Tetrachlorocyclopentadienone *O*-oxide, a facile oxygen-atom transfer reagent: the oxidation of cyclohexene

Ian R. Dunkin, Adam McCluskey [1]

Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK

Abstract

The photolysis of tetrachlorodiazocyclopentadiene (1) in oxygen-saturated cyclohexene results in the transient formation of tetrachlorocyclopentadienone *O*-oxide (3), which rapidly decomposes to give cyclohex-2-en-1-one (7) (150%) and cyclohex-2-en-1-ol (8) (150%) as the major products. The product yields are consistent with a radical chain reaction, and conflict with a mechanism involving the dimerization of cycloalkylperoxy radicals, which has been proposed for related oxidations.

1. Introduction

Carbonyl *O*-oxides, such as tetrachlorocyclopenta-dienone *O*-oxide (3), have been implicated as key intermediates in numerous oxidations ever since Criegee's original report on olefin ozonolysis [1–3]. Cyclo-pentadienone *O*-oxide, the unchlorinated analogue of 3, was the first such species to be observed spectro-scopically. This was achieved in matrix isolation studies conducted in our laboratory [4–6]. A recent review by Sander [7] describes the generation and characterization of carbonyl oxides by matrix isolation and laser flash photolysis techniques, and discusses their electronic structures and photochemistry. Even before carbonyl oxides had been studied spectroscopically, extensive work on photo-oxidations brought about by the pho-tolysis of diazo compounds in the presence of O_2 had been carried out, particularly by Murray's [8–15] and Ando's [16–20] research groups.

In a previous paper in this series [21], we described how information derived from matrix isolation studies of carbonyl oxides could be applied to the room-temperature photo-oxidation of cyclohexane. Earlier low-temperature spectroscopic work [22] showed that 3, to a greater extent than other carbonyl oxides, preferentially expels an oxygen atom, generating tetra-chlorocyclopentadienone (4), rather than rearranging to lactone 6 via dioxirane 5 (Scheme 1). We concluded
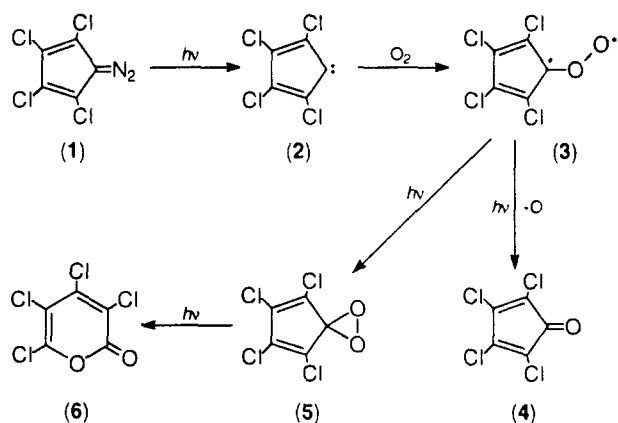
Scheme 1.

that the photolysis of tetrachlorodiazocyclopentadiene (1) in O_2-saturated solutions should provide efficient O-atom transfer conditions. The photo-oxidation of cyclohexane by this means was found to be efficient with either the neat liquid or solutions of cyclohexane in CCl_4, and yields of the oxidized products, cyclohexanol and cyclohexanone, were the highest so far reported for oxidations of this type. From these results, the carbonyl oxide (3) appears to be 30–50 times more efficient than the unchlorinated parent, cyclopentadi-enone *O*-oxide. This increased efficiency is attributed to the electronic nature of the chlorine substituents. In this paper, we report the oxidation of cyclohexene as part of our continuing investigation into the range of synthetic applications of 1.

2. Results and discussion

2.1. Products

Solutions of 1 (about 0.2 M) in cyclohexene were placed in the 20 cm^3 Pyrex vessel described in Section 4, kept saturated with O_2 by the continuous passage of a gentle stream of the gas and irradiated with a medium-pressure Hg arc. The reaction mixtures were separated by preparative gas chromatography (GC) to provide, typically, cyclohex-2-en-1-one (7) (150%), cyclohex-2-en-1-ol (8) (150%) and a third component, which was shown by further GC and mass spectral analysis to contain at least two isomeric chlorocyclohexanols (approximately 28%) (Scheme 2). These minor components were not investigated further, but the presence of chlorinated products implies that some Cl-atom abstraction occurred, probably from 1, 4 or decomposition products of the latter. Yields are based on the consumption of the diazo compound (1), since cyclohexene was in large excess.

Control reactions showed that, for the photo-oxidation to proceed, 1, O_2 and UV irradiation are required. This is in keeping with other work [23]. Moreover, experiments carried out by ourselves and other research groups have shown that secondary alcohols are not oxidized to ketones in the conditions of our reaction or similar conditions [12,14,20,21,24,25]. Therefore the ketone product (7) does not arise from secondary oxidation of the alcohol product (8).

The high yield and C-3 selectivity observed in the reaction of 1 and O_2 with cyclohexene were somewhat surprising, because Sawaki et al. [26] reported that cyclohexene gave only low yields of 1,2-epoxycyclohexane and cyclohexenylhydroperoxide in analogous reaction conditions. With 1 and O_2 no epoxycyclohexane is produced, while the hydroperoxide is unlikely to have survived our reaction and work-up conditions. The high overall yield of products (about 328% based on the consumption of 1) is strong evidence for a radical chain mechanism.

The fate of 4 in this oxidation has not been determined. This ketone is probably unstable at room temperature and will rapidly polymerize; it has so far been observed only in low-temperature matrices [22].
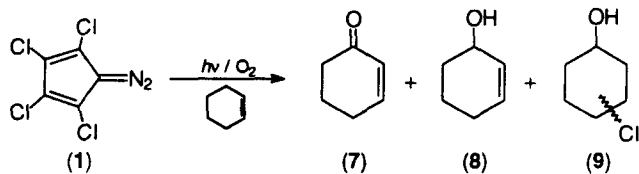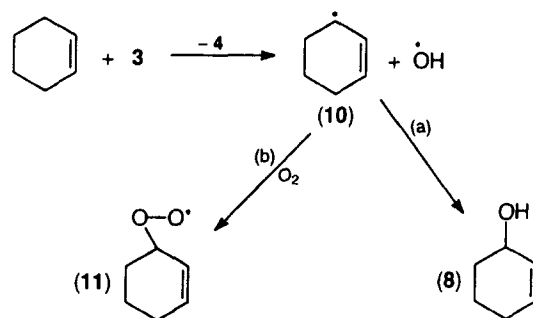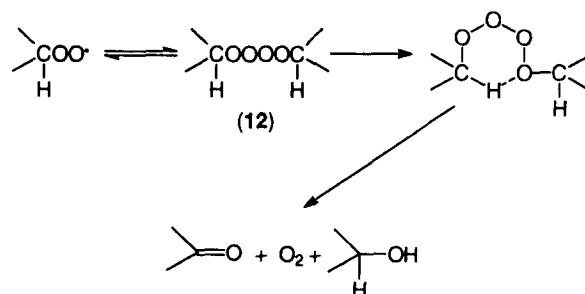
Scheme 2.

2.2. Mechanism

A striking feature of our results for both cyclohexane and cyclohexene photo-oxidation is the 1 : 1 formation of ketone and alcohol products. Any mechanism proposed must therefore account for this equimolarity. Related photo-oxidations of cyclohexane studied by other groups have not always indicated such a close equimolarity, however [23].

As suggested previously [21,23], it is probable that the reaction is initiated by H-atom abstraction from the hydrocarbon by the reactive carbonyl oxide 3. With cyclohexene, this would yield the cyclohexenyl radical 10 and a hydroxyl radical (Scheme 3). These two radicals could combine to yield cyclohexenol (8) (path (a)). In our previous study [21], we suggested that the analogous radical recombination might well contribute significantly to the formation of cyclohexanol. With cyclohexene, however, path (a) cannot contribute significantly to the observed process, because it consumes a molecule of 1 for each molecule of 8 generated, and is thus inconsistent with the high overall yield (150% based on 1). The cyclohexenyl radical (10) is therefore most likely to react with O_2 to give the cyclohexenylperoxy radical 11, while the hydroxyl radical could react with cyclohexene to give a second molecule of 10, and thence a second peroxy radical (11).

Kinetic studies of the oxidation of cyclohexane [27,28], in which the near equimolarity of ketone and alcohol products was also noted, suggest that alkylperoxy radicals such as 11 decompose via dimerization to the corresponding dialkyl tetroxide (12) (Scheme 4). Low-temperature kinetic electron spin resonance (ESR) studies
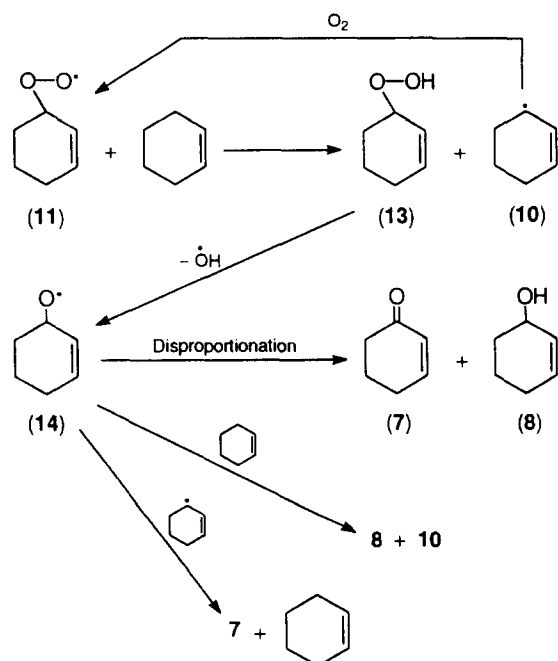
Scheme 3.

Scheme 4.

of isopropylperoxy radicals are also in accord with this mechanism [29].

Analysis of the mechanism of Scheme 4 shows that one molecule each of the ketone and alcohol products is generated from two molecules of the precursor alkylperoxy radicals. The mechanism neatly accounts for the equimolar formation of both products. In our systems, the alkylperoxy radicals are formed as shown in Scheme 3, although a second alkylperoxy radical can be formed from each molecule of **1** via reaction of the initial hydroxyl radical with cyclohexene. Thus, at most, two cyclohexenylperoxy radicals (**11**) may be generated from each molecule of **1**. According to Scheme 4, the highest theoretical yields of **7** and **8** (based on **1**) would be 100% each. The observed yields (150% of each plus additional oxidation products) are therefore inconsistent with the exclusive operation of the pathway of Scheme 4.

An alternative decomposition route for the cyclohexenylperoxy radicals (**11**) is suggested in Scheme 5. Firstly, H abstraction from cyclohexene would regenerate a cyclohexenyl radical (**10**) and give the hydroperoxide (**13**). Subsequent O–O bond cleavage would give a cyclohexenyloxy radical (**14**) and a hydroxyl radical. The latter could then regenerate yet another cyclohexenyl radical. The cyclohexenyloxy radical (**14**) could decompose via several different paths, e.g. disproportionation to give one molecule each of **7** and **8**, H abstraction from the cyclohexene solvent to give **8** or loss of an H atom by reaction with a cyclohexenyl or OH radical to give **7**.

The key features of Scheme 5 are (i) the regeneration of the cyclohexenyl radical by several plausible pathways,

thus accounting for the very high yields of **7** and **8**, and (ii) the disproportionation of cyclohexenyloxy radicals (**14**), which accounts for the equimolar formation of these two products. In our earlier study of the photo-oxidation of cyclohexane [21], the yields of oxidized products did not exceed 100%, so we could only speculate as to the preferred mechanism of cyclohexanone and cyclohexanol formation. With cyclohexene, however, the high observed yields necessitate a radical chain mechanism. Although ketone and alcohol products can arise in independent pathways (as shown in Scheme 5), it would be surprisingly coincidental if these two products were produced in a 1 : 1 ratio in all the reactions carried out. The disproportionation of two cyclohexenyloxy radicals is therefore the most likely termination step.

We have attempted to confirm the intermediacy of **3** in our reactions by trapping experiments with nitriles or aldehydes, which can act as 1,3-dipolarophiles. In all cases these reactions were unsuccessful, with only oxidized species being recovered. Nevertheless, the intermediacy of the carbonyl oxide is highly probable, although it apparently does not take part in 1,3-dipolar cycloadditions.

Overall, the evidence suggests that the carbonyl oxide (**3**) has the ability to initiate or accelerate the autoxidation of cyclohexene. These photo-oxidations were carried out in the absence of a triplet sensitizer. The observed products differ from those obtained with other, similarly mild, oxidizing agents. Thus 1,2-epoxycyclohexane was the only isolable product (more than 95%) from the dimethyldioxirane-mediated oxidation of cyclohexene reported by Baumstark and Vasquez [30], while Sawaki et al. [26] found that the oxidation of cyclohexene by fluorene *O*-oxide, generated by the sensitized photo-oxidation of 9-diazofluorene, gave only 1,2-epoxycyclohexane (2%) and cyclohexenylhydroperoxide (16%). The latter workers also reported that control reactions in the absence of 9-diazofluorene (singlet O_2 reaction with cyclohexene) resulted in higher yields with similar product ratios, and that the azoisobutyronitrile-initiated autoxidation of cyclohexene yielded 1,2-epoxycyclohexane and cyclohexenylhydroperoxide in almost exactly the same ratio. On the other hand, a second series of experiments showed that β-carotene (a known singlet oxygen quencher [31,32]) had no effect on the product yield or ratio, which seems to preclude singlet oxygen as the oxidant.

Scheme 5.

3. Conclusions

This study reveals that tetrachlorocyclopentadienone *O*-oxide (**3**), generated from tetrachlorodiazocyclopentadiene (**1**) in the presence of O_2, is a radical initiator for the photo-oxidation of cyclohexene. The major

products are cyclohex-2-en-1-one (7) and cyclohex-2-en-1-ol (8), both obtained in 150% yield based on the precursor (1) consumed. The oxygen transfer ability of the carbonyl oxide (3) surpasses that of α-phenyl- and α-carbonyl-stabilized carbonyl oxides. Results to date indicate a high propensity to expel an oxygen atom, which is in agreement with our low-temperature spectroscopic studies. They also indicate that oxygen transfer from carbonyl oxides occurs via a radical mechanism, and that tetrachlorocyclopentadienone O-oxide does not act in the same manner as previously studied carbonyl oxides. The oxidations of cyclohexene by tetrachlorocyclopentadienone O-oxide and dimethyldioxirane occur by quite different mechanistic pathways.

4. Experimental details

Tetrachlorodiazocyclopentadiene (1) was prepared from hexachlorocyclopentadiene (Aldrich Chemical Co.), as described previously [21], by a slight modification of the method of McBee and Sienkowski for the tetrabromo analogue [33]. Cyclohexene was redistilled prior to use.

Photo-oxidations were carried out in a specially constructed Pyrex vessel of approximately 20 cm³ capacity. This had two concentric annular containers fused together, the inner for the sample and the outer acting as a cooling jacket, through which a stream of cold water was passed. The annular design allowed a Philips HPK 125 W medium-pressure Hg arc lamp to be placed in the centre so as to maximize the photon flux through the samples. Oxygen was passed through the sample by means of a capillary tube, which provided gentle agitation as well as keeping the samples saturated with O_2.

In a typical experiment, tetrachlorodiazocyclopentadiene (1) (1.0 g, 4.35 mmol) was dissolved in cyclohexene (20 cm³); the solution was placed in the special Pyrex vessel described above, kept saturated with O_2 and irradiated for several hours with a medium-pressure Hg arc lamp. Irradiation was terminated when the orange–yellow colour of 1 had disappeared. The reaction mixture was separated by preparative GC on one of several available columns: carbowax, FFAP, E301 and OV-101. The products identified were cyclohex-2-en-1-one (7) (639 mg, 150%), cyclohex-2-en-1-ol (8) (646 mg, 150%) and at least two minor products, probably chlorocyclohexanols (129 mg, approximately 28%). The two major products were identified firstly by GC analysis involving co-injection of authentic samples, and subsequently by gas chromatography–mass spectrometry (GC–MS), ¹H nuclear magnetic resonance (NMR) and ¹³C NMR. The minor products could not be adequately separated on any of the available GC columns, so that more than two components may have

been present. GC–MS analysis, however, indicated two compounds with molecular weights of 135 (consistent with $C_6H_{11}ClO$). These minor components were not investigated further.

The following control experiments were carried out: (1) UV irradiation of O_2-saturated cyclohexene; (2) photolysis of 1 in deoxygenated cyclohexene; (3) bubbling of O_2 through a solution of 1 in cyclohexene in the dark. In none of these controls was the oxidation of cyclohexene observed.

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