Studies on Photochemical Reactions of Air Pollutants. XII.
Photochemical Epoxidation of Aldrin with Suspended Particulates in Air

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Suspended particulates collected in Yokohama, Japan over various 24-h periods were found to cause the photochemical epoxidation of aldrin to dieldrin in good yield. trans-Stilbene did not undergo the epoxidation. Upon irradiation of aldrin together with the suspended particulates in quasi-air consisting of $^{18}$O, 100% incorporation of $^{18}$O into dieldrin was obtained. Thus, the oxygen atom in dieldrin originated not from the particulates, but from oxygen in air.

Keywords  suspended particulate; vehicular exhaust gas; photochemical epoxidation; aldrin; dieldrin; metal oxide

We have shown that nitrogen dioxide, an air pollutant, in air causes photochemical epoxidation, converting olefins such as trans-stilbene, cis-stilbene, cyclohexene, 4,5-dibromo-cyclohexene and aldrin to their corresponding epoxides in good yield.3) Further, x-diketones such as glyoxal, methylglyoxal, biacetyl, phenylglyoxal, 1-phenyl-1,2-propanedione, and benzil, of which the former three were observed when a mixture of aromatic hydrocarbons (benzene, toluene and three xylenes) and nitrogen dioxide was exposed to light emitted from the xenon lamp in air,2,3) can convert aldrin photochemically to dieldrin in good yield. Peroxycetyl nitrate (PAN),5) derived from the photochemical reaction of olefins with nitrogen dioxide in air, is also known to be an epoxidizing agent.6)

Many types of pollutants, both organic and inorganic compounds, are released into the atmosphere, and their chemical reactivities are often unknown. We are interested in the photochemistry of suspended particulates as air pollutants. Suspended particulates are known to adsorb photoproducts (polycyclic quinones,7) aliphatic dicarboxylic acids,8) nitratet polycyclic aromatic hydrocarbons9) and nitrophenols10) derived from the photochemical reactions of air pollutants with each other, but have not been identified as reactants in photo reactions. We wish to report herein the participation of suspended particulates in photochemical epoxidation.

MATERIALS AND METHODS

Materials  Aldrin was supplied by Wako Chemical Co., Ltd. Dieldrin, trans-stilbene and trans-stilbene oxide were supplied by Tokyo Kasei Chemical Co., Ltd. 18O2 (99.5%) was purchased from ICON Co., Ltd. Chemicals used were purified before use, if necessary.

Analytical Equipment  Gas liquid chromatography (GLC) was carried out with a Shimadzu 9A gas chromatograph equipped with a flame ionization detector. A coiled glass column (1.1 m x 3 mm i.d.) packed with 1.5% Silicone SE-30 on Chromosorb WAW-DMCS (60—80 mesh) was employed. Other conditions were the same as described in the previous paper.1)

Gas liquid chromatography-mass spectrometry (GLCMS) was done with a JEOL DX-300 spectrometer. A coiled glass column (2 m x 3 mm i.d.) packed with 1.5% Silicone SE-30 on Chromosorb WAW-DMCS (60—80 mesh) was used. Other conditions were the same as described in the previous paper.1)

Ion chromatography was done with a Dionex 450i ion chromatograph equipped with a conductivity detector and a 50 μl sample loop. A Dionex AMMS micromembrane suppressor and an Erma ERC-3312 on-line degasser were also used. The separator column consisted of a Sarace AN-1 guard cartridge and a Sarace AN-1 column. The eluent (1.7 mm Na2CO3/1.8 mm NaHCO3) was used at a flow rate of 1.0 ml/min.

Wavelength-dispersive X-ray fluorescence spectrometry was done with a Siemens SRS 303 instrument. Measurement conditions were as follows: crystals of LiF 100, PET and OVO 55 were prepared, and the X-ray tube (rhodium anode) was run at 60 kV and 40 mA, 50 kV and 48 mA, and 40 kV and 60 mA, respectively, for excitation. A thin beryllium window (125 μm thick) is incorporated for optimum excitation of the elements. Computer control of the collimator apertures was used to suppress the characteristic spectral lines of the sample cup mask material; when analyzing light elements, the sensitivity was increased by using a coarse collimator. Pulse counting was carried out using a proportional flow counter for light elements, or a scintillation detector for heavy elements.

Collection of Suspended Particulates in the Atmosphere and of Particulates from Vehicular Exhaust Gas  Suspended particulates in the atmosphere were collected on GB-100R glass fiber filters (203 x 254 mm) or No. 1 cellulose fiber filters (203 x 254 mm) using a high-volume air sampler at the flow rate of 1.0 m3/min over various 24-h periods on the campus of the Industrial Research Institute of Kanagawa Prefecture, while particulates from vehicular exhaust gas were collected on a GB-100R glass fiber filter using the above sampler over a 10-h period at the Sanyu-cho crossing of the Hachioji bypass.

Photochemical Reaction of Aldrin or trans-Stilbene with Suspended Particulates in Air  One milliliter of a solution of aldrin or trans-stilbene in acetone (44.6 μmol/ml = 1000 μl gas/ml) was uniformly applied on each filter (50 mm i.d.) bearing collected particulates, followed by evaporation of the acetone under reduced pressure. The
RESULTS AND DISCUSSION

In a study of nitrophenols in suspended particulates collected in Yokohama in 1982, we concluded that the nitrophenols were derived from the photochemical reactions of aromatic hydrocarbons with nitrogen dioxide in the atmosphere, followed by adsorption on suspended particulates. Nevertheless, suspended particulates in the atmosphere may participate directly in some photoreactions. Accordingly, in this work, olefins such as aldrin and trans-stilbene were irradiated in air in the presence of suspended particulates, collected by using a high-volume air sampler, as described in the previous paper.

The quantity of suspended particulates collected in Yokohama in 1993 was not markedly different from samples collected in 1982. The campus of the Industrial Research Institute of Kanagawa Prefecture has remained the same, except for some changes in the traffic network around its perimeter. The quantities of particulates collected are listed in Table I. Aldrin gave the corresponding epoxide, dieldrin, in good yield when it was irradiated in the presence of suspended particulates in air using the xenon lamp operated through a Pyrex filter (cut-off below 290 nm), while trans-stilbene essentially failed to give the corresponding epoxide, trans-stilbene oxide. Apparently, suspended particulates have limited photochemical epoxidation ability, compared with nitrogen dioxide. As shown in Table I, the ratio of product yield to suspended particulates used ranged from 3.8 to 9.1 (%/mg). GB-100R glass fiber filters were usually used for the collection of suspended particulates. In some experiments, No. 1 cellulose fiber filters were also employed to allow the determination of elements in suspended particulates by wavelength-dispersive X-ray fluorescence spectrometry after collection, since glass fiber filters interfere with the determination. The use of different filters did not affect the product yield.

In order to clarify the nature of the photochemical epoxidation of aldrin in the presence of suspended particulates in air, irradiation of aldrin with suspended particulates in quasi-air consisting of \(^{18}\text{O}_2\) was carried out. As shown in Table II, there was 100% incorporation of \(^{18}\text{O}\) into the epoxide, dieldrin. In other words, the oxygen atom in dieldrin originated not from the suspended particulates, but from oxygen in air. This might mean that oxygen was converted to activated species when irradiated in the presence of suspended particulates.

Table 1. Photochemical Epoxidation of Aldrin with Suspended Particulates in Air

<table>
<thead>
<tr>
<th>Run</th>
<th>Day</th>
<th>Particulate (mg/d)</th>
<th>Reactants</th>
<th>Ratio of conversion</th>
<th>Product (yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/21—1/22</td>
<td>30</td>
<td>Aldrin + 1.7 mg particulate</td>
<td>39 ± 18%</td>
<td>Dieldrin (14 ± 6.5%)</td>
</tr>
<tr>
<td>2</td>
<td>3/3</td>
<td>60</td>
<td>Aldrin + 3.4 mg particulate</td>
<td>37 ± 15%</td>
<td>Dieldrin (17 ± 0.7%)</td>
</tr>
<tr>
<td>3</td>
<td>4/6—4/7</td>
<td>47</td>
<td>Aldrin + 2.4 mg particulate</td>
<td>30 ± 13%</td>
<td>Dieldrin (9 ± 0.4%)</td>
</tr>
<tr>
<td>4</td>
<td>4/12—4/13</td>
<td>46</td>
<td>Aldrin + 2.3 mg particulate</td>
<td>41 ± 20%</td>
<td>Dieldrin (21 ± 9.9%)</td>
</tr>
<tr>
<td>5</td>
<td>4/19—4/20</td>
<td>55</td>
<td>Aldrin + 2.8 mg particulate</td>
<td>22 ± 1.1%</td>
<td>Dieldrin (14 ± 0.7%)</td>
</tr>
</tbody>
</table>

Data reported represents the mean ± S.D. of three experiments. a) Aldrin, 44.6 μmol; irradiation time, 5 h. b) Ratio of conversions are [the molar amounts of aldrin reacted/the molar amounts of aldrin used] × 100. c) Yields are [the molar amounts of dieldrin formed/the molar amounts of aldrin used] × 100. d) Cellulose fiber filter. e) Glass fiber filter.
TABLE II. Quantity of $^{14}$O and $^{18}$O in Dieldrin Obtained by Photochemical Epoxidation of Dieldrin with Suspended Particulates in Quasi-Air Consisting of $^{18}$O$_2$

<table>
<thead>
<tr>
<th>Product</th>
<th>Quantity$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[{}^{18}\text{O}]Dieldrin</td>
<td>0%</td>
</tr>
<tr>
<td>[{}^{16}\text{O}]Dieldrin</td>
<td>100%</td>
</tr>
</tbody>
</table>

\textit{a)} Aldrin, 44.6\,$\mu$mol; particulate in run 3, 1.5 mg; N$_2$, 120 ml; $^{18}$O$_2$, 30 ml.
\textit{b)} Quantity is based on the quantity of dieldrin formed.

TABLE III. Photochemical Epoxidation of Aldrin with Metal Oxides and with Particulates$^a$ in Air

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product (yield)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin + TiO$_2$</td>
<td>Dieldrin (7%)</td>
</tr>
<tr>
<td>Aldrin + ZnO</td>
<td>Dieldrin (&lt;1%)</td>
</tr>
<tr>
<td>Aldrin + PbO$_2$</td>
<td>Dieldrin (&lt;1%)</td>
</tr>
<tr>
<td>Aldrin + 5.9 mg particulate</td>
<td>Dieldrin (2%)</td>
</tr>
</tbody>
</table>

\textit{a)} Aldrin, 44.6\,$\mu$mol; metal oxide, 44.6\,$\mu$mol; irradiation time, 5 h. \textit{b)} Particulates emitted from vehicular exhaust gas were collected using a glass fiber filter. \textit{c)} Yields are (the molar amounts of dieldrin formed/the molar amounts of aldrin used) $\times$ 100.

It is well known that suspended particulates contain inorganic compounds such as metal oxides.\textsuperscript{11-13} So, three metal oxides, TiO$_2$, ZnO and PbO$_2$, of which the former two are photo-sensitizers,\textsuperscript{14-20} were examined to see whether or not they participate in the photochemical epoxidation which converts aldrin to dieldrin. The results are shown in Table III. Of the three metal oxides, TiO$_2$ was more effective for epoxidation than the others. The ratio of product yield to TiO$_2$ used was 1.9 ($\%$/mg), which is quite low compared with the value obtained from suspended particulates (Table I). According to the wavelength-dispersive X-ray fluorescence spectrometry analysis, the major elements (more than 1%) were Na, Mg, Al, Si, S, Cl, and Ca, while K, Fe and Zn were present at concentrations between 0.1 and 1%. However, Ti and Pb were almost undetectable in the suspended particulates. The concentrations did not directly correlate with those of sand or sea water obtained in the neighborhood of the sampling location. Accordingly, it is clear that TiO$_2$, ZnO and PbO$_2$ in the suspended particulates cannot account for the results observed in the photochemical reaction of aldrin with suspended particulates. The concentration levels of sulfate and nitrate ions in suspended particulates are summarized in Table IV; these ions are known to be components of suspended particulates.\textsuperscript{11} We investigated whether there is any correlation between the yields of dieldrin and the concentrations of sulfate ions and nitrate ions, which are shown in Table IV. There was a high correlation between the yields of dieldrin and the concentration of nitrate ions ($\gamma = -0.92$). However, the concentration of sulfate ions did not correlate with the yields of dieldrin.

As shown in Table III, particulates emitted from vehicular exhaust gas (\textit{i.e.}, collected near heavy traffic) gave dieldrin in poor yield. The ratio of product yield to the particulates used was 0.34 ($\%$/mg), which is very low compared with the value obtained from suspended particulates, as shown in Table I. Therefore, the particulates derived from vehicular exhaust gas do not account for the epoxidation.

Next, $\alpha$-diketones in suspended particulates were analyzed using the $\alpha$-phenylenediamine method, leading to quinoxaline derivatives, instead of the 4-chloro-$\alpha$-phenylenediamine method,\textsuperscript{21} since $\alpha$-diketones such as glyoxal, methylglyoxal, biacetyl, phenylglyoxal, 1-phenyl-1,2-propanedione and benzil, of which the former three were observed in our smog chamber experiments,\textsuperscript{23} are known to have the ability to cause photochemical epoxidation.\textsuperscript{41} No $\alpha$-diketones were detected in the suspended particulates. Further, suspended particulates showed virtually no decrease in photo-epoxidation ability during the three months after collection. Thus, PAN (peroxycetyl nitrate) is not likely to participate in the epoxidation, since PAN is an unstable substance with a short lifetime.\textsuperscript{21-23}

It is concluded that the photo-epoxidation ability of suspended particulates is mainly due to unidentified substances; metal oxides such as TiO$_2$, ZnO and PbO$_2$, the particulates emitted from vehicular exhaust gas, $\alpha$-diketones such as glyoxal, methylglyoxal, biacetyl, phenylglyoxal, 1-phenyl-1,2-propanedione and benzil, and PAN, are not primarily responsible. Regardless, it is important to human health to realize that suspended particulates in the environment have the capability to participate in photochemical epoxidation, since the epoxy form of organic compounds appears in a lot of carcinogens. Further investigations are in progress.

REFERENCES


