Cyclopentadienone *O*-Oxide: A Highly Labile Intermediate in the Matrix Reaction between Cyclopentadienylidene and Oxygen

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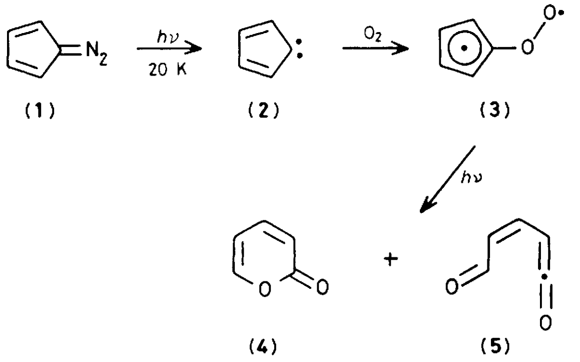
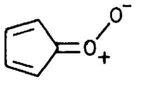
Cyclopentadienylidene reacts with oxygen in low-temperature matrices, giving a photolabile intermediate, the i.r. spectrum of which suggests that it is the carbonyl oxide, cyclopentadienone *O*-oxide.

Recent studies of the photolysis of diazocyclopentadiene (**1**) in low-temperature matrices have provided i.r. and u.v. absorption spectra of cyclopentadienylidene (**2**), and have shown that thermal dimerization of this carbene and its reaction with

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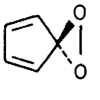
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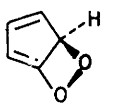
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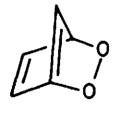
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carbon monoxide follow straightforward pathways to give fulvalene and the corresponding ketene, respectively.[1] In contrast, the reaction between (**2**) and O_2 is relatively complicated, yielding a number of oxygen-containing products.[2] Amongst these are α-pyrone (**4**) and its ring-opened isomer (**5**).[3] Chapman[2] has proposed the intermediacy of cyclopentadienone *O*-oxide, formulated as (**6**), in the reaction between (**2**) and O_2, but so far no i.r. spectrum of this or any other carbonyl oxide has been published. Ogata and co-workers[4] have examined the formation of carbonyl oxides in the photo-oxidation of diazo compounds, and have discussed whether these species are best formulated as zwitterions, *cf.* (**6**), biradicals, *cf.* (**3**), or dioxiranes, *cf.* (**7**), without reaching a definite conclusion. We now report the observation of a highly photolabile intermediate, arising from the reaction between (**2**) and O_2, the i.r. spectrum of which suggests that it is indeed the carbonyl oxide, cyclopentadienone *O*-oxide, and that this species is best formulated as the biradical (**3**).

Mercury-arc photolysis of (**1**) at 20 K in an N_2 matrix containing 10% O_2 resulted in the disappearance of the i.r. bands of (**1**) and the appearance of many new bands.† In accord with previous reports,[2] the product i.r. bands could nearly all be attributed to (**4**), (**5**), cyclopentadienone, and varying amounts of the carbene (**2**), although the presence of additional weak bands indicated other minor products. When a similar photolysis was carried out with an interference filter in the beam (λ 296 ± 5 nm), a similar change in the i.r. spectrum occurred, with the additional appearance of fourteen new bands, the strongest of which were at 1 398, 1 321, 1 014, 947, 940, 888, and 758 cm^{-1}.‡ All fourteen bands belonged to a highly photolabile species, and disappeared within a few seconds upon irradiation of the matrix with a Pyrex- or soda glass-filtered Hg-arc. This secondary photolysis was accompanied by the further growth of the i.r. bands of (**4**) and (**5**). The photolabile species is, therefore, a precursor of α-pyrone.

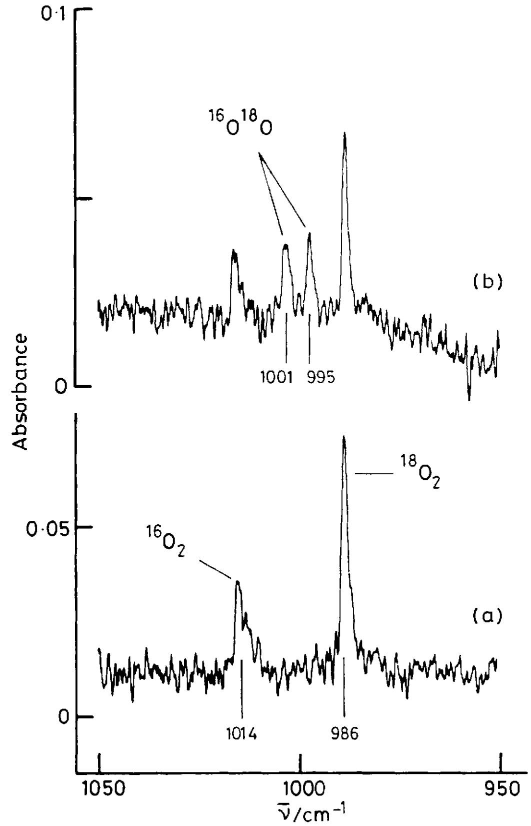

Figure 1. I.r. spectra in the 1 000 cm^{-1} region recorded after photolysis (λ 296 ± 5 nm) of diazocyclopentadiene (**1**) at 20 K in N_2 matrices containing 4—5% of O_2 labelled with 70 atom-% ^{18}O. (a) Only $^{16}O_2$ and $^{18}O_2$ present, (b) $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ present. All the bands shown belonged to the photolabile intermediate, and disappeared rapidly on further photolysis with quartz, Pyrex, or soda glass filtration.

The same species could also be obtained in N_2 matrices containing only 1% O_2. Under these conditions, filtered or unfiltered irradiation of (**1**) produced substantial amounts of the carbene (**2**) as well as the products formed in matrices containing 10% O_2. Subsequent annealing (30—35 K) resulted in the growth of the i.r. bands attributed to the α-pyrone precursor. The mode of formation of the photolabile intermediate and its photo-decomposition to α-pyrone suggest that it is an adduct derived from one molecule each of (**2**) and O_2. Such an adduct would most probably have the biradical (**3**), zwitterionic (**6**), or dioxirane structure (**7**). The zwitterionic structure (**6**), however, appears to be ruled out by the absence of an i.r. band that could be assigned to the stretching of a carbon–oxygen double bond.

The experiments were repeated with matrices containing mixtures of $^{16}O_2$ and $^{18}O_2$ (ratio 30:70), and $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ (70 atom-% ^{18}O).§ Isotope shifts for the $^{18}O_2$-derived intermediate were largest for those bands which occurred at 1 014 (−28), 947 (−22), and 940 (−15) cm^{-1} in the spectrum of the $^{16}O_2$-species. The first of these bands split into two additional absorptions for the $^{16}O^{18}O$-adduct (Figure 1). Such splitting for the mixed isotope indicates that the two oxygen atoms are not equivalent in the intermediate, and therefore rules out the dioxirane structure (**7**).[5] Similar splitting of the bands at 947

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† Matrix gas mixtures were prepared manometrically and deposited on a CsBr window cooled to 20 K by an Air Products Displex model CSA-202. I.r. spectra were recorded on a Perkin-Elmer PE684 spectrometer interfaced to a Perkin-Elmer model 3600 Data Station. The spectrometer was calibrated with a polystyrene film, and quoted frequencies are accurate ±2 cm^{-1}. U.v.-irradiation was carried out by means of a 200 W high-pressure Hg-arc, and a water filter with quartz windows was used at all times to remove i.r. radiation.

‡ The weaker bands were observed at 3 158, 1 481, 1 303, 1 066, 694, 606, and 498 cm^{-1}.

§ Labelled oxygen was obtained from BOC Prochem Ltd. as a 30:70 mixture of $^{16}O_2$ and $^{18}O_2$. Scrambling to give a near-statistical mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ was achieved by subjecting a bulb at 20 Torr of the original mixture to the discharge from a Tesla coil.

and 940 cm^{-1} was not resolved, probably owing to the close proximity of the two bands, especially for the ^{18}O-labelled species. The vibrations showing the largest isotope shifts absorb at frequencies typical of single bond stretching, and are likely to involve substantial contributions from both C–O and O–O stretching.

Although the i.r. results for the intermediate rule out structures (**6**) and (**7**), bicyclic structures with non-equivalent oxygen atoms, such as (**8**) or the highly improbable anti-Bredt adduct (**9**), remain consistent with the observations. These alternatives, however, seem unlikely on chemical grounds. We therefore propose that the labile intermediate formed in the reaction between (**2**) and O_2 is cyclopentadienone *O*-oxide and that structure (**3**) seems to represent this molecule best.

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