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Studies on Photochemical Reactions of Air Pollutants. IX.[1] Formation of *o*-Nitrophenol and *p*-Nitrophenol by Reaction of Benzene Oxide with NO_2 in Air

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When benzene oxide was brought into contact with nitrogen dioxide in air, *o*-nitrophenol and *p*-nitrophenol were formed together with fog. Benzene oxide seems to be an intermediate in the photochemical reaction of benzene with nitrogen dioxide in air.

Keywords——benzene oxide; nitrogen dioxide; air pollutant; fog; oxygen atom; epoxidation; nitro-nitrite rearrangement; phenol; *o*-nitrophenol; *p*-nitrophenol

In the previous paper of this series, we reported that irradiation of benzene in the presence of nitrogen dioxide in air gave *o*-nitrophenol and *p*-nitrophenol as a part of the products,[2] and that nitrogen dioxide in air can act as an epoxidizing agent not only for olefins such as *trans*-stilbene, cyclohexene, 4,5-dibromocyclohexene and aldrin but also for polycyclic aromatic hydrocarbons such as phenanthrene.[1] In the formation of the nitrophenols, benzene oxide may be an intermediate, since *o*-nitrophenol and *p*-nitrophenol were also formed in the photochemical and dark reactions of benzene oxide with nitrogen dioxide in air.

Experimental

1. **Materials**——*o*-Nitroanisole, *p*-nitroanisole and maleic anhydride were supplied by Tokyo Kasei Chemical Co., Ltd. Benzene oxide was prepared from 4,5-dibromocyclohexene oxide[3] according to the method described by Vogel *et al.*[4,5] The adduct (3) of benzene oxide (1) and maleic anhydride (2) was synthesized by the method of Vogel *et al.*[5] as shown in Chart 1. Diazomethane was obtained from the reaction of *p*-tolylsulfonylmethylnitrosamide with potassium hydroxide aqueous solution.[6] Other chemicals used were purified before use, if necessary.

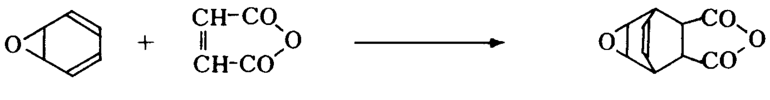

Chart 1

2. **Reaction Conditions and Preparation of Test Solutions**——2-1. Photochemical and Dark Reactions of Benzene Oxide with Nitrogen Dioxide in Air: Benzene oxide (5 µl)[7] was taken in a 1 liter reaction vessel made of Pyrex glass, and then nitrogen dioxide gas (1000 µl, 44.6 µmol) was injected into the vessel. The mixture was irradiated with a xenon lamp[8] (ozoneless type, Ushio Co.) or allowed to stand in the dark at 25—30°C for 3 h. The resulting reaction mixture was dissolved in methanol (10 ml). This solution served as the test solution (A).

2-2. Reaction of Maleic Anhydride with Photo-Products from a Mixture of Benzene and Nitrogen Dioxide in Air: Benzene (4 µl, 44.6 µmol) was taken in a 1 liter Pyrex reaction vessel, and then nitrogen dioxide gas (1000 µl, 44.6 µmol) was injected into the vessel. The mixture was irradiated with the xenon lamp at 25—30°C for 3 h. The resulting reaction mixture was dissolved in benzene (10 ml) containing maleic anhydride (22 mg, 224 µmol) and allowed to stand in the dark overnight at room temperature. The resulting reaction mixture was evaporated to dryness under reduced pressure, and then dissolved in acetone (1 ml).

This solution served as the test solution (B).

3. **Analytical Equipment**——Gas Chromatography–Mass Spectrometry (GC–MS): GC–MS was carried out with a Shimadzu LKB-9000 gas chromatograph–mass spectrometer equipped with a multiple ion detector. A coiled glass column (3 mm i.d. × 2 m) was packed with 5% Silicone SE-30 on Chromosorb WAW (60—80 mesh). The flow rate of helium was 15 ml/min. The column temperatures were kept at 160°C for nitroanisoles and 220°C for the adduct of benzene oxide and maleic anhydride. 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, 70 eV and 60 μA, respectively. When the gas chromatograph–mass spectrometer was used for mass fragmentography (MF), the ionizing voltage was adjusted to 20 eV.

4. **Analytical Procedure**——4-1. Nitrophenols: To determine nitrophenols in the test solution (A), an aliquot of the test solution was concentrated, and then treated with ethereal diazomethane overnight at room temperature. The resulting solution was concentrated, and then subjected to GC–MS.

4-2. Adduct of Benzene Oxide and Maleic Anhydride: The adduct in the test solution (B) was determined by MF.

Results and Discussion

Results on the photochemical and dark reactions of benzene oxide with nitrogen dioxide in air are summarized in Table I. It was found that *o*-nitrophenol and *p*-nitrophenol were produced when a mixture of benzene oxide and nitrogen dioxide in air was irradiated or allowed to stand in the dark, and that the irradiation did not affect the products distribution. Fog was formed on contacting benzene oxide with nitrogen dioxide in air.

TABLE I.[a] Products obtained by Photochemical and Dark Reactions of Benzene Oxide with Nitrogen Dioxide in Air

Reactants	Products (yield)[b]
Benzene oxide + NO_2[c]	*o*-Nitrophenol (16%) *p*-Nitrophenol (17%)
Benzene oxide + NO_2[d]	*o*-Nitrophenol (12%) *p*-Nitrophenol (11%)

a) Benzene oxide: 5 μl,[7] NO_2: 44.6 μmol.
b) Yields are based on the quantity of NO_2 used.
c) On standing for 3 h in the dark.
d) Irradiated for 3 h.

It is generally recognized that benzene oxide readily isomerizes under the influence of Brönsted (proton) and Lewis acids to form phenol.[9] Since nitrogen dioxide is regarded as a Lewis acid according to the classification of electron donors and acceptors by Mulliken,[10] nitrogen dioxide can catalyze this isomerization. However, Holovka and Gardner reported that photo-isomerization of benzene oxide to phenol under irradiation using a soft glass filter (λ>310 nm) does not occur.[11] We have already reported that phenol reacted with nitrogen dioxide in air to give *o*-nitrophenol and *p*-nitrophenol.[12] Therefore, the reaction process of benzene oxide (**1**) and nitrogen dioxide can be explained by the mechanisms shown in Chart 2. Compound **1** isomerizes under the influence of nitrogen dioxide to form phenol (**4**), which is nitrated with nitrogen dioxide to give *o*-nitrophenol (**5**) and *p*-nitrophenol (**6**).

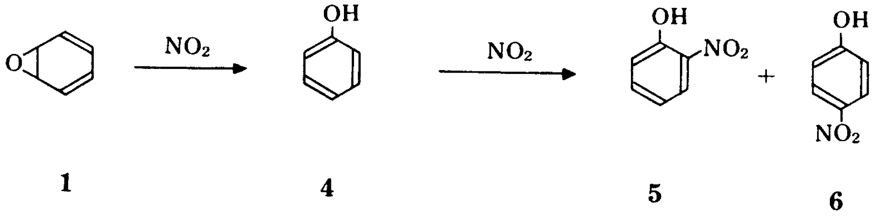

Chart 2

Thus, benzene oxide was found to be a precursor in the formation of *o*-nitrophenol and *p*-nitrophenol. We also reported that nitrogen dioxide in air can act as an epoxidizing agent not only for olefins such as *trans*-stilbene, cyclohexene, 4,5-dibromocyclohexene and aldrin, but also for polycyclic aromatic hydrocarbons such as phenanthrene.1) However, benzene oxide could not be detected in the photo-products obtained from a mixture of benzene and nitrogen dioxide in air, as shown in Fig. 1. This result suggests that benzene oxide is so reactive that it might be immediately converted into nitrophenols in the presence of nitrogen dioxide.

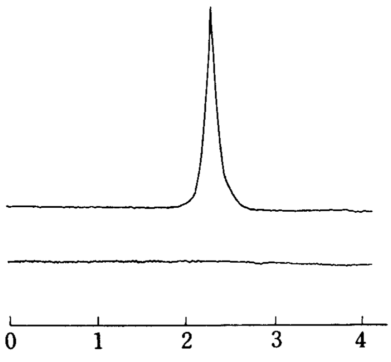

Fig. 1. Mass Fragmentogram at *m/e* 92 of the Adduct of Benzene Oxide and Maleic Anhydride

Lower line: reaction products of maleic anhydride and photo-products from a mixture of benzene and nitrogen dioxide in air.
Upper line: authentic adduct of benzene oxide and maleic anhydride.

These considerations suggest that *o*-nitrophenol and *p*-nitrophenol from benzene could be formed through benzene oxide as an intermediate. We have already clarified that *o*-nitrophenol and *p*-nitrophenol are formed through the nitro-nitrite rearrangement13,14) of nitrobenzene.12) Therefore, two processes for the formation of *o*-nitrophenol and *p*-nitrophenol can be considered, the one *via* benzene oxide and the other *via* nitrobenzene, as shown in Chart 3. The first process is: benzene is epoxidized by an oxygen atom $O(^3P)$15) resulting from the photolysis of nitrogen dioxide to form benzene oxide (**1**), followed by isomerization of **1** under the influence of nitrogen dioxide to phenol (**4**). The second one is: benzene is nitrated with nitrogen dioxide under irradiation to give nitrobenzene (**7**),12,16) followed by rearrangement of **7** under irradiation to aryl nitrite (**8**), which is hydrolyzed to form **4**. Finally **4** is nitrated with nitrogen dioxide to give *o*-nitrophenol (**5**) and *p*-nitrophenol (**6**).

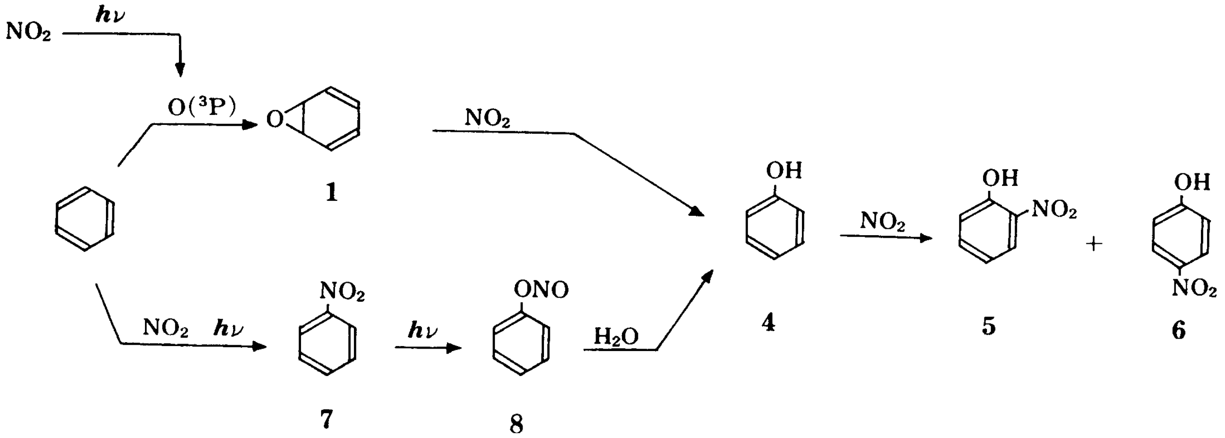

Chart 3

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