Studies on Photochemical Reactions of Air Pollutants. XV. Photoactivity of Heptachloro-3′-cyclopentenylidioxo Heptachloro-2-cyclopentene Formed by Exposure of Hexachlorocyclopentadiene to Ultraviolet Light in Air

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Hexachlorocyclopentadiene (HCCP, 1), one of the starting materials in the synthesis of aldrin (3), was found to be able to epoxidize aldrin (3) to give dieldrin (4) when exposed to artificial light at wavelengths longer than 290 nm. In this photochemical reaction, heptachloro-3′-cyclopentenylidioxo heptachloro-2-cyclopentene (2) was isolated as a key intermediate, which appears to be derived from the interaction between the triplet state of photo-excited HCCP (1) and triplet oxygen ($\Sigma_g^+$), but not from that between the ground state of HCCP (1) and singlet oxygen ($\Delta_g$). The peroxy (2) plays an important role in the formation of dieldrin (4), because it utilized oxygen atom derived from oxygen in air for the epoxidation.

Key words aldrin; dieldrin; hexachlorocyclopentadiene; peroxy; heptachloro-3′-cyclopentenylidioxo heptachloro-2-cyclopentene; photooxidation

Aldrin 3 has been used as an agricultural and domestic insecticide in many countries, but presents an environmental problem because it is not readily degraded.1–6 Many researchers have examined its transformations on exposure to sunlight in air,7 to sunlight in the presence of photosensitizer in air,8,9 or to UV at wavelengths longer than 290 nm in a vapor-phase system in air,10 as well as in the presence of nitrogen dioxide in air,11 in the presence of $\alpha$-diketones including glyoxyxyl, methylglyoxyxyl and biacetyl in air,12 in the presence of suspended particulates in air13 and in the presence of benzaldehyde in air.14

Interestingly, it was observed that crude 3 gave 4 in moderately week when exposed to light at wavelengths longer than 290 nm. Thus, impurities in crude 3 may play a role in the formation of 4. Therefore, the photochemical reactivity of residual HCCP (1) and 2,5-norbornadiene, used as starting materials in the synthesis of 3 through Diels–Alder reaction, was investigated. The involvement of 1 in the formation of 4 from 3 was confirmed here, and the peroxy (2) was isolated as a key intermediate. Compound 2 was shown to be generated via the interaction between the triplet state of photo-excited HCCP (1) and triplet oxygen ($\Sigma_g^+$), but not via the ground state of HCCP (1) and singlet oxygen ($\Delta_g$).

Experimental

Apparatus Melting points were measured on a Yamato melting point apparatus using a capillary tube and are uncorrected. IR spectra were determined with a JASCO FT/IR-410 spectrometer. Here, KCl instead of KBr was employed, because the peroxide ($\alpha$-HCCP, 1) might oxidize Br$^-$. FAB-MS spectra were measured on a Hitachi U-2000 spectrophotometer. Single crystal X-ray diffraction analysis was done with a Rigaku RFC-5.

Materials Oxygen-18 (99.5 atom %) was purchased from ICON. Ultra pure nitrogen (99.9999%) and pure oxygen (99.9%) were supplied by Tokyo Kourouzu Co. Ltd. Aldrin [3: (1α,4α,4β,5α,5β,8α,8β)-1,2,3,4,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanophthalene] and dieldrin [4: (1α,4α,4β,5α,5β,8α,8β)-1,2,3,4,10-hexachloro-1,4,5,8-dimethanophthalene] were supplied by Wako Pure Chemicals Industries Ltd. Since commercial 3 contained 1 as an impurity, 3 was purified using activated charcoal in methanol, followed by recrystallization from methanol. Other chemicals used in the experiments were supplied by Wako Pure Chemicals Industries Ltd. or Tokyo Kasei Kogyo Co. Ltd., and were purified before use, if necessary.

Analytical Method Gas liquid chromatography-mass spectrometry (GLC-MS) was carried out with a JEOL JMS-700 spectrometer coupled with a Hewlett Packard HP5890 gas chromatograph. A coiled glass column (0.32 mm i.d. x 30 m) coated with HP-5 (film thickness, 0.25 µm), supplied by Hewlett Packard, was employed. The column temperature, injection port temperature and helium carrier gas flow rate were 200 °C, 250 °C and 30 ml/min, respectively.

High-performance liquid chromatography (HPLC) was done with a GL Sciences PU 614 equipped with an ultraviolet-visible detector and a 20 µl sample loop. A stainless steel column (4.6 mm i.d. x 150 mm) packed with ODS was used. Acetonitrile and H$_2$O (92.5:7.5) was employed as the mobile phase. The flow rate was 1.0 ml/min.

Preparation of Heptachloro-3′-cyclopentenylidioxo Heptachloro-2-cyclopentene (2) Forty microliters of 1 was taken into a 180 ml Pyrex reaction vessel filled with pure oxygen, followed by irradiation with a xenon lamp (300 W, ozoneless type, Ushio Inc.) at room temperature for 40 min (see Fig. 5). After irradiation, the reaction mixture was extracted with 8 ml of n-hexane twice. The resulting solution was subjected to HPLC analysis.

Irradiation of Aldrin (3) in the Presence of HCCP (1) in Air One milliliter of a n-hexane solution containing 3 (22.3 µmol/ml = 500 µl gas/ml) was injected into a 180 ml Pyrex reaction vessel. n-Hexane vapor was flushed out with air (ca. 40% humidity), leaving the material deposited in the vessel. Then, 3.6 µl (22.3 µmol = 500 µl of gas) of 1 was injected into the reaction vessel, followed by irradiation with the xenon lamp at room temperature for 0.5, 1.0 or 2.0 h. After irradiation, the reaction mixture was dissolved in 10 ml of n-hexane. The resulting solution was subjected to HPLC analysis.

Irradiation of HCCP (1) in Air Three point six microliters (22.3 µmol = 500 µl of gas) of 1 was injected into a 180 ml Pyrex reaction vessel filled with air (ca. 40% humidity), followed by irradiation with the xenon lamp at room temperature for 0.5, 1.0 or 2.0 h. After irradiation, the reaction mixture was dissolved in 10 ml of n-hexane. The resulting solution was subjected to HPLC analysis.

Photochemical or Dark Reaction of Aldrin (3) with Peroxide (2) in Air One milliliter of a n-hexane solution containing 2 and 3 (each
22.3 μmol/ml = 500 μl/gas/ml was taken into a 180 ml Pyrex reaction vessel. n-Hexane vapor was replaced with air (ca. 40% humidity), leaving the material deposited in the vessel. Then, the mixture was irradiated with the xenon lamp or allowed to stand in the dark at room temperature for 0.5, 1.0 or 2.0 h. After irradiation or standing, the content was dissolved in 10 ml of n-hexane, and subjected to HPLC analysis.

**Reaction of Peroxide (2) with 2,6-Dimethylhydroquinone in the Presence of Aldrin (3) or Dieldrin (4)**

To 10 ml of a n-hexane and ethanol (1:1) solution of 2 and 3, or 2 and 4 (each 2.23 μmol/ml) was added 2,6-dimethylhydroquinone (22.3×5 μmol). The resulting mixture was heated at 55±1°C for 3 h under no light, and then subjected to HPLC analysis.

**Photoreaction of Aldrin (3) with Peroxide (2) in Quasi-Air Containing 18O2**

One milliliter of a n-hexane solution of 2 and 3 (each 22.3 μmol/ml = 500 μl gas/ml) was taken into a 180 ml Pyrex reaction vessel filled with pure nitrogen. n-Hexane vapor was flushed out with pure nitrogen, leaving the material deposited in the vessel. Then, 40 ml of nitrogen was removed from the vessel through a syringe, followed by injection of 40 ml of 18O2. The mixture was irradiated with the xenon lamp at room temperature for 1 h. After irradiation, the reaction mixture was dissolved in 10 ml of n-hexane and ethanol (1:1), to which 2,6-dimethylhydroquinone (22.3×5 μmol) was added. The resulting mixture was heated at 55±1°C for 3 h, then concentrated to 2 ml under reduced pressure, and subjected to GLC-MS analysis.

**Results and Discussion**

We observed that when crude 3 was irradiated with a xenon lamp through a Pyrex filter (cut-off below 290 nm) in air, compound 4 was formed. This result suggested that impurities in crude 3 might have epoxidation ability under irradiation, so the photochemical reactivity of residual 1 and 2,5-norbornadiene (starting materials in the synthesis of 3 through Diels–Alder reaction) was investigated. It was confirmed that 1 was responsible for the formation of 4 from 3.

We first examined whether or not an active species is produced when 1 alone is irradiated in air. One of the photoproducts was found to liberate I2 from potassium iodide aqueous solution. It was isolated by column chromatography on Kieselgel 60 as colorless needles, and was subjected to single-crystal X-ray diffraction analysis. As shown in Fig. 1, the product was confirmed to be heptachloro-3'–cyclopentenyldioxy heptachloro-2-cyclopentene (2).

Two routes for its formation can be considered: in one, a triplet state obtained through intersystem crossing from the singlet state of photo-excited HCCP (1) transfers its energy to triplet oxygen (3Σg−) to result in the formation of singlet oxygen (1Δg), and undergoes Diels–Alder reaction with ground-state 1 to give an adduct which leads to 2; in the other, the triplet state derived from photo-excited HCCP (1) directly reacts with triplet oxygen (3Σg−) to afford an adduct which yields 2. Whenever 1 was exposed to irradiation cut off below 400 nm (with a Toshiba L-39 glass filter), the formation of 2 was not observed. In other words, 2 was not obtained if 1 was not excited photochemically. In fact, 1 itself showed little light absorption (see Fig. 2). That is to say, light transmitted through the 400 nm cut-off filter did not excite 1.

Then, we examined whether or not 2 is produced when the ground state of 1 is brought into contact with singlet oxygen (1Δg) generated by the reaction of hypochlorite with hydrogen peroxyde,[16–24] because it has already been reported that cyclopentadiene derivatives and singlet oxygen (1Δg) undergo adduct formation.25–30 However, no reaction was observed. It is well known that a triplet state is biradical in nature and has a longer lifetime than a singlet state.31,32 Accordingly, the interaction between the triplet state of photo-excited HCCP (1) and triplet oxygen (3Σg−) was concluded to be im-

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<th>Species</th>
<th>Computational methods</th>
<th>State</th>
<th>Multiplicity</th>
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<tbody>
<tr>
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<td>Single Point Energy</td>
<td>First excited</td>
<td>Triplet</td>
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<td>Density Functional B3LYP 6-31G*</td>
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<td>Hartree–Fock 3-21G*</td>
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<td>Single Point Energy</td>
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Table 1. Parameters for Calculation Using Spartan ‘04 Version 1.0.3
important for the formation of 2.

Next, we examined the feasibility of the two routes in terms of the structures and spin density of candidate participating radicals, and the structure, HOMO and LUMO of 1 (see Figs. 3-1—3-3). Calculations were done with Spartan '04 Version 1.0.3 (WAVEFUNCTION, INC., U.S.A.) (see Table 1).

First, triplet oxygen ($^3\Sigma_g^-$) reacts with the triplet state (biradical, a) derived from photo-excited HCCP (1), which has higher spin density at the C-1 carbon, to give the biradical intermediate (b) bearing higher spin density at the C-2 and C-4 carbons than other carbons, and terminal oxygen, followed immediately by the abstraction of chlorine atom attached to the sp$^3$ carbon (C-5 carbon$^{37}$) of 1 by the C-2 carbon in b to afford the dioxy radical (c; heptachloro-3-cyclopentenyl-dioxy radical). In this case, C-2 carbon is probably superior in the steric factor for 1 to approach to C-4 carbon. Abstraction of chlorine atom by a radical has already been reported by Fisher et al. in the reaction of $\beta$-pinene with carbon tetrachloride.$^{38}$ Next, the interaction between SOMO of the dioxy radical (c), and HOMO and LUMO of 1 as postulated by Fukui et al.$^{39,40}$ would afford the radical intermediate (d), which has high spin density at the C-2 carbon and C-4 carbon. In the above interaction, the dioxy radical (c) would attack the C-1 carbon having larger coefficient of HOMO and LUMO in Fig. 3-3 than the C-2 carbon in compound 1. Then, the C-4 carbon abstracts chlorine atom for steric reasons, generating heptachloro-3'-cyclopentenyldioxy heptachloro-2-cyclopentene (2).

Figure 4 shows plots of consumption of 1 and 3 and concomitant formation of 2 and 4 versus irradiation time. Apparently 1 acts as a photochemical epoxidizing agent in air. The yields of 4 and 2 reached a maximum after about 2 h irradiation and 0.5 h irradiation, respectively, while 1 had almost disappeared after 2 h. The data in Fig. 4 do not indicate
whether or not 2 participates in the formation of 4, so we attempted to isolate 2.

Figure 5 shows plots of consumption of 1 and concomitant formation of 2 versus irradiation time. Clearly 2 was formed when 1 was irradiated in air. In this case, also, the yield of 2 reached a maximum after about 0.5 h irradiation, while 1 had almost disappeared after 2 h. Compound 2 was isolated from the reaction mixture by column chromatography using Kieselgel 60 with n-hexane as the mobile phase to give colorless needles, which oxidized iodide ion to iodine.

Figure 6 shows plots of consumption of 2 and 3 and concomitant formation of 4 versus irradiation time. The results suggest that 2 is an intermediate in the formation of 4. The yield of 4 reached a maximum after about 0.5 h irradiation, while 3 had almost disappeared after 2 h. Moreover, we examined whether or not irradiation is required for the epoxidation. As shown in Fig. 7, the epoxidation did not proceed in the absence of irradiation. It is also clear that 2 is stable at room temperature.

In order to investigate the mechanism of the photochemical epoxidation, we examined in detail 4, which was obtained by irradiation of 3 in the presence of 2 in quasi-air containing 18O2, by means of gas liquid chromatography-mass spectrometry (GLC-MS). Since residual 2 may directly react with residual 3 to give 4 during GLC-MS, we decided to decompose residual 2 with a reducing agent prior to the analysis. For this purpose, 2,6-dimethylhydroquinone was found to be superior to other reducing agents examined. Figure 8 shows plots of consumption of 2 and 3 versus reaction time. After 3 h, 2 was completely decomposed by 2,6-dimethylhydroquinone, while 3 remained unchanged.

It is also possible that the reducing agent (2,6-dimethylhydroquinone) may convert 4 into some other compounds. To examine this possibility, the reaction of 2 with 2,6-dimethylhydroquinone under the same conditions as above was carried out in the presence of 4. Figure 9 shows plots of consumption of 2 and 4 versus reaction time. Again, it was found that after 3 h, 2 was completely decomposed by 2,6-di-
methylhydroquinone, while 4 remained unchanged. Thus, 2,6-dimethylhydroquinone would not affect the determination of 4 in the photochemical reaction products by GLC-MS analysis.

On the basis of these experimental results, GLC-MS analysis of 4 obtained from the irradiation of 3 in the presence of 2 in quasi-air containing 18O2 was carried out. Table 2 indicates the abundance of 18O in 4 thus obtained. It is clear that the oxygen atom introduced into 4 originated from 18O2, but not from 2.

These results indicate that the formation of 4 during irradiation of 3 with 2 in air may proceed as follows: first 2 is photolytically cleaved to generate an oxy radical (FAB-MS data in the experimental section are consistent with this), followed by combination with oxygen in air to give trioxo radicals e (heptachloro-2-cyclopentenyltrioxy radical) and e’ (heptachloro-3-cyclopentenyltrioxy radical) as active species which epoxidize 3 to afford 4. Peroxy radicals are known to have epoxidizing ability.41)

The overall process of the formation of 4 from a mixture of 3 and 1 irradiated in air is summarized in Chart 1. The possible contribution of the dioxy radical (c) remains to be examined.

Elucidation of the transformations of pollutants in the environment is important in assessing the impact of pollutants on human health, because it is possible that highly toxic compounds may be generated via photochemical reactions in air. Thus, it is important to examine the fates of pollutants, including insecticides such as aldrin (3), in the environment.

Acknowledgments  The authors thank Dr. M. Aida of Hiroshima University for the advice on calculation of molecular orbitals.

References and Notes

Table 2. Abundance of 18O in Dieldrin Obtained from Irradiation of Aldrin (3) in the Presence of Peroxide (2) in Quasi-Air Containing 18O2

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product (yield)</th>
</tr>
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<tr>
<td>Aldrin (3) + Peroxide (2)</td>
<td>18O-Dieldrin (100%)</td>
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</table>

a) Aldrin (3), 22.3 μmol; peroxide (2), 22.3 μmol; irradiation time, 1 h.  b) Yield is [molar amount of 18O-dieldrin formed/molar amount of dieldrin formed]×100.

Fig. 9. Decomposition of Peroxide (2) by 2,6-Dimethylhydroquinone in the Presence of Dieldrin (4) in n-Hexane/Ethanol Solution ○: dieldrin (4), □: peroxide (2).

Chart 1
(1989).


15) Crystal Data: C_{10}Cl_{14}O_{2}; M=648.46; Monoclinic, space group: P2_{1}/n, Z=4 with a=8.2766(9) Å, b=23.204(3) Å, c=11.041(1) Å, β=92.073(3)°; V=2119.2(4) Å³, T=296(1) K; Absorption coefficient: 18.2 cm⁻¹ (transmission factors: 0.6814—0.8397). 23952 reflections measured, 4287 unique (R int=0.118); Final R indices: R1=0.090, wR2=0.078. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 289269.


