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Studies on Photochemical Reaction of Air Pollutants. X.[1] Identification of Nitrophenols in Suspended Particulates

KAZUHIRO NOJIMA,*,[a] AKIHIRO KAWAGUCHI,[b] TAKESHI OHYA,[a]
SABURO KANNO[a] and MASAAKI HIROBE[c]

Faculty of Pharmaceutical Sciences, Josai University,[a] 1-1, Keyakidai, Sakado, Saitama 350-02, Japan, Industrial Research Institute of Kanagawa Prefecture,[b] 3137, Showa-machi, Kanazawa-ku, Yokohama, Kanagawa 236, Japan and Faculty of Pharmaceutical Sciences, Tokyo University,[c] Hongo, Bunkyo-ku, Tokyo 113, Japan

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In suspended particulates collected in Yokohama over various 24-h periods, the following seven nitrophenols were detected; *o*-nitrophenol, *p*-nitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenol, 2-methyl-6-nitrophenol, 2-methyl-4-nitrophenol and 3-methyl-4-nitrophenol. These nitrophenols were also observed in smog chamber experiments carried out with benzene and toluene in the presence of nitrogen dioxide in air.

Keywords——suspended particulate; mass fragmentography; photochemical reaction; photochemical smog; nitrophenol; oxidant; nitrogen monoxide; nitrogen dioxide; high-volume sampler; automobile exhaust gas

Introduction

Investigations on polycyclic quinones and aliphatic dicarboxylic acids in suspended particulates have recently been reported by Pierce and Katz[2] and by Pitts, Jr. *et al.*,[3] respectively. They suggested that these organic compounds might be derived from the photooxidation of hydrocarbon precursors. Previously we reported that nitrophenols were formed in smog chamber experiments.[4-6] However, the presence of nitrophenols in suspended particulates has not yet been investigated. In this paper we report the identification of nitrophenols in suspended particulates collected in Yokohama, where photochemical smog has frequently been observed.

Experimental

Materials——*o*-Nitroanisole, *p*-nitroanisole, 2,4-dinitroanisole and 2,6-dinitrophenol were supplied by Tokyo Kasei Chemical Co., Ltd. 3-Methyl-4-nitroanisole was purchased from Aldrich Chemical Co., Ltd. 2,6-Dinitroanisole, 2-methyl-6-nitroanisole, 2-methyl-4-nitroanisole and 9-methoxy-10-nitrophenanthrene were prepared from 2,6-dinitrophenol, 2-methyl-6-nitrophenol,[7] 2-methyl-4-nitrophenol[7] and 9-hydroxy-10-nitrophenanthrene,[6] respectively, by reaction with ethereal diazomethane[8] in methanol. Other chamicals used were purified before use, if necessary.

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 (3 mm i.d. ×2 m) was packed with 5% Silicone SE-30 on Chromosorb WAW (60—80 mesh). The flow rate of carrier gas (helium) was 20 ml/min. The column temperatures were kept at 160°C for nitroanisoles, 190°C for dinitroanisoles and 230°C for 9-methoxy-10-nitrophenanthrene. The injection, separator and ion source were kept at 250, 250 and 290°C, respectively. The accelerating voltage, ionizing voltage and trap current were set at 3.5 kV, 20 eV and 60 μA, respectively. Other conditions are described later.

Preparation of Test Solution from Suspended Particulates for MF——Suspended particulate samples were collected on GB-100R glass fiber filters using a high-volume sampler over various 24-h periods on the campus of the Industrial Research Institute of Kanagawa Prefecture, and were extracted for 5 h with 0.1 N sodium hydroxide aqueous solution (150 ml). The extract was filtered, and the filtrate was washed with ethyl ether (50 ml) twice. The aqueous fraction was acidified with 1 N sulfuric acid aqueous solution (20 ml) and extracted with ethyl ether (50 ml). The resulting ethyl ether layer was washed with distilled water (50 ml), dried over anhydrous sodium sulfate, and concentrated. The residue was treated with ethereal diazomethane (7 ml) in methanol (1 ml) overnight at room temperature, and then the reaction mixture was concentrated to 2 ml. The resulting solution served as the test solution for MF.

Preparation of Test Solution from Vehicular Exhaust Gas for MF——Vehicular exhaust gas was bubbled through 0.5 N sodium hydroxide aqueous solution (100 ml) for 15 min at a flow rate of 1 l/min. The resulting aqueous solution was washed with ethyl ether (50 ml) twice. The aqueous fraction was acidified with 5 N sulfuric acid aqueous solution (15 ml) and extracted with ethyl ether (50 ml). The resulting ethyl ether layer was washed with distilled water (50 ml) twice and treated as mentioned above. The resulting solution served as the test solution for MF.

Analysis——Five microliters of a test solution for MF was injected into the gas chromatography–mass spectrometer under the conditions described above, and the mass fragmentogram of each nitroanisole derivative was obtained. Determination of each nitroanisole derivative in the test solution was carried out by referring to the calibration curve obtained from standards containing 0.025, 0.050, 0.100 and 0.125 μl gas (0°C, 760 mmHg)/ml of each nitroanisole derivative in methanol.

Results and Discussion

Seven nitrophenols including *o*-nitrophenol (I), *p*-nitrophenol (II), 2,6-dinitrophenol (III), 2,4-dinitrophenol (IV), 2-methyl-6-nitrophenol (V), 2-methyl-4-nitrophenol (VI) and 3-methyl-4-nitrophenol (VII) were detected in suspended particulates collected in Yokohama, where photochemical smog has frequently been observed. 9-Hydroxy-10-nitrophenanthrene (VIII) was not detected during the measurements. The structures of these nitrophenols (I—VIII) are shown in Fig. 1. The content of each nitrophenol is shown in Table I. The authors have already reported that these nitrophenols (I—VIII) were obtained by the photochemical reactions of aromatic hydrocarbons such as benzene, toluene and phenanthrene with nitrogen

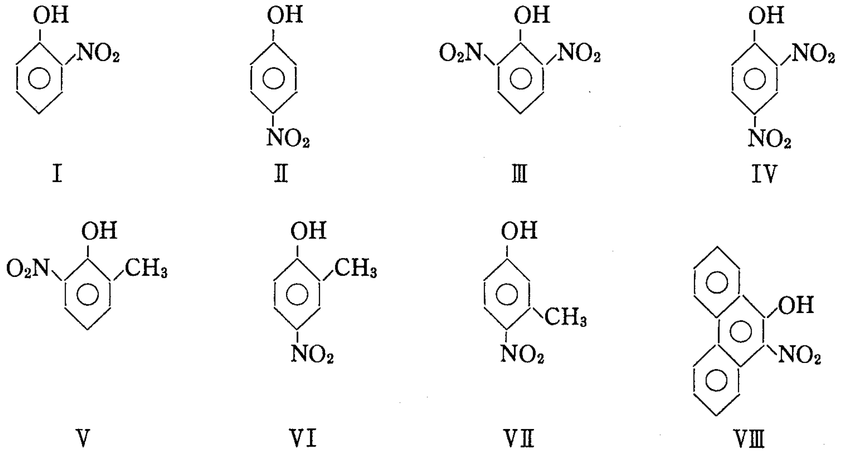

Fig. 1. Chemical Structures of Nitrophenols obtained from Photochemical Reactions of Aromatic Hydrocarbons with Nitrogen Dioxide in Air

Table I. Nitrophenols in Suspended Particulates

Day	Particulate (mg/d)	Nitrophenols (μg/g particulate)							
		I	II	III	IV	V	VI	VII	VIII
1982									
5/24—5/25	28.7	ND[a]	5.1	3.0	2.4	0.52	1.9	1.7	ND[a]
5/25—5/26	28.1	ND[a]	7.3	3.2	2.6	1.1	3.0	2.7	ND[a]
5/26—5/27	54·2	Tr[b]	42	3.7	4.5	2.7	18	4.2	ND[a]
5/27—5/28	67.0	3.9	10	5.8	12	0.75	4.0	1.2	ND[a]
5/28—5/29	62.7	3.4	8.0	9.2	6.0	0.67	2.6	0.35	ND[a]

a) Not detected. b) Tr$<$0.05 μg/g particulate.

dioxide in air.4—6) Some typical mass fragmentograms of the methylated nitrophenols are shown in Figs. 2—5. Among these nitrophenols, the contents of *p*-nitrophenol (II) and 2-methyl-4-nitrophenol (VI) in the particulates of May 26—27 were high. These two compounds had been detected in rain collected in Yokohama during photochemical smog episodes (July 21, 1975), as already reported in a previous paper.5) These results might be related to the

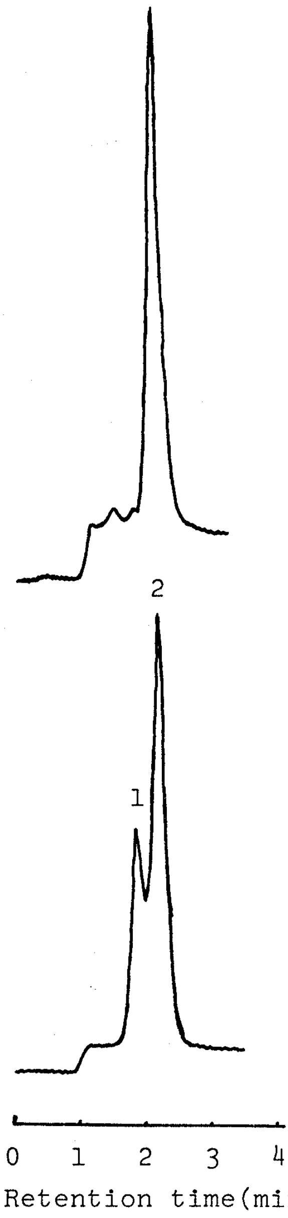

Fig. 2. Mass Fragmentogram, at *m/e* 153, of Nitroanisole

Lower line: authentic *o*-nitroanisole (peak 1) and *p*-nitroanisole (peak 2).
Upper line: methyl derivatives of nitrophenols in suspended particulates (May 26—27, 1982).

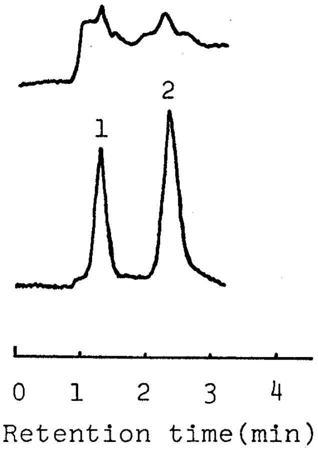

Fig. 3. Mass Fragmentogram, at *m/e* 198, of Dinitroanisole

Lower line: authentic 2,6-dinitroanisole (peak 1) and 2,4-dinitroanisole (peak 2).
Upper line: methyl derivatives of nitrophenols in suspended particulates (May 26—27, 1982).

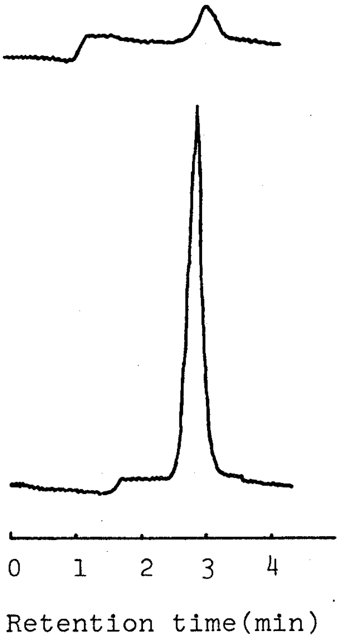

Fig. 4. Mass Fragmentogram, at *m/e* 253, of 9-Methoxy-10-nitrophenanthrene

Lower line: authentic 9-methoxy-10-nitrophenanthrene.
Upper line: methyl derivatives of nitrophenols in suspended particulates (May 26—27, 1982).

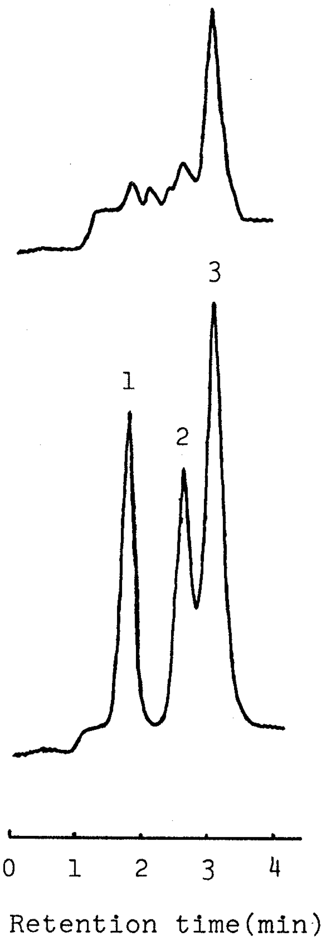

Fig. 5. Mass Fragmentogram, at *m/e* 167, of Methylnitroanisole

Lower line: authentic 2-methyl-6-nitroanisole (peak 1), 3-methyl-4-nitroaniole (peak 2) and 2-methyl-4-nitroanisole (peak 3).
Upper line: methyl derivatives of nitrophenols in suspended particulates (May 26—27, 1982).

fact that *p*-nitrophenol (II) and 2-methyl-4-nitrophenol (VI) were the main nitrophenols obtained by the photochemical reactions of benzene and toluene, respectively, with nitrogen dioxide in air.[4,5]

We investigated whether there is any correlation between the contents of the two nitrophenols (II and VI) and the concentrations of oxidants, nitrogen monoxide (NO) and nitrogen dioxide (NO_2), which are shown in Table II. There was a high correlation between the contents of the nitrophenols and the concentration of NO (II, $r=0.972$; VI, $r=0.971$). However, the concentration of oxidants or NO_2 was not significantly correlated with the contents of the two nitrophenols (II and VI).

TABLE II. Contents of Nitrophenols (II and VI) and Concentrations of Oxidants, NO and NO_2

Day	Nitrophenol (μg/d)		Oxidants (ppm)[a]	NO (ppm)[a]	NO_2 (ppm)[a]
	II	VI			
1982			Ave	Ave	Ave
5/24—5/25	0.147	0.055	0.0442	0.00675	0.0251
5/25—5/26	0.205	0.084	0.0287	0.00854	0.0270
5/26—5/27	2.278	0.976	0.0282	0.01338	0.0306
5/27—5/28	0.670	0.268	0.0528	0.00910	0.0332
5/28—5/29	0.503	0.163	0.0367	0.00860	0.0228

[a] These data were supplied by the Government of Kanagawa Prefecture, Yokohama, Kanagawa.

Subsequently, nitrophenols in automobile exhaust gas were examined to determine whether they might contribute to those in suspended particulates. Results on the concentrations of nitrophenols (I—VIII) in vehicular exhaust gas are shown in Table III. Four nitrophenols[*o*-nitrophenol (I), *p*-nitrophenol (II), 2,6-dinitrophenol (III) and 2,4-dinitrophenol (IV)] were detected, and their distribution did not appear to be affected by the type of engine. As shown in Table I and III, the distribution of nitrophenols in suspended particulates was not similar to that of nitrophenols in automobile exhaust gas.

TABLE III. Nitrophenols in Vehicular Exhaust Gas[a]

Type	Nitrophenols (ppb)							
	I	II	III	IV	V	VI	VII	VIII
Gasoline engine[b]	3.1	Tr[d]	13	2.1	ND[e]	ND[e]	ND[e]	ND[e]
Diesel engine[c]	6.4	2.5	10	2.7	ND[e]	ND[e]	ND[e]	ND[e]

[a] Engine idling. [b] Crown 2600 cc (Toyota, 1975). [c] Fuso bus 7000 cc (Mitsubishi, 1981). [d] Tr<. 0.5 ppb. [e] Not detected.

On the basis of these experimental results and considerations, it is suggested that nitrophenols in suspended particulates originate mostly from secondary photochemical reactions in the atmosphere and partly from primary emission of automobile exhaust gas.

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