oxygen atoms are retained. Recent evidence indicates that the latter process probably takes place via a dioxirane intermediate [26]. So far, these photochemical studies have been carried out only for cyclopentadienone *O*-oxide and its close analogues, indenone *O*-oxide and fluorenone *O*-oxide. In this paper we report a similar matrix i.r. study of the formation and photochemical decomposition of the fully chlorinated analogue, tetrachlorocyclopentadienone *O*-oxide (**4**), in which the chlorine substituents might be expected to influence or inhibit the reaction.



1a 1b 1c

EXPERIMENTAL

Equipment

The matrix isolation cold cell has been described in detail previously [27]. It consisted of a CsBr window enclosed in a glass and metal vacuum shroud and cooled by an Air Products Displex CSA-202 closed cycle helium refrigerator. The base temperature was 12 K, and higher temperatures could be attained by means of a small resistance heater connected to an Air Products APD-B temperature controller. Infrared spectra were recorded on a Perkin–Elmer 684 spectrometer interfaced with a Perkin–Elmer 3600 data station. Photolysis was carried out with an Oriel 200 W high pressure Hg arc. In all circumstances, a water filter (13 cm pathlength) with quartz windows (λ > 200 nm) was used to remove i.r. radiation. Additional filters, used as necessary, included Pyrex (λ > 300 nm), soda glass (λ > 330 nm), Schott glass sharp cut-off filters (λ > 290 and 395 nm), and narrow band (10 nm) interference filters (296 and 312 nm). An Applied Photophysics high radiance f/3.4 monochromator with variable slits was also employed in some of the experiments.

Materials

Research grade Ar ($\nless$ 99.9997 %), N_2 ($\nless$ 99.994 %) and O_2 ($\nless$ 99.97 %) were obtained from B.O.C. Ltd., and were used without further purification. $^{18}O_2$ (99 atom %) was obtained from Amersham International plc, and statistical or near-statistical mixtures of $^{16}O_2$, $^{18}O_2$ and $^{16}O^{18}O$ were prepared by subjecting mixtures of $^{16}O_2$ and $^{18}O_2$ at ca 20 torr to about 30 min discharge from a Tesla coil, followed by standing overnight at room temperature. Tetrachlorodiazocyclopentadiene (**2**) was prepared from hexachlorocyclopentadiene [28]; tetrachloro-2-pyrone (**7**) was prepared from hexachloropropene and trichloroethylene [29, 30]; and tetrachloro-1,2-benzoquinone (**8**) was a commercial sample.

Matrix deposition

Mixtures of Ar or N_2 with O_2 were prepared on a conventional vacuum line by standard manometric procedures. Compounds (2), (7) and (8) were insufficiently volatile for convenient measurement of their vapour pressures, so they were sublimed directly on to the cold window at 12–20 K, while a large excess of the O_2/Ar or O_2/N_2 mixture was allowed to condense simultaneously through a needle valve. In typical depositions, 4–6 mmol of the gas mixture was allowed into the vacuum-shroud during 60–90 min. Matrices which were deposited at temperatures above 12 K were cooled to 12 K immediately after deposition. Although adequate isolation seems to have been achieved in these experiments, matrix host: guest ratios could not be estimated.

RESULTS

The major photoproducts

When tetrachlorodiazocyclopentadiene (2) was isolated at 12 K in Ar or N_2 matrices containing 10% O_2 and photolysed with wide-band light ($\lambda > 200$, or $\lambda > 300$ nm), the i.r. bands of (2) disappeared and new bands arose. In typical experiments (2) was removed almost completely in a few minutes. The product absorptions in the range 2000–400 cm^{-1} are given in Table 1. In addition, weak bands appeared at ca 2345 (CO_2) and 2140 cm^{-1}, both of which resulted from secondary photolysis of one of the major products (see below). About half the product bands were shown to belong to tetrachloro-2-pyrone (7) by comparison with Ar and N_2 matrix spectra of an authentic sample [Table 1 and Fig. 1(e)]. As is usual, the agreement between the spectra of (7) in Ar and N_2 matrices is very close in both frequency (± 5 cm^{-1}) and relative intensity, although some slight differences in band shape or site splittings can be noted. The only exceptions are a band at 931 cm^{-1} in Ar, which is shifted to 938 cm^{-1} in N_2, and a much weaker band at 1853 cm^{-1} in Ar, which is shifted to 1868 cm^{-1} in N_2. The weaker of these two bands occurs at almost exactly twice the frequency of the stronger and exhibits twice the matrix shift. It is thus neatly identified as the first overtone of the stronger band. As indicated in Table 1, the weakest bands of (7) did not appear above the noise level in the spectra of the photoproducts from (2), but the identification based on the medium and strong bands of (7) is very satisfactory.

When (7) was irradiated ($\lambda > 200$ nm) in Ar or N_2 matrices at 12 K, it underwent photolysis only very slowly. After 1 or 2 h of irradiation, less than 10 or 20% of the starting material had decomposed and weak bands at 2142 cm^{-1} (Ar) or 2139 cm^{-1} (N_2) had grown. These were accompanied otherwise only by very weak bands at lower frequencies. The photoproduct giving rise to the absorptions at ca 2140 cm^{-1} could have been carbon monoxide, but was most probably the ketene isomer (9), resulting from electrocyclic ring opening, as in the analogous photolysis of 2-pyrone [31–34]. When (7) was irradiated ($\lambda > 200$ nm) in Ar or N_2 matrices containing 10% O_2, however, the additional formation of CO_2 (ν_{as} 2345 cm^{-1}) was observed. Experiments with isotopically labelled O_2 have indicated that CO_2 arises by a photo-oxidation of (7) involving O_2 molecules in the matrix, and not simply by photo-elimination of CO_2 from (7) or one of its isomers [35].

Nearly all the remaining i.r. bands arising during the matrix photo-oxidation of (2) are assigned to the hitherto unknown tetrachlorocyclopentadienone (5). This ketone was generated independently in Ar and N_2 matrices at 12 K, by photolysis ($\lambda > 200$ nm) of tetrachloro-1,2-benzoquinone (8). In this reaction, the starting-material disappeared almost completely in about 1 h of irradiation, with the elimination of CO (ν_{CO} 2140 cm^{-1} in Ar, 2142 cm^{-1} in N_2), as previously observed in the pyrolysis of 1,2-benzoquinone [36], and a new compound was formed with i.r. spectra which matched those of the other photoproduct of (2) very closely [Table 1 and Fig. 1(d)]. We identify this new compound, which appears to be resistant to further photodecomposition, as tetrachlorocyclopentadienone (5) (see below). Although we have no estimate for the relative extinction coefficients of the i.r. absorptions of (5) and (7) and thus no quantitative basis, it is nevertheless clear from the general appearance of the spectra that (5) is the more abundant of the two major products formed in the matrix photo-oxidation of (2) [*cf.* Fig. 1 (c)–(e)].

There remain only four weak bands belonging to the products from (2) that do not seem to belong to either (5) or (7). The most important of these are bands at 1043 and 1038 cm^{-1} which were observed in both Ar and N_2 matrices (Table 1). These occur very close to the frequency of the strongest i.r absorption (ν_3) of ozone, which has been reported at 1040 cm^{-1} for Ar matrices at 16 K [37]. Since O_3 is an expected product of the reaction (see below), it is plausible to assign the bands at 1043 and 1038 cm^{-1} to this species, the splitting being due to a matrix site effect, possibly a perturbation by neighbouring molecules of (5). The other two i.r. bands of O_3 are much weaker, and therefore it is not surprising that they were not observed in our experiments. Two more weak bands at 1206 cm^{-1} (Ar matrices) and 1579 cm^{-1} (N_2 matrices) have not been accounted for. These do not belong to the carbene (3) [38], O_3 [37], N_2O [39] or a photodecomposition product of (5) or (7) (see above), and must therefore remain unassigned for the present.

The photolabile intermediate

When (2) was photolysed ($\lambda > 290$ nm) at 12 K in Ar or N_2 matrices containing only 1% O_2, the initial product spectrum showed the presence of carbene (3) (strongest band at 1127 cm^{-1}) [38] as well as small amounts of (5) and (7). When such matrices were annealed at 30–35 K and recooled to 12 K, the absorptions of (3) diminished in intensity while those of a new species appeared. The new species was very photolabile, and disappeared after 1 or 2 min photolysis with light of $\lambda > 395$ nm, with concomitant formation of (5) and (7). We identify this labile intermediate as the carbonyl oxide, tetrachlorocyclopentadienone *O*-oxide (4) (see below), and Table 2 gives the i.r. absorptions which have been assigned to it. Figure 1 shows parts of

Table 1. Infrared absorptions (cm^{-1}) in the region 2000–400 cm^{-1} of the products from λ > 200 nm photolysis of (2) in Ar and N_2 matrices doped with O_2, and a comparison with spectra of (5) and (7) in pure Ar and N_2 matrices

Ar matrices			N_2 matrices		
Photoproducts	(5)	(7)	Photoproducts	(5)	(7)
		1853*			1868
1796		1795 vs	1797		1797 s
	1778			1783	
1775		1775 vs	1776		1775 s
1773					
				1765 sh	
1760 m	1759 s		1760 m	1760 s	
				1746	
				1729	
1685	1682				
			1616		
1607	1606 m	1610 sh	1607	1607 m	1612
		1600			1597 sh
1592		1590 s	1594		1592 m
			1579		
	1536			1540	
1512		1510 m	1511		1512 m
		1494			1497
		1303			
1289		1289 m	1285		1293
		1276			
1239		1235 s	1239		1238 s
1206					
	1196			1196	
1189 m	1188 s		1190 m	1189 s	
1174	1173		1174	1175	
				1129	
		1107			1109
		1096			1098
1079	1079		1082	1083	
		1069			1072
		1059			1061
1043			1043		
1038			1038		
				989	
					955
930		931 s	939		938 m
	918			922	
849		849 m	852		850 m
835	834		836	836	
	810			813	
				752	
745	744 m	747 m	746	746 m	748 m
732		731	733		733
	640			642	
				624	

*Qualitative band intensities: bands were weak but distinct, unless denoted vs very strong, s strong, m medium, or sh shoulder.

the i.r. spectra recorded in one such experiment. The same labile intermediate was also detected when (2) was isolated at 12 K in an N_2 matrix containing 10% O_2, and photolysed for 36 min with narrow-band (10 nm) light of λ = 312 nm. Subsequent irradiation for 20 s with light of λ > 200 nm removed the intermediate entirely.

Experiments with $^{18}O_2$ *and* $^{16}O^{18}O$

Experiments using isotopically labelled O_2 were directed primarily towards determining isotope shifts in the i.r. spectrum of the carbonyl oxide (4). For this we chose to concentrate on Ar matrices, and sought to optimize the conditions for the highest possible yield of (4) at a low percentage of O_2 doping. The successful interpretation of the results, however, has been somewhat hampered by the relative weakness, even under the optimum experimental conditions, of the i.r. bands of (4), particularly those showing significant isotope shifts.

In the first set of experiments, (2) was isolated at 12 K in Ar matrices containing 1 % of a 1 : 1 mixture of $^{16}O_2$ and $^{18}O_2$. The resulting matrices were irradiated for 2 min with light of λ > 200 nm, then annealed at 30–35 K and recooled to 12 K. Finally, irradiation for a further 2 min with light of λ > 395 nm converted the

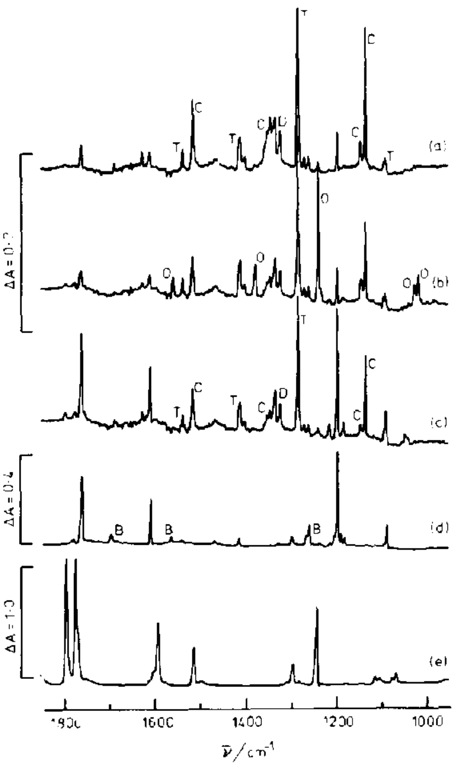


Fig. 1. Matrix i.r. spectra, after background subtraction, in the region 1850–950 cm^{-1}; all recorded at 12 K. (a) (2) in Ar doped with 1 % O_2, after 60 s photolysis with $\lambda > 290$ nm; (b) the same matrix after annealing at 30 K; and (c) after a further 120 s photolysis with $\lambda > 395$ nm. (d) (5) obtained from 60 min $\lambda > 200$ nm photolysis of (8) in pure Ar; (e) (7) in pure Ar. Assignments of prominent bands are shown as follows. C carbene (3); D the dimer of (3); T residual (2); B residual (8); O carbonyl oxide (4). The last of these can be seen to have grown on annealing and to have disappeared on subsequent photolysis.

Table 2. Infrared absorptions (cm^{-1}) assigned to carbonyl oxide (4) in Ar and N_2 matrices at 12 K

Ar matrices	N_2 matrices
1555*	1558
1371	1380
1231 m	1230 m
1135	1137
1016	1017
1007	1005
974 vw	976
835	833
748	750
668	669
506	508

*Qualitative band intensities: bands were weak unless denoted m medium, or vw very weak.

intermediate (4) into the products (5) and (7). Infrared bands belonging to the two isotopomers of (4) were identified as usual by their growth on annealing and rapid disappearance during the final photolysis, and were observed at 1554 (w), 1371 (w), 1360 (w), 1231 (m), 1136 (vw, br), 1016 (vw), 1007 (w), 979 (vw), 962 (w), 748 (sh, overlapping with bands of (5) and (7) at 744–747 cm^{-1}) and 670 (vw) cm^{-1}. Other very weak absorptions of (4) at 974 and 835 cm^{-1} (*cf.* Table 2) did not appear clearly above the noise level, while that at 506 cm^{-1} was just observable and was possibly associated with an equally weak isotopically shifted band at 491 cm^{-1}. Unfortunately the strongest band of (4) at 1231 cm^{-1} showed no discernible isotopic splitting. Significant $^{18}O_2$ shifts were seen only for the 1371 cm^{-1} band (1360 cm^{-1} in the $^{18}O_2$ isotopomer) and for the pair of bands at 1016 and 1007 cm^{-1} (shifted to 979 and 962 cm^{-1}). To these might be added the doubtful shift of the very weak 506 cm^{-1} band to 491 cm^{-1}. Even these are not all straightforward, because the 962 cm^{-1} band of the $^{18}O_2$ species is stronger than its presumed $^{16}O_2$ counterpart at 1007 cm^{-1}, whereas the band at 979 cm^{-1} is weaker than its presumed counterpart at 1016 cm^{-1}. This behaviour indicates that the vibrations associated with these two absorptions undergo a significant change in character upon isotopic substitution, a conclusion which is also consistent with the comparatively large magnitudes of the shifts (-37 and -45 cm^{-1}). One possibility is that in the $^{16}O_2$ species these two modes are affected by Fermi resonance, whereas in the $^{18}O_2$ species this does not occur or is much reduced. In the final products, ν_{CO} for (5) is shifted by -32 cm^{-1}, from 1760 to 1728 cm^{-1}, in its $^{18}O_2$ isotopomer, while the 1775 cm^{-1} ν_{CO} band of (7) has a similar shift of -30 cm^{-1}. The position of the shifted band corresponding to the 1795 cm^{-1} component of the ν_{CO} doublet of (7) could not be determined, however, because it was obscured by the much stronger 1760 cm^{-1} absorption of (5).

In the second set of experiments, 1 : 1 mixtures of $^{16}O_2$ and $^{18}O_2$ were scrambled by Tesla discharge to yield approximately 1 : 2 : 1 mixtures of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$, and these were then incorporated into Ar matrices as before. Problems in detecting very weak absorptions were exacerbated even further with these isotope mixtures. Significant results were obtained only for the 1371, 1016, and 1007 cm^{-1} absorptions of (4). Figure 2 shows portions of the i.r. spectra recorded after (4) was generated in an Ar matrix doped with 1 % of the scrambled O_2, and after it was subsequently removed by photolysis. The band at 1231 cm^{-1} is included for comparison, but shows no discernible isotope splitting. Despite the very low intensity of the absorptions of (4) in this experiment, two interesting results emerge. Firstly the 1371 cm^{-1} band of (4), shifted to 1360 cm^{-1} in the $^{18}O_2$ isotopomer, shows no additional splitting due to $^{16}O^{18}O$ isotopomers. Secondly three bands due to $^{16}O^{18}O$ isotopomers appear in the region just below 1000 cm^{-1}: at 995, 987 and 972 cm^{-1}. The last of these is definitely not the very weak band of (4) at 974 cm^{-1} (Table 2), since it can be seen in Fig. 2 to be at least as strong as the band at 1007 cm^{-1} whereas in the $^{16}O_2$ isotopomer of (4) the absorption at 974 cm^{-1} is very much weaker than

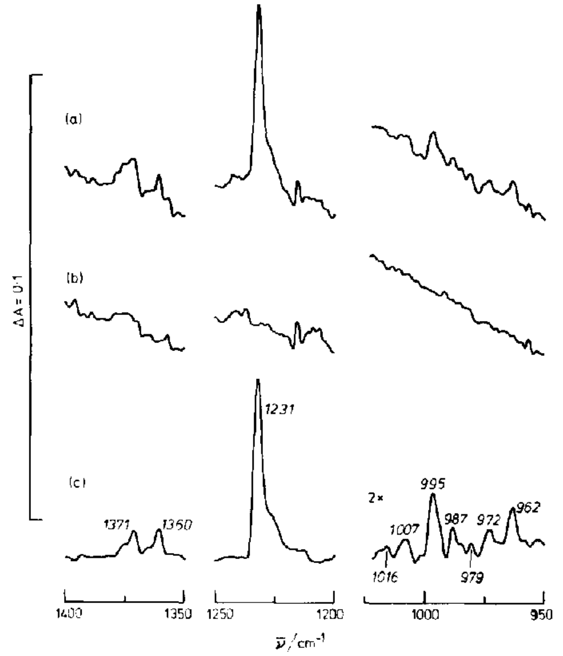


Fig. 2. Infrared spectra, after background subtraction, of matrices at 12 K. (a) (2) in Ar containing 1 % of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ in a ratio of approximately 1 : 2 : 1, after generation of (4) by 120 s photolysis with $\lambda > 295$ nm followed by annealing at 35 K; (b) the same matrix after removal of (4) by further 120 s photolysis with $\lambda > 395$ nm; (c) difference spectrum [(a)–(b)].

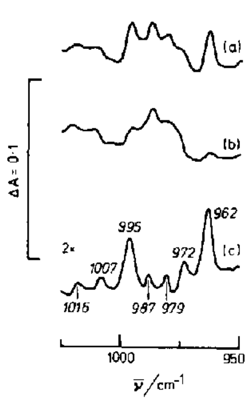


Fig. 3. Infrared spectra, after background subtraction, of matrices at 12 K. (a) (2) in Ar containing 1 % of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ in a ratio of approximately 1 : 2 : 1, after 120 min deposition with simultaneous irradiation with $\lambda = 300 \pm 10$ nm; (b) the same matrix after additional photolysis for 120 s with $\lambda > 395$ nm; (c) difference spectrum [(a)–(b)].

this band. In attempts to improve the yield of (4), we discovered that the intensity of its spectrum could be increased if it was generated by photolysing (2) during matrix deposition. Thus (2) was sublimed on to the cold window at 12 K over 2 h, with simultaneous deposition of ca 3 mmol of Ar doped with 1 % of scrambled O_2, and with simultaneous irradiation with monochromated light ($\lambda = 300 \pm 10$ nm). Figure 3(a) shows the 1000 cm^{-1} region of the i.r. spectrum recorded after this combined deposition and photolysis. The whole spectrum is complicated, because substantial amounts of (5) and (7) were already present in the matrix, but it shows an increased yield of (4) compared with the earlier experiments. The isotopomers of (4) were then removed by 2 min irradiation with $\lambda > 395$ nm [Fig. 3(b)]. Although the spectra were necessarily complicated by the presence of many product bands, the difference spectrum shown in Fig. 3(c), which separates out the absorptions of the photolabile intermediate (4), is in very good agreement with the difference spectrum shown in Fig. 2(c) of the same intermediate, obtained with a similar mixture of O_2 isotopes but under different conditions. We thus assign bands at 995, 987 and 972 cm^{-1} to $^{16}O^{18}O$ isotopomers of (4).

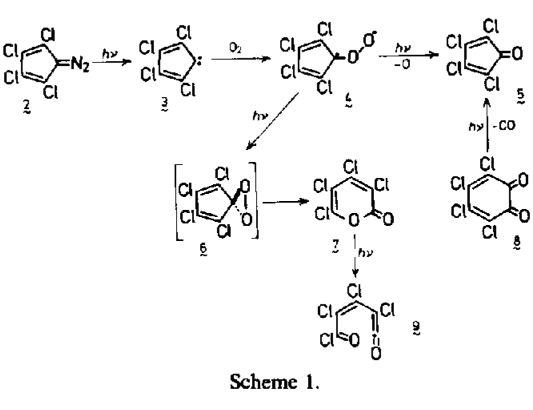
Control experiments

In view of an earlier report [40] that low temperature Hg arc photolysis of O_2 can produce ozone, we carried out two blank experiments in which Ar and N_2 doped with 10 % O_2 were subjected to irradiation at $\lambda = 296 \pm 5$ nm for 60–75 min, followed by $\lambda > 290$ nm for a further 60 min. The matrices were examined by i.r. spectroscopy at intervals during the irradiation, but no absorptions were seen to grow at any stage. Thus O_3 [37] and N_2O [39], which might be expected in N_2 matrices, were not formed directly from O_2 under these conditions.

DISCUSSION

Identification of products

From earlier studies [18, 19, 25], two compounds were expected as ultimate products in the matrix photo-oxidation of tetrachlorodiazocyclopentadiene (2): tetrachlorocyclopentadienone (5) and tetrachloro-2-pyrone (7). Since the pyrone (7) is a stable compound, it was an easy matter to show that it is indeed the minor product of the reaction (Table 1 and Fig. 1). The ketone (5), on the other hand, was previously unknown, attempts to generate it in solution, in the absence of dienophiles, having yielded only a dimer and its further decomposition product [41–46]. It



Scheme 1.

seemed likely, however, that photolysis of the readily available tetrachloro-1,2-benzoquinone (**8**) would provide an independent route to this ketone, especially since cyclopentadienone itself can be generated by pyrolysis of 1,2-benzoquinone [36]. Ultraviolet photolysis of (**8**) in Ar and N_2 matrices turned out to be fairly efficient, and resulted in the elimination of CO and the formation of a carbonyl compound whose i.r. spectra were a very close match to those of the major photo-oxidation product of (**2**) (Table 1 and Fig. 1). The carbonyl stretching frequency of this compound at 1760 cm^{-1} falls quite close to that of matrix-isolated tetrafluorocyclopentadienone at 1756 cm^{-1} [47]. It is therefore clear that matrix photo-oxidation of (**2**) yields ketone (**5**) as the major product and a minor amount of (**7**). These two products are comparatively stable towards further photodecomposition, except that on prolonged u.v.-irradiation (**7**) apparently undergoes an inefficient ring opening to ketene (**9**) and, in the presence of O_2, a slow photo-oxidation in which CO_2 is formed. Ring opening of 2-pyrone to penta-1,3-dien-1,5-dione is a well known photoprocess in matrices [31–34], although the corresponding reaction of the chlorinated analogue (**7**) seems less efficient.

In matrices containing only 1% O_2, the initial product from photolysis of (**2**) is the carbene (**3**). This carbene has been characterized recently by i.r. and u.v.-visible spectroscopy [38]. When Ar or N_2 matrices containing both carbene (**3**) and O_2 are annealed at 30–35 K, some of the carbene is converted into a new species, which is a very photolabile precursor of (**5**) and (**7**). Only a single species seems to be formed, since the i.r. bands assigned to it (Table 2) all grew and disappeared together. That this intermediate in the photo-oxidation of (**2**) is an adduct of (**3**) and O_2 is supported by the following observations. (i) It is formed in a thermal reaction at 30–35 K in matrices containing (**3**) and O_2, but not in the absence of O_2 [38]. (ii) Some of the i.r. absorptions belonging to the intermediate show significant isotopic shifts in matrices containing $^{18}O_2$, demonstrating that it contains oxygen. (iii) Separate bands are observed for the $^{16}O^{18}O$ species, demonstrating that it contains at least two O atoms. (iv) Photo-decomposition of the intermediate yields pyrone (**7**) as well as ketone (**5**), also suggesting the presence of two O atoms. (v) The possible involvement of ozone in its formation seems ruled out by negative blank experiments, in which no ozone was formed from O_2 under conditions typical of the photo-oxidation experiments.

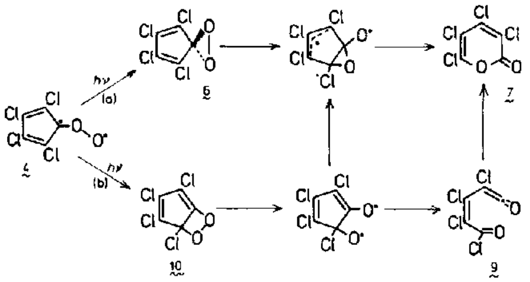
Although several alternatives can be envisaged [18], there are only two reasonably likely structures for the adduct of (**3**) and O_2. They are the end-on bonded carbonyl oxide (**4**) and the sideways bonded dioxirane (**6**). In dioxirane (**6**) the two O atoms are equivalent, so that only one $^{16}O^{18}O$ isotopomer is possible. There are two distinct $^{16}O^{18}O$ isotopomers of the carbonyl oxide (**4**), however. If the intermediate observed in our experiments were dioxirane (**6**), only one i.r. band belonging to its $^{16}O^{18}O$ isotopomer would be seen corresponding to each band of the $^{16}O_2$ species. Despite the weakness of the absorptions, three bands belonging to $^{16}O^{18}O$ isotopomers of the intermediate have been identified between 1000 and 970 cm^{-1}, corresponding to only the two bands at 1016 and 1007 cm^{-1} of the $^{16}O_2$ species. This leads to the conclusion that the intermediate has non-equivalent O atoms, and that a fourth $^{16}O^{18}O$ band is unresolved in our spectra. We thus identify the intermediate as the carbonyl oxide, tetrachlorocyclopentadienone *O*-oxide (**4**).

The thermal addition of O_2 to carbenes has already been observed for cyclopentadienylidene [18], indenylidene [19] and fluorenylidene [19], and in each case the corresponding carbonyl oxide seems to be formed. Infrared studies with $^{16}O^{18}O$ gave a very clear demonstration of the non-equivalence of the two O atoms in cyclopentadienone *O*-oxide [18], for which the intensity of the crucial i.r. absorption was found to be more favourable than in the case of (**4**). We have already reported that a photolabile adduct of (**3**) and O_2 has an electronic absorption with $\lambda_{max} = 395$ nm [20], and this species is clearly the same as the intermediate (**4**), which has now been characterized by i.r. spectroscopy.

Reaction mechanisms for the photolysis of (4)

The major photo-decomposition route for (**4**) is the loss of an oxygen atom, to give the ketone (**5**). The most probable fate of the eliminated O atom is reaction with a second molecule of O_2, giving ozone. CHAPMAN and HESS have observed ozone as a product in the matrix photo-oxidation of diazocyclopentadiene [25], although until now we have been unable to confirm its presence among the photoproducts of the carbonyl oxides which we have examined. In the case of (**4**), however, the photo-elimination of an O atom is the predominant pathway, and weak product i.r. bands at 1043 and 1038 cm^{-1}, which we cannot assign to any other species, occur where the strongest absorption of O_3 is expected [37]. Alternative fates for the eliminated O atom include dimerization to O_2, which does not absorb in the i.r., and combination with one or more of the carbon species, to yield epoxides or other oxygenated organic molecules. The latter possibility might account for the very few weak bands in the product spectrum which we have been unable to assign. Finally, ozone is photolabile and will itself eliminate an oxygen atom, which could then recombine with O_2 or diffuse away from the matrix cage and follow one of the alternative reaction pathways.

A second photodecomposition of (**4**) is the rearrangement to pyrone (**7**), but it seems to be a much less important pathway than photo-elimination of oxygen. This behaviour contrasts with that of the previously studied unchlorinated carbonyl oxides, for which both routes seem of comparable importance [18, 19]. Mechanisms for reactions analogous to the conversion of (**4**) into (**7**) have been discussed recently [19, 25]. Two possible routes, which could be interrelated, seem to be favoured, and these are outlined in Scheme 2. Route (a) involves a dioxirane intermediate (**6**) and route (b) a dioxetane (**10**). Because the rearrangement of (**4**) is such a minor pathway, we have obtained no direct evidence of a second intermediate lying on the route between (**4**) and (**7**). Recent observations on the photorearrangement of cyclopentadienone *O*-oxide, however, have led to the identification of a dioxirane, analogous to (**6**), as an intermediate between the carbonyl oxide and 2-pyrone [26]. Thus route (a) (Scheme 2) seems the most likely at present, despite some theoretical reasons for preferring route (b) [25].



Scheme 2.

Bonding in carbonyl oxides

Various calculations on simple carbonyl oxides agree that the ground states of such species should be singlets [12, 48–50]. According to *ab initio* predictions, formaldehyde *O*-oxide is best represented as a singlet biradical (**1a**, R = H), while for acetone *O*-oxide the biradical (**1a**, R = Me) and zwitterionic (**1b**, R = Me) structures are of equal energy [48, 49]. In contrast, MINDO/3 calculations indicate pronounced zwitterionic character even for formaldehyde *O*-oxide, and suggest that substituents should exert little influence on the relative biradical or zwitterionic contributions to the structures [12, 50]. In experimental terms, a carbonyl oxide with a zwitterionic structure like (**1b**) would be expected to give rise to a carbonyl stretching band in the i.r. spectrum. It is not known exactly where this band should occur. CHAPMAN and HESS have suggested that it might be found in the range 1400–1350 cm^{-1}, i.e. about halfway between the normal double and single bond frequencies for carbon–oxygen bonds, and have claimed that bands in this range, with $^{18}O_2$-shifts of about -12 cm^{-1}, do indeed belong to cyclopentadienone *O*-oxide and should be identified as primarily C–O stretching bands [25]. In view of other evidence [18, 26], it is unlikely that these bands belong to a carbonyl oxide, but the suggestion that zwitterionic carbonyl oxides might have ν_{CO} bands as low as 1400–1350 cm^{-1} is not unreasonable. In the i.r. spectrum of (**4**), three bands clearly show significant $^{18}O_2$ shifts. Two of these at 1016 and 1007 cm^{-1} are in the single bond region of the spectrum, but the third at 1371 cm^{-1} falls in the range where ν_{CO} of a zwitterionic carbonyl oxide might be expected. The magnitude of the $^{18}O_2$ shift, however, does not support this assignment. The ^{18}O shift of a genuine carbonyl compound, tetrachlorocyclopentadienone (**5**), provides a good comparison, and has been measured in this work (see above) as -32 cm^{-1}, or about -1.8%. In the harmonic oscillator approximation, the theoretical maximum ^{18}O shift for a completely isolated C=O bond with a $^{12}C^{16}O$ frequency of 1760 cm^{-1} is -42 cm^{-1}, or about -2.4%. The observed ^{18}O shift for the 1760 cm^{-1} band of (**5**) is therefore about 75% of the theoretical maximum, confirming the predominant ν_{CO} character of the vibration. The observed $^{18}O_2$ shift of the 1371 cm^{-1} band of (**4**), however, is only -11 cm^{-1} (see above), or about -0.8%. An interesting feature of this vibration is that no corresponding bands for the $^{16}O^{18}O$ isotopomers of (**4**) were resolved in our spectra. Since there is little doubt that the band does indeed belong to (**4**), it must be concluded that the vibrational mode which gives rise to this absorption involves only one of the O atoms to any appreciable extent. We can thus assign it as predominantly a ring mode of (**4**), with a minor contribution from C–O stretching. The two bands of (**4**) at 1016 and 1007 cm^{-1} show much larger $^{18}O_2$ shifts: -37 and -45 cm^{-1}, respectively. These can be identified as having single bond stretching character, probably mainly $\nu_{O\text{–}O}$.

The i.r. absorptions of (**4**) and the associated isotopic shifts are not consistent with what we should expect for a carbonyl oxide with a pronounced zwitterionic contribution from a structure like (**1b**). They are much more consistent with a biradical structure like (**1a**) or possibly a zwitterionic structure like (**1c**). We thus continue tentatively to represent carbonyl oxides as singlet biradicals as in Schemes 1 and 2.

CONCLUSIONS

The work described in this paper was a study of the photolysis of tetrachlorodiazocyclopentadiene (**2**) isolated at 12 K in Ar and N_2 matrices containing O_2. The ultimate products in the reaction are tetrachlorocyclopentadienone (**5**) and a smaller amount of tetrachloro-2-pyrone (**7**). The reaction takes place by addition of O_2 to the initially formed carbene (**3**), yielding a photolabile intermediate. The i.r. spectra of the intermediate, including data for oxygen-isotope shifts, suggest that it is the carbonyl oxide (**4**). Furthermore, the i.r. data do not seem consistent with a structure for this carbonyl oxide which has pronounced carbon–oxygen double bond character. Mechanisms for the photolysis of (**4**) are discussed briefly, in the light of these results and those for other carbonyl oxides which have been reported recently.

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