Chem. Pharm. Bull.
30(12)4500—4506(1982)

Studies on Photochemical Reactions of Air Pollutants. VIII.[1] Photochemical Epoxidation of Olefins with NO_2 in a Solid-Gas Phase System

Kazuhiro Nojima,*,[a] Takeshi Ohya,[a] Saburo Kanno[a]
and Masaaki Hirobe[b]

Faculty of Pharmaceutical Sciences, Josai University,[a] 1-1, Keyakidai, Sakado, Saitama, 350-02, Japan and Faculty of Pharmaceutical Sciences, Tokyo University,[b] Hongo, Bunkyo-ku, Tokyo, 113, Japan

(Received May 12, 1982)

Upon irradiation with a xenon lamp through a Pyrex filter (cut-off below 290 nm), olefinic compounds such as *trans*-stilbene, cyclohexene, 4,5-dibromocyclohexene and aldrin reacted with nitrogen dioxide, an air pollutant which induces photochemical smog, in air and gave the corresponding epoxides in good yields, while phenanthrene gave 9,10-phenanthrenequinone and 9-hydroxy-10-nitrophenanthrene. Furthermore, the photochemical and dark reactions of phenanthrene 9,10-oxide with nitrogen dioxide in air both resulted in the same products as above. Therefore, phenanthrene 9,10-oxide seems to be an intermediate in the photochemical reaction of phenanthrene with nitrogen dioxide in air.

Keywords——nitrogen dioxide; air pollutant; photochemical smog; epoxide; dieldrin; arene oxide; phenanthrene 9,10-oxide; 9,10-phenanthrenequinone; 9-hydroxy-10-nitrophenanthrene

Introduction

During investigations on the photochemical reactions of some low-molecular-weight olefins with nitrogen dioxide in nitrogen,[2-4] Jaffe observed that ethylene oxide was produced in very poor yield when a mixture of ethylene and nitrogen dioxide in nitrogen was irradiated at 366 nm.

However, photochemical smog is induced when air pollutants are exposed to sunlight ($\lambda > 290$ nm) in the presence of nitrogen dioxide not in nitrogen, but in air, so the experimental conditions employed by Jaffe were different from the atmospheric conditions under which smog production occurs. Therefore, in order to examine the epoxidation ability of nitrogen dioxide in air, olefinic compounds such as *trans*-stilbene, cyclohexene, 4,5-dibromocyclohexene and aldrin were irradiated in the presence of nitrogen dioxide in air with a xenon lamp operating through a Pyrex filter (cut-off below 290 nm). These olefinic compounds were converted to the corresponding epoxides in good yields. Furthermore, phenanthrene, which is known to be present in the atmosphere,[5] and its epoxide were also irradiated in the presence of nitrogen dioxide in air. Both phenanthrene and its epoxide gave 9,10-phenanthrenequinone and 9-hydroxy-10-nitrophenanthrene. Accordingly, phenanthrene 9,10-oxide seems to be an intermediate in the formation of 9,10-phenanthrenequinone and 9-hydroxy-10-nitrophenanthrene.

Thus, it is suggested that nitrogen dioxide in air can be an epoxidizing agent not only for simple olefins but also for polycyclic aromatic hydrocarbons.

Experimental

1. **Materials**——Cyclohexene oxide, aldrin and dieldrin were supplied by Wako Chemical Co., Ltd. 4,5-Dibromocyclohexene oxide was prepared from 4,5-dibromocyclohexene[6] according to the method described by van Tamelen.[7] *cis*-Stilbene oxide was prepared by the reaction of *cis*-stilbene with *m*-chloro-

perbenzoic acid in benzene. Phenanthrene and 9,10-phenanthrenequinone were supplied by Tokyo Kasei Chemical Co., Ltd. 9-Phenanthrol was purchased from Aldrich Chemical Co., Ltd. Phenanthrene 9,10-oxide was prepared by the method described by Krishnan *et al.*[8) 9-Hydroxy-10-nitrophenanthrene was synthesized as described below.

A mixture of 9,10-phenanthrenequinone monoxime[9) (112 mg, 0.5 mmol) and *m*-chloroperbenzoic acid (170 mg, 1.0 mmol) in benzene (10 ml) was allowed to stand for 3 d at room temperature. After standing, the reaction mixture was concentrated and chromatographed on a column of Kieselgel 60 (70 g). The benzene eluates were concentrated under reduced pressure to give yellow crystals, which were recrystallized from benzene to afford 9-hydroxy-10-nitrophenanthrene as yellow needles (48 mg, 40%), mp 144°C (dec.). *Anal.* Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.77; N, 5.86. Found: C, 70.25; H, 4.00; N, 5.84. IR ν_{max}^{KBr} cm^{-1}: 1590, 1570, 1525, 1335, 1310, 765, 740, 720. MS *m/e*: 239 (M^+).

9-Methoxy-10-nitrophenanthrene was prepared by the reaction of 9-hydroxy-10-nitrophenanthrene with ethereal diazomethane in methanol.

Other chemicals used were purified before use, if necessary.

2. **Irradiation Conditions and Preparation of Test Solutions**——2-1. Photochemical Reactions of Olefinic Compounds with Nitrogen Dioxide in Air: One milliliter of *trans*-stilbene, 4,5-dibromocyclohexene or aldrin solution in acetone (44.6 μmol/ml = 1000 μl gas/ml) was taken in a 1 liter reaction vessel made of Pyrex glass, and acetone vapor was replaced with air. The olefinic compound was deposited in the vessel. In the case of cyclohexene, 4.5 μl of cyclohexene was directly injected into the 1 liter Pyrex reaction vessel. The cyclohexene vaporized immediately. Then, 1000 μl of nitrogen dioxide gas was injected into the vessel. The mixture was irradiated at 25—30°C with a xenon lamp[10) (ozoneless type, Ushio Co., Ltd.).

After irradiation, the reaction mixture was dissolved in 10 ml of benzene. This solution served as test solution (A).

2-2. Photochemical Reaction of Phenanthrene with Nitrogen Dioxide in Air: One milliliter of a solution of phenanthrene in acetone (44.6 μmol/ml = 1000 μl gas/ml) was taken in a 1 liter Pyrex reaction vessel, and acetone vapor was replaced with air. The phenanthrene was deposited in the vessel. Then, 1000 μl of nitrogen dioxide gas was injected into the vessel. The mixture was treated as mentioned above. The resulting reaction mixture was dissolved in 10 ml of benzene. This solution served as test solution (B).

2-3. Photolysis of Phenanthrene 9,10-Oxide in Air or Nitrogen: One milliliter of a solution of phenanthrene 9,10-oxide in acetone (2.23 μmol/ml = 50 μl gas/ml) was taken in a 1 liter Pyrex reaction vessel, and acetone vapor was replaced with air or nitrogen. The phenanthrene 9,10-oxide was deposited in the vessel. The content was treated as mentioned above, and the resulting reaction mixture was dissolved in 10 ml of benzene. This solution served as test solution (C).

2-4. Photochemical and Dark Reactions of Phenanthrene-9,10-Oxide or 9-Phenanthrol with Nitrogen Dioxide in Air: One milliliter of a solution of phenanthrene 9,10-oxide or 9-phenanthrol in acetone (44.6 μmol/ml = 1000 μl gas/ml) was taken in a 1 liter Pyrex reaction vessel, and acetone vapor was replaced with air. The compound was deposited in the vessel. Then, 1000 μl of nitrogen dioxide gas was injected into the vessel. The mixture was irradiated as mentioned above or allowed to stand in the dark. The resulting reaction mixture was dissolved in 10 ml of benzene, and this solution served as test solution (D).

3. **Analytical Equipment**——3-1. Gas Chromatography (GC): GC was carried out with a Shimadzu 6A gas chromatograph equipped with a flame ionization detector. The columns were 1.5 m × 3 mm i.d. glass tubes. The column packing was 5% Silicone SE-30 on Chromosorb WAW (60—80 mesh). The column temperatures were 170°C for *trans*-stilbene, 140°C for 4,5-dibromocyclohexene, 210°C for aldrin and 220°C for phenanthrene. The flow rate of nitrogen was in the range of 30—40 ml/min.

3-2. Mass Fragmentography (MF): MF measurements were made with a Shimadzu LKB-9000 gas chromatograph–mass spectrometer equipped with a multiple ion detector. A coiled glass column (1 m × 3 mm i.d.) was packed with 5% Silicone SE-30 on Chromosorb WAW (60—80 mesh). The column temperatures were 50°C for cyclohexene oxide, 140°C for 4,5-dibromocyclohexene oxide, 160°C for *trans*-stilbene oxide, 200°C for phenanthrene oxide or 9-phenanthrol, 220°C for dieldrin or 9,10-phenanthrenequinone, and 230°C for 9-methoxy-10-nitrophenanthrene. The flow rate of helium was in the range of 10—20 ml/min. The injection, separator and ion source were kept at 250°C. The accelerating voltage, ionizing voltage and trap current were set at 3.5 kV, 20 eV and 60 μA, respectively. The mass fragment ions selected were the parent ions (M^+) for cyclohexene oxide, *trans*-stilbene oxide, dieldrin, phenanthrene 9,10-oxide, 9-phenanthrol and 9-methoxy-10-nitrophenanthrene, $(M-79)^+$ ion for 4,5-dibromocyclohexene oxide, and $(M-28)^+$ ion for 9,10-phenanthrenequinone.

4. **Analytical Procedure**——4-1. Olefinic Compounds: Olefinic compounds in the test solution (A) were directly determined by the GC method.

4-2. Epoxides: Epoxides in the test solution (A) were directly determined by the MF method.

4-3. Phenanthrene: Phenanthrene in the test solution (B) was directly determined by the GC method.

4-4. Phenanthrene 9,10-Oxide and 9-Phenanthrol: The separation of the two compounds by the MF method was unsuccessful, since phenanthrene 9,10-oxide isomerized to 9-phenanthrol when heated for GC injection. Therefore, the test solutions (B) and (C) were treated as follows: 10 ml of 0.1 N sodium hydroxide aqueous solution was added to the test solution and the mixture was shaken vigorously. The resulting benzene layer was washed with distilled water, then dried over anhydrous sodium sulfate. This benzene solution was directly used for the determination of phenanthrene 9,10-oxide by the MF method. On the other hand, 2 ml of 1 N sulfuric acid aqueous solution and 10 ml of benzene were added to the alkaline aqueous solution obtained above, and the mixture was shaken vigorously. The resulting benzene layer was washed with distilled water, then dried over anhydrous sodium sulfate. This benzene solution was directly employed for the determination of 9-phenanthrol by the MF method.

4-5. 9,10-Phenanthrenequinone: 9,10-Phenanthrenequinone in the test solutions (B), (C) and (D) was directly determined by the MF method.

4-6. 9-Hydroxy-10-nitrophenanthrene: To determine 9-hydroxy-10-nitrophenanthrene in the test solutions (B) and (D), an aliquot of each test solution was concentrated, then treated with ethereal diazomethane containing methanol overnight at room temperature. The resulting solution was concentrated, then analyzed by the MF method.

Results and Discussion

Photochemical Reactions of Olefinic Compounds with Nitrogen Dioxide in Air

Jaffe[2-4] reported that ethylene oxide was obtained in 0.004% yield when a mixture of ethylene (5.5 mmol/l) and nitrogen dioxide (0.25 mmol/l) was irradiated in nitrogen at 366 nm for 1 h, and that the oxygen atom O(^{3}P)[11] resulting from the photolysis of nitrogen dioxide participated in the formation of the epoxide.

Table I.[a] Formation of Epoxides by Photochemical Reactions of Olefinic Compounds with Nitrogen Dioxide in Air

Olefinic compound	Ratio of conversion	Product (yield)
trans-Stilbene	44%	*trans*-Stilbene oxide (23%)[b]
Cyclohexene	—	Cyclohexene oxide (51%)[c]
4,5-Dibromocyclohexene	51%	4,5-Dibromocyclohexene oxide (20%)[b]
Aldrin	32%	Dieldrin (34%)[b]

a) Olefinic compound, 44.6 μmol; NO_2, 44.6 μmol; irradiation time, 1 h.
b) Yields are based on the quantity of olefinic compound converted.
c) Yield is based on the quantity of olefinic compound used.

However, photochemical smog is induced when air pollutants are exposed to sunlight (λ>290 nm) in the presence of nitrogen dioxide not in nitrogen, but in air, so the experimental conditions employed by Jaffe were different from the atmospheric conditions under which smog production occurs. Therefore, the epoxidation ability of nitrogen dioxide in air was examined. The epoxides obtained by the photochemical reactions of *trans*-stilbene, cyclohexene, 4,5-dibromocyclohexene and aldrin with nitrogen dioxide in air were analyzed by comparison of their mass fragmentograms with those of authentic substances. The yields of the epoxides are shown in Table I. It was found that the olefinic com-

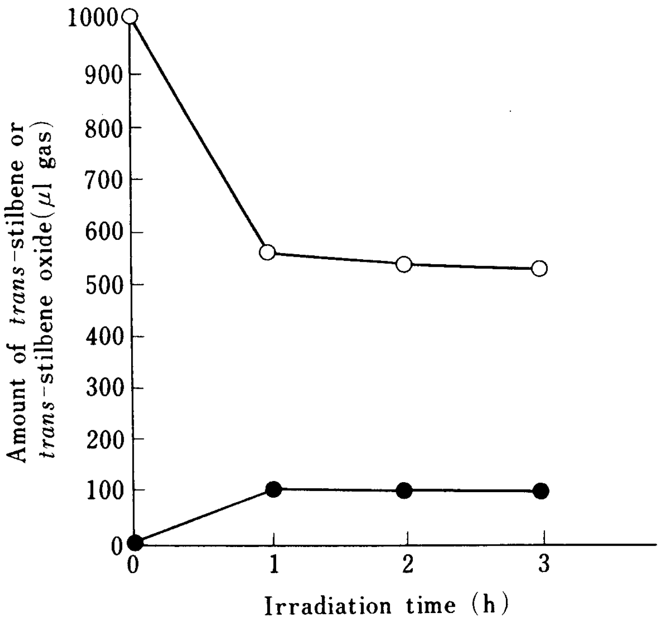

Fig. 1. Time Course of Formation of *trans*-Stilbene Oxide

○, *trans*-Stilbene; ●, *trans*-stilbene oxide.

pounds irradiated in the presence of nitrogen dioxide in air gave the corresponding epoxides in good yields. Cyclohexene oxide was obtained in particularly high yield, which may be due to the high volatility of cyclohexene as a starting material. The formation of these epoxides could be explained in terms of the reaction of an oxygen atom with olefinic compounds.

The time course of the formation of epoxide, taking *trans*-stilbene as an example, is shown in Fig. 1. The formation of *trans*-stilbene oxide was found to be maximum after one hour's irradiation.

It is known that *trans*-stilbene isomerizes to the *cis*-isomer when irradiated at 313 nm[12] or when brought into contact with nitrogen dioxide.[13] However, *cis*-stilbene oxide could not be observed in the photo-products. This shows that the epoxidation of *trans*-stilbene proceeds faster than the isomerization.

Photochemical Reaction of Phenanthrene with Nitrogen Dioxide in Air

Phenanthrene was irradiated in the presence of nitrogen dioxide in air to give 9,10-phenanthrenequinone and 9-hydroxy-10-nitrophenanthrene. The products were analyzed by comparison of their mass fragmentograms with those of authentic substances. 9-Hydroxy-10-nitrophenanthrene was converted into the methyl derivative prior to analysis, since the compound decomposed when heated for GC injection. The yields of the photo-products are shown in Table II. However, phenanthrene 9,10-oxide was not detected in the photo-products. This result suggests that phenanthrene 9,10-oxide is so reactive that it is converted into other compounds. To check this possibility, further experiments were carried out.

TABLE II.[a] Products obtained by Photochemical Reaction of Phenanthrene with Nitrogen Dioxide in Air

Reactants	Ratio of conversion of phenanthrene	Products (yield)[b]
Phenanthrene + NO_2	8.0%	Phenanthrene 9,10-oxide (ND)[c] 9-Phenanthrol (ND)[c] 9,10-Phenanthrenequinone (6.5%) 9-Hydroxy-10-nitrophenanthrene (1.3%)

a) Phenanthrene, 44.6 μmol; NO_2, 44.6 μmol; irradiation time, 3 h.
b) Yields are based on the quantity of phenanthrene converted.
c) ND: Not detected.

Photolysis of Phenanthrene 9,10-Oxide in Air or Nitrogen

Results on the photolysis of phenanthrene 9,10-oxide in air or nitrogen are summarized in Table III. Irradiation of phenanthrene 9,10-oxide in nitrogen gave 9-phenanthrol, while the irradiation in air gave mostly 9,10-phenanthrenequinone and partly 9-phenanthrol. Shudo and Okamoto reported that the photolysis of phenanthrene 9,10-oxide in methylene chloride

TABLE III.[a] Products obtained by Photolysis of Phenanthrene 9,10-Oxide in Air or Nitrogen

Reactant	Ratio of conversion	Products (yield)[b]
Phenanthrene 9,10-oxide[c]	96%	9-Phenanthrol (8.4%) 9,10-Phenanthrenequinone (79%)
Phenanthrene 9,10-oxide[d]	84%	9-Phenanthrol (94%)

a) Phenanthrene 9,10-oxide, 2.23 μmol; irradiation time, 1 h.
b) Yields are based on the quantity of phenanthrene 9,10-oxide converted.
c) In air.
d) In nitrogen.

gave 9-phenanthrol.[14] Isomerization of phenanthrene 9,10-oxide to 9-phenanthrol in nitrogen is thus consistent with their result.

On the basis of these results, the photolysis of phenanthrene 9,10-oxide (**1**) can be explained in terms of the processes shown in Chart 1. **1** isomerizes under irradiation to 9-phenanthrol (**2**), which is oxidized by oxygen in air to give 9,10-phenanthrenequinone (**3**).

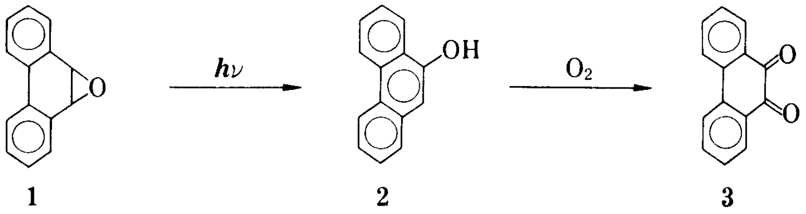

Chart 1

Photochemical and Dark Reactions of Phenanthrene 9,10-Oxide or 9-Phenanthrol with Nitrogen Dioxide in Air

The results on the photochemical and dark reactions of phenanthrene 9,10-oxide or 9-phenanthrol with nitrogen dioxide in air are summarized in Table IV. It was observed that 9,10-phenanthrenequinone and 9-hydroxy-10-nitrophenanthrene were produced when a mixture of phenanthrene 9,10-oxide and nitrogen dioxide in air was irradiated or allowed to stand in the dark. In the case of 9-phenanthrol, the products distribution was similar to that of phenanthrene 9,10-oxide.

Table IV.[a] Products obtained by Photochemical and Dark Reactions of Phenanthrene 9,10-Oxide or 9-Phenanthrol with Nitrogen Dioxide in Air

Reactants	Products (yield)[b]
Phenanthrene 9,10-oxide + NO_2[c]	9,10-Phenanthrenequinone (35%) 9-Hydroxy-10-nitrophenanthrene (55%)
Phenanthrene 9,10-oxide + NO_2[d]	9,10-Phenanthrenequinone (41%) 9-Hydroxy-10-nitrophenanthrene (51%)
9-Phenanthrol + NO_2[c]	9,10-Phenanthrenequinone (53%) 9-Hydroxy-10-nitrophenanthrene (42%)
9-Phenanthrol + NO_2[d]	9,10-Phenanthrenequinone (81%) 9-Hydroxy-10-nitrophenanthrene (14%)

a) Phenanthrene 9,10-oxide, 44.6 μmol; 9-phenanthrol, 44.6 μmol; NO_2, 44.6 μmol.
b) Yields are based on the quantity of phenanthrene 9,10-oxide or 9-phenanthrol used.
c) On standing for 1 h in the dark.
d) Irradiated for 1 h

It is generally recognized that arene oxides readily isomerize under the influence of Brönsted (proton) and Lewis acids to the corresponding phenols.[15] Since nitrogen dioxide is regarded as a Lewis acid according to the classification of electron donors and acceptors by Mulliken,[16] nitrogen dioxide can catalyze this isomerization. Also, nitrogen dioxide is known to act as an oxidizing agent for the conversion of hydroquinones to quinones.[17] In addition, the formation of 9-hydroxy-10-nitrophenanthrene from 9-phenanthrol can be explained on the basis of the present authors' reports[18–21] that phenols react with nitrogen dioxide in air to give the corresponding nitrophenols.

On the basis of these results, the reaction of phenanthrene 9,10-oxide (**1**) with nitrogen dioxide in air can explained by the processes shown in Chart 2. Compound **1** isomerizes in nitrogen dioxide or under irradiation to 9-phenanthrol (**2**), which is partly oxidized by nitrogen

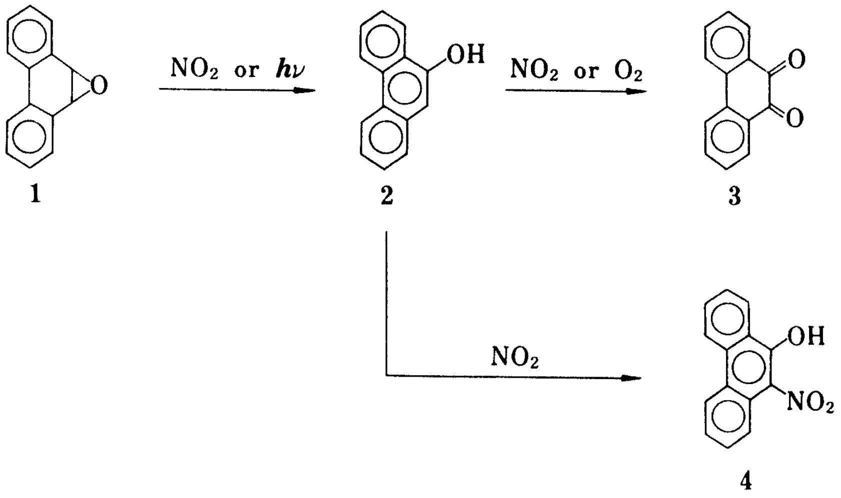

Chart 2

dioxide or oxygen in air to give 9,10-phenanthrenequinone (**3**) and partly nitrated by nitrogen dioxide to give 9-hydroxy-10-nitrophenanthrene (**4**).

Mechanism of the Photochemical Reaction of Phenanthrene with Nitrogen Dioxide in Air

On the basis of these experimental results, 9,10-phenanthrenequinone and 9-hydroxy-10-nitrophenanthrene could be formed from phenanthrene through phenanthrene 9,10-oxide as an intermediate.

Cvetanovic *et al.* reported that the arene oxide might be an intermediate in the reaction of oxygen atoms with benzene and toluene.22,23) However, the source of oxygen atoms used in their experiments was not nitrogen dioxide (NO_2), but nitrous oxide (N_2O). In other words, their experimental conditions were entirely different from atmospheric conditions, as used here.

Thus, it is suggested that nitrogen dioxide in air can act as an epoxidizing agent not only for simple olefins but also for polycyclic aromatic hydrocarbons.

Acknowledgement The authors thank Dr. T. Nagano, Pharmaceutical Sciences, Tokyo University, for providing an authentic sample of *trans*-stilbene oxide.

References and Notes

1) The main title of this series (I—VII) was "Studies on Photochemistry of Aromatic Hydrocarbons."
2) S. Jaffe and J. Keith, *J. Chem. Phys.*, **48**, 2805 (1968).
3) S. Jaffe and R.C.S. Grant, *J. Chem. Phys.*, **50**, 3477 (1969).
4) S. Jaffe, in "Chemical Reactions in Urban Atmosphere," ed. by C.S. Tuesday, Elsevier, New York, 1969, p. 103.
5) U.S. Environmental Protection Agency: Scientific and Technical Assessment Report on Particulate Polycyclic Organic Matter, EPA-600/6-74-001 (1975).
6) J.P. Wibaut and F.A. Haak, *Recl. Trav. Chim. Pays-Bas*, **67**, 85 (1948).
7) E.E. van Tamelen, *J. Am. Chem. Soc.*, **77**, 1704 (1955).
8) S. Krishnan, D.G. Kuhn and G.A. Hamilton, *J. Am. Chem. Soc.*, **99**, 8121 (1977).
9) H. Goldschmidt, *Chem. Ber.*, **16**, 2178 (1883).
10) K. Nojima, K. Fukaya, S. Fukui and S. Kanno, *Chemosphere*, **3**, 247 (1974).
11) F.E. Blacet, T.C. Hall and P.A. Leighton, *J. Am. Chem. Soc.*, **84**, 4011 (1962).
12) J. Saltiel and E.D. Megarity, *J. Am. Chem. Soc.*, **94**, 2742 (1972).
13) K.R. Darnall and J.N. Pitts, Jr., *J. Chem. Soc.*, *Chem. Commun.*, **1970**, 1305.
14) K. Shudo and T. Okamoto, *Chem. Pharm. Bull.*, **21**, 2809 (1973).
15) E. Vogel and H. Günther, *Angew. Chem.*, **79**, 427 (1967).
16) R.S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

17) A.G. Brook, *J. Chem. Soc.*, **1952**, 5040.
18) K. Nojima and S. Kanno, *Chemosphere*, **6**, 371 (1977).
19) S. Kanno and K. Nojima, *Chemosphere*, **8**, 225 (1979).
20) K. Nojima, T. Ikarigawa and S. Kanno, *Chemosphere*, **9**, 421 (1980).
21) K. Nojima and S. Kanno, *Chemosphere*, **9**, 437 (1980).
22) G. Boocock and R.J. Cvetanovic, *Can. J. Chem.*, **39**, 2436 (1961).
23) G.R.H. Jones and R.J. Cvetanovic, *Can. J. Chem.*, **39**, 2444 (1961).