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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 $^{18}O_2$. 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-dibromocyclohexene and aldrin to their corresponding epoxides in good yield.[1] Further, α-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 the light emitted from a xenon lamp in air,[2,3] can convert aldrin photochemically to dieldrin in good yield.[4] Peroxyacetyl 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] nitrated polycyclic aromatic hydrocarbons[9] and nitrophenols[10]) derived from the photochemical reactions of air pollutants with each other, but have not been identified as reactants in photoreactions. 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. $^{18}O_2$ (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 × 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 (GLC-MS) was done with a JEOL DX-300 spectrometer. A coiled glass column (2 m × 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 4500i 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 Saracep AN-1 guard cartridge and a Saracep AN-1 column. The eluent (1.7 mM Na_2CO_3/1.8 mM Na_2CO_3) 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 × 254 mm) or No. 1 cellulose fiber filters (203 × 254 mm) using a high-volume air sampler at the flow rate of 1.0 m^3/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 resulting filter was placed in a vessel (150 ml) made of Pyrex glass and irradiated with a xenon lamp operating through a Pyrex filter (cut-off below 290 nm) for 5 h at 25—30 °C. After irradiation, the reaction mixture was extracted with methanol (50 ml × 2). The resulting solution was filtered through a 25 mm Millex Filter Unit. The filtrate was concentrated and the residue was analyzed by GLC and GLC-MS.

Photochemical Reaction of Aldrin with Suspended Particulates in Quasi-Air Consisting of $^{18}O_2$ One milliliter of a solution of aldrin in acetone (44.6 μmol/ml = 1000 μl gas/ml) was treated as described above. After the filter was placed in the vessel, air was evacuated from the vessel, followed by the injection of $^{18}O_2$ (30 ml) and N_2 (120 ml). The mixture was treated and analyzed, as described above.

Photochemical Reaction of Aldrin with TiO_2, ZnO or PbO_2 in Air One milliliter of a solution of aldrin in acetone (44.6 μmol/ml = 1000 μl gas/ml) and 1 ml of a suspension of TiO_2, ZnO or PbO_2 in acetone (44.6 μmol/ml) were taken in a 1 l reaction vessel made of Pyrex glass. Then, acetone was removed by flushing with air. The resulting mixture was irradiated with the xenon lamp for 5 h at 25—30 °C. After irradiation, the reaction mixture was extracted with methanol (50 ml). The resulting solution was filtered through a 25 mm Millex Filter Unit, followed by concentration and analysis, as described above.

Analysis of SO_4^{2-} and NO_3^- in Suspended Particulates by Ion Chromatography Each filter, on which suspended particulates had been collected, was divided into four equal parts, one of which was finely cut, and extracted with distilled water (45 ml × 2). The resulting aqueous solution was filtered through the 25 mm Millex Filter Unit, adjusted to 100 ml with distilled water and analyzed by ion chromatography.

Analysis of Elements in Suspended Particulates by Wavelength-Dispersive X-Ray Fluorescence Spectrometry Each filter (23 mm i.d.) was irradiated with an X-ray beam of short wavelength. The characteristic atomic emission or fluorescence upon absorption of the primary or incident X-ray is dispersed, and intensities at selected wavelengths are measured with sensitive detectors. The K spectral lines were used for elements of atomic numbers 11 to 50. Concentrations of the elements were estimated from calibration curves, with corrections for elements present in the No. 1 cellulose fiber filters.

RESULTS AND DISCUSSION

In a study of nitrophenols in suspended particulates collected in Yokohama in 1982,[10] 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.[10]

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 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.[1] 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-despersive 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 $^{18}O_2$ was carried out. As shown in Table II, there was 100% incorporation of ^{18}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 I.[a] Photochemical Epoxidation of Aldrin with Suspended Particulates in Air

Run	Day	Particulate (mg/d)	Reactants	Ratio of conversion[b]	Product (yield)[c]
	1993				
1[d]	1/21—1/22	30	Aldrin + 1.7 mg particulate	39 ± 1.8%	Dieldrin (14 ± 0.6%)
2[d]	3/3 —3/4	60	Aldrin + 3.4 mg particulate	37 ± 1.5%	Dieldrin (17 ± 0.7%)
3[e]	4/6 —4/7	47	Aldrin + 2.4 mg particulate	30 ± 1.3%	Dieldrin (9 ± 0.4%)
4[e]	4/12—4/13	46	Aldrin + 2.3 mg particulate	41 ± 2.0%	Dieldrin (21 ± 0.9%)
5[e]	4/19—4/20	55	Aldrin + 2.8 mg particulate	22 ± 1.1%	Dieldrin (14 ± 0.7%)

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.[a] Quantity of ^{16}O and ^{18}O in Dieldrin Obtained by Photochemical Epoxidation of Aldrin with Suspended Particulates in Quasi-Air Consisting of $^{18}O_2$

Product	Quantity[b]
$[^{16}O]$Dieldrin	0%
$[^{18}O]$Dieldrin	100%

a) Aldrin, 44.6 μmol; particulate in run 3, 1.5 mg; N_2, 120 ml; $^{18}O_2$, 30 ml. *b)* Quantity is based on the quantity of dieldrin formed.

Table III.[a] Photochemical Epoxidation of Aldrin with Metal Oxides and with Particulates[b] in Air

Reactants	Product (yield)[c]
Aldrin + TiO_2	Dieldrin (7%)
Aldrin + ZnO	Dieldrin (<1%)
Aldrin + PbO_2	Dieldrin (<1%)
Aldrin + 5.9 mg particulate	Dieldrin (2%)

a) Aldrin, 44.6 μmol; metal oxide, 44.6 μmol; irradiation time, 5 h. *b)* Particulates emitted from vehicular exhaust gas were collected using a glass fiber filter. *c)* Yields are [the molar amounts of dieldrin formed/the molar amounts of aldrin used] × 100.

It is well known that suspended particulates contain inorganic compounds such as metal oxides.[11-13] So, three metal oxides, TiO_2, ZnO and PbO_2, of which the former two are photo-sensitizers,[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.[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 correlates with the yields of dieldrin.

As shown in Table III, particulates emitted from vehicular exhaust gas (*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.

Table IV. Sulfate Ions and Nitrate Ions in Suspended Particulates Collected on the GB-100R Glass Fiber Filter

Run	Day	Particulate (mg/d)	SO_4^{2-} (μg/mg particulate)	NO_3^- (μg/mg particulate)
	1993			
3	4/6 —4/7	47	213 ± 2	128 ± 1
4	4/12—4/13	46	228 ± 1	94 ± 1
5	4/19—4/20	55	187 ± 1	102 ± 1

Data reported represents the mean ± S.D. of three experiments.

Next, α-diketones in suspended particulates were analyzed using the *o*-phenylenediamine method, leading to quinoxaline derivatives, instead of the 4-chloro-*o*-phenylenediamine method,[2] since α-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,[2] are known to have the ability to cause photochemical epoxidation.[4] No α-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 (peroxyacetyl nitrate) is not linely to participate in the epoxidation, since PAN is an unstable substance with a short lifetime.[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, α-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

1) K. Nojima, T. Ohya, S. Kanno, M. Hirobe, *Chem. Pharm. Bull.*, **30**, 4500 (1982).
2) K. Nojima, K. Fukaya, S. Fukui, S. Kanno, *Chemosphere*, **3**, 247 (1974).
3) E. C. Tuazon, H. M. Leod, R. Atkinson, W. R. L. Carter, *Environ. Sci. Technol.*, **20**, 383 (1986).
4) K. Nojima, C. Isogami, *Chemosphere*, **26**, 921 (1993).
5) E. R. Stephens, *Adv. Environ. Sci. Technol.*, **1**, 119 (1969).
6) K. R. Darnall, J. N. Pitts, Jr., *J. Chem. Soc. D*, **1970**, 1305.
7) R. C. Pierce, M. Katz, *Environ. Sci. Technol.*, **10**, 45 (1976).
8) D. Grosjean, K. Van Cauwenberghe, J. P. Schmid, P. E. Kelley, J. N. Pitts, Jr., *Environ. Sci. Technol.*, **12**, 313 (1978).
9) T. Ramdahl, G. Becher, A. Bjørseth, *Environ. Sci. Technol.*, **16**, 861 (1982).
10) K. Nojima, A. Kawaguchi, T. Ohya, S. Kanno, M. Hirobe, *Chem. Pharm. Bull.*, **31**, 1047 (1983).
11) P. F. Fennelly, *J. Air Pollut. Contr. Assoc.*, **25**, 697 (1975).
12) B. E. Saltzman, J. Cholak, L. J. Schafer, D. W. Yeager, B. G. Meiners, J. Svetlik, *Environ. Sci. Technol.*, **19**, 328 (1985).
13) C. I. Davidson, W. D. Goold, T. P. Mathison, G. B. Wiersma, K.

W. Brown, M. T. Reilly, *Environ. Sci. Technol.*, **19**, 27 (1985).

14) E. Baur, *Helv. Chim. Acta*, **10**, 901 (1927).

15) C. Yun, M. Anpo, S. Kodama, Y. Kubohara, *J. Chem. Soc., Chem. Commun.*, **1980**, 609.

16) S. Sato, J. M. White, *Chem. Phys. Lett.*, **70**, 131 (1980).

17) A. L. Pruden, D. F. Ollis, *Environ. Sci. Technol.*, **17**, 628 (1983).

18) G. K.-C. Low, S. R. McEvoy, R. W. Matthews, *Environ. Sci. Technol.*, **25**, 460 (1991).

19) C. Kormann, D. W. Bahnemann, M. R. Hoffmann, *Environ. Sci. Technol.*, **25**, 494 (1991).

20) M. R. Nimlos, W. A. Jacoby, D. M. Blake, T. A. Milne, *Environ. Sci. Technol.*, **27**, 732 (1993).

21) C. T. Pate, R. Atkinson, J. N. Pitts, Jr., *J. Environ. Sci. Health*, **A11**, 19 (1976).

22) R. A. Cox, M. J. Roffey, *Environ. Sci. Technol.*, **11**, 900 (1977).

23) P. W. Bruckmann, H. Willner, *Environ. Sci. Technol.*, **17**, 352 (1983).