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ANALYTICAL STUDY OF LOW-CONCENTRATION GASES

IV*. INVESTIGATION OF THE REACTION BY TRAPPING NITROGEN DIOXIDE IN AIR USING THE TRIETHANOLAMINE METHOD

TAIKI AOYAMA*
Environmental Pollution Research Institute, 1–14, Chudo-cho, Minami-ku, Nagoya City (Japan)
and
TAMOTSU YASHIRO
Faculty of Pharmaceutical Sciences, Nagoya City University, 3-1, Tanabe-dori, Mizuho-ku, Nagoya City (Japan)
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SUMMARY

An investigation was made of the absorption of nitrogen dioxide (NO_2) by the triethanolamine (TEA) plate method, which is simple for determination of NO_2 in air.

NO_2 generated from a permeation tube was exposed to a TEA plate and to TEA-coated glass beads. One of the reaction products was found to be N-nitrosodiethanolamine (NDEA). It was also detected on a TEA plate subjected to exposure to NO_2 in air, as in the case with the permeation tube reaction. The product was positive to the Liebermann nitroso reaction, and the product and NDEA synthesized by NO_2 and diethanolamine were identified by gas chromatography, gas chromatography–mass spectrometry and UV spectrometry.

INTRODUCTION

Nitrogen dioxide (NO_2) concentrations in air have been determined by the Saltzmann method[1], the Jacobs and Hochmeister method[2] and the modified Jacobs and Hochheiser method[3]. Because of the instruments and manpower required, however, it is difficult to use these methods to gain an understanding of the present situation with regard to the widespread air pollution by automobile exhausts. The triethanolamine (TEA) filter method and the plate method, reported by Levaggi *et al.*[4], are simple methods for the determination of relative degrees of NO_2 pollution. These methods, however, left many problems unsolved, such as susceptibility to meterological conditions. We have now investigated the reaction of TEA and NO_2 in

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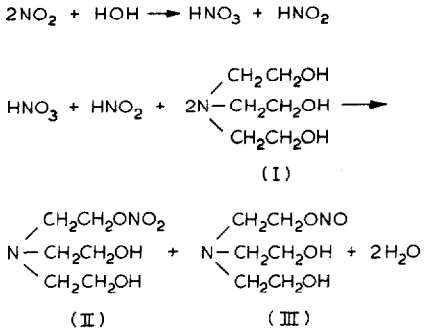
order to make the TEA plate method a simpler, more established method for the determination of NO_2.

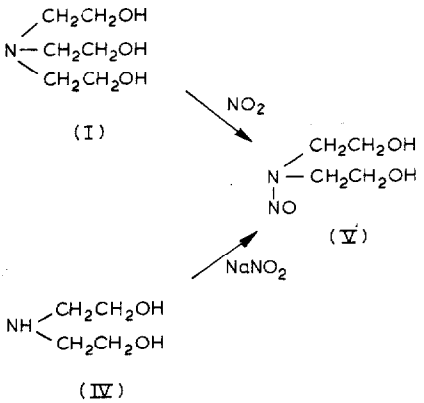
Concerning the trapping reaction of NO_2 in TEA, Levaggi *et al.*[4] reported that, as shown in Scheme 1, TEA (I) would be trapped to produce triethanolamine nitrate (II) and triethanolamine nitrite (III). However, there is also a report that, unlike unsubstituted aliphatic alcohols, nitrogen-containing aliphatic alcohols do not readily form nitrite esters[5]. We have attempted the esterification of three amine compounds, mono-, di- and triethanolamine, with sodium nitrite under various conditions but no esters could be obtained.



Scheme 1.

Gold[6] has reported that an aqueous solution of TEA reacted with NO_2 to form the nitrate of TEA via an unstable nitrosoammonium salt in the solution. However, it is difficult to regard the product as the nitrate of TEA because the dichloromethane extract of the product gave a peak other than TEA on gas chromatography. Fan *et al.*[7] reported the presence of nitrosodiethanolamine (NDEA) in human hepatic cancer caused by cutting oil and Kawano *et al.*[8] reported the easy formation of NDEA by reacting TEA in cutting oil with sodium nitrite.

We expected NDEA to be formed by the reaction of TEA with NO_2 and identified it by gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS) and other methods. NDEA synthesized from sodium nitrite and diethanolamine was identified qualitatively. The outline is reported in Scheme 2.



Scheme 2.

EXPERIMENTAL

Apparatus

A Shimazu 5A gas chromatograph, a Nippon Denshi JMS-D300/JMA-200 gas chromatograph–mass spectrometer, a Shimazu UV-210A UV spectrophotometer and a Gastec PD-1B standard gas generator were used.

Reagents

All reagents were of special grade.

Triethanolamine and diethanolamine were obtained from Tokyo Kasei, sodium nitrite from Wako and dichloromethane (for pesticide residue analysis grade), ethanol (for precise analysis grade), pyridine and acetic anhydride from Katayama. The permeation tube (NO_2-H type) was purchased from Gastec and glass beads (GB 733) from Gaschro.

Preparation of TEA plate[9]

A 2-ml volume of 20% TEA solution was mixed with 15 g of 250–300-mesh glass beads, then 25 g of the mixture were placed on a plate prepared by attaching a glass disk, 80 mm in diameter, to the bottom of a commercial glass laboratory dish, 60 mm in diameter. The plate was dried at 70–80°C to constant weight.

Absorption of NO_2 in TEA

A 1-g amount of TEA was dissolved in 30 ml of dichloromethane, into which 10 g of glass beads were placed, and the solvent was distilled off under reduced pressure. Five grams of the TEA-coated glass beads, 3–5 mm in diameter, were placed in the apparatus as shown in Fig. 1. NO_2 generated from the permeation tube in the apparatus as shown in Fig. 2 was exposed to the glass beads at a flow-rate of 1 l/min for about 3 h. The concentration of NO_2 generated from the permeation tube was about 10 ppm and exposure was carried out for 3 h. The TEA plate was placed in a 500-ml three-necked flask as shown in Fig. 3, in which NO_2 was exposed to the plate as with the glass beads.

Acetylation of TEA and NO_2-trapped product

Takeuchi *et al.*[10] determined NDEA in cosmetics using a thermal energy analyser, a high-performance liquid chromatograph, a gas chromatograph with an electron-capture detector and a gas chromatograph–mass spectrometer after the NDEA had been acetylated. We acetylated TEA and the NO_2-trapped product in accordance with the method of Takeuchi *et al.*[10]. Five grams of glass beads were reacted with NO_2 and the late contents prepared in accordance with the method of Sato *et al.*[9] were placed in each beaker. A 300-mg amount of ammonium sulphate and 30 ml of acetonitrile were placed in the beakers, and the contents were stirred for 10 min to remove unreacted NO_2. Then 10 g of anhydrous sodium sulphate were added and the mixture was stirred for 5 min and then filtered. The residues were washed with two 10-ml portions of acetonitrile and the washings were combined with the filtrates. The filtrates were concentrated to about 0.5–1 ml under reduced pressure at a temperature below 30°C and the solvent was distilled off under the same conditions as in the concentration step. Acetic anhydride and absolute pyridine (1 ml of each) were added

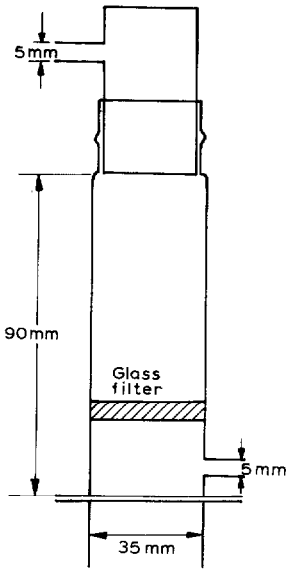


Fig. 1. Absorption tube.

to the residues, which were allowed to stand for 30 min at 60°C or overnight at room temperature prior to use as the test solutions.

Preparation of N-nitrosodiethanolamine

NDEA was synthesized from DEA and sodium nitrite according to the methods of Uno *et al.*[11] and Kawano *et al.*[8], because a commercial preparation was difficult to obtain. DEA (100 mg) was weighed into a 300-ml erlenmeyer flask, to which 5 ml of acetic acid was added to dissolve the DEA. To the solution were added gradually 2 ml of an aqueous solution of sodium nitrite with stirring at 30°C for 15 min to effect a nitroso reaction. After completion of the reaction, 2% urea solution was added to decompose the excess of sodium nitrite. Ethanol was added to the solution after it had been allowed to stand for a while and no bubbles were observed. The solution was distilled in a stream of nitrogen under reduced pressure to remove the solvent. The process was repeated several times until no odour of acetic acid was perceptible.

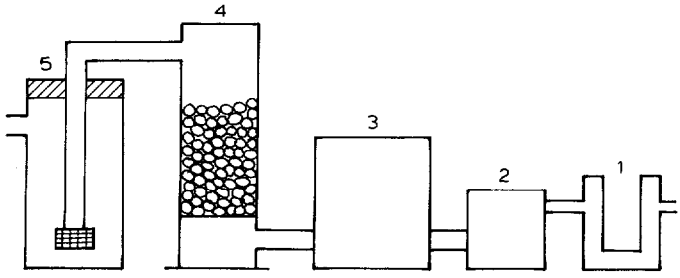


Fig. 2. Apparatus for absorption of NO_2 stream into TEA on glass beads. 1 = Drying tube (charcoal + $CaCl_2$); 2 = diaphragm pump; 3 = NO_2 generator; 4 = absorber; 5 = bubbler (NaOH solution).

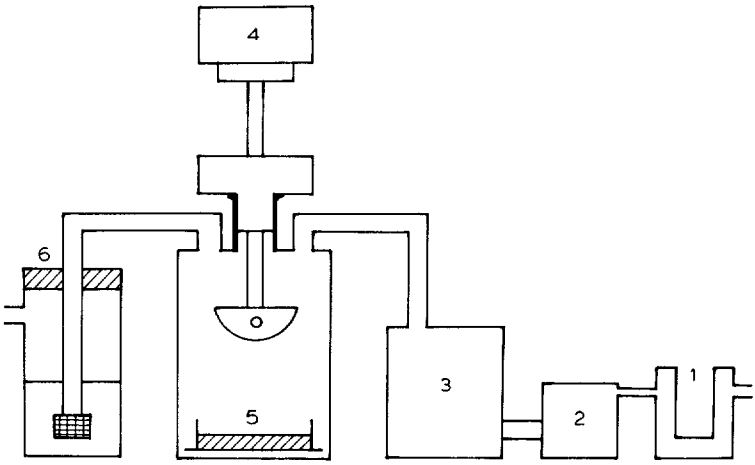


Fig. 3. Apparatus for absorption of NO_2 stream on TEA plate. 1 = Drying tube (charcoal + $CaCl_2$); 2 = diaphragm pump; 3 = NO_2 generator; 4 = motor; 5 = TEA plate; 6 = bubbler (NaOH solution).

RESULTS AND DISCUSSION

Gas chromatographic analysis

Figs. 4 and 5 show the gas chromatograms of TEA, DEA, NDEA and NO_2-exposed glass beads that had been treated by the methods described above. The GC operating conditions were as follows: glass column (2 m × 3 mm I.D.), 1.5% OV-17

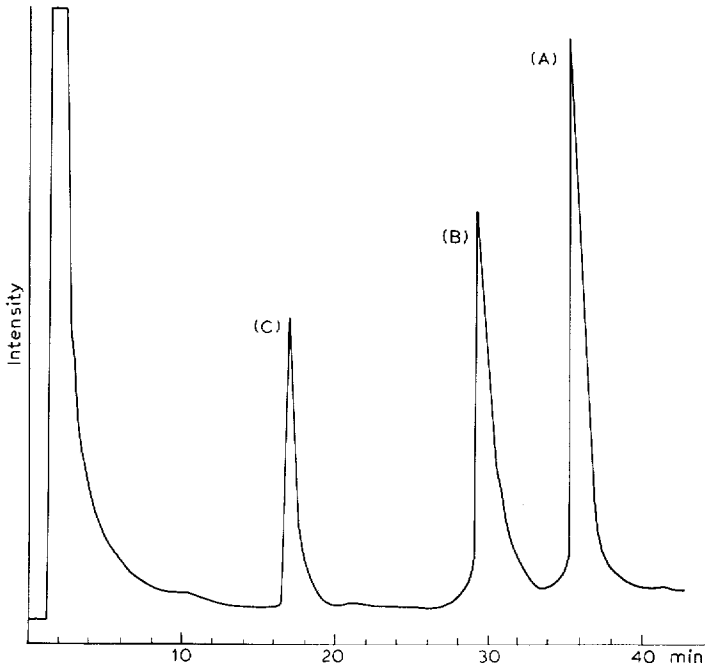


Fig. 4. Gas chromatogram of acetyl derivatives. A, TEA; B, DEA; C, NDEA.

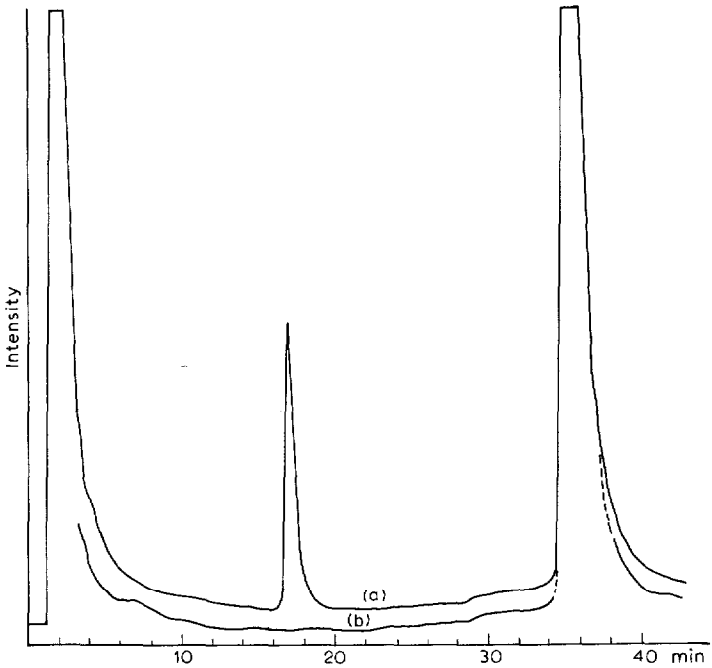


Fig. 5. Gas chromatograms of (a) reaction product and (b) blank.

Chromosorb W (60–80 mesh); column temperature, 130°C; injection temperature, 200°C; flow-rates, nitrogen 1 kg/cm^2, hydrogen 60 ml/min, air 0.8 l/min; detector, FID.

The gas chromatogram of the plate contents treated similarly was in agreement with that of the glass beads. A peak that was not observed with the blank extracts appeared at a retention time of 17 min. This peak suggested the formation of a substance other than TEA by the reaction of NO_2 with TEA. Peak A (Fig. 5) was expected to correspond to NDEA. The gas chromatogram of the acetylated NDEA synthesized from DEA and $NaNO_2$ was in good agreement with the gas chromatogram in Fig. 5 with regard to the retention time. Although the NDEA was expected to be the reaction product of DEA as an impurity in TEA with NO_2, the peak developed here was larger than that in the gas chromatogram of impurity-free TEA. For this reason, NDEA was considered to be the reaction product of TEA, but not of DEA, with NO_2.

Identification by gas chromatographic–mass spectrometric analysis

The mass spectrum of peak A (Fig. 5) was measured because the reaction product would be insufficiently identified by the GC retention time alone. The conditions were as follows: glass column (2 m × 2 mm I.D.), 1.5% OV-17 on Chromosorb W (60–80 mesh); column temperature, 130°C; injection temperature, 200°C; flow-rate (helium), 1.5 kg/cm^2; ionizing current, 100 μA; ionizing voltage, 20 eV; ion source temperature, 220°C. The results are shown in Fig. 6.

The mass spectrum in Fig. 6 has peaks corresponding to the molecular ion,

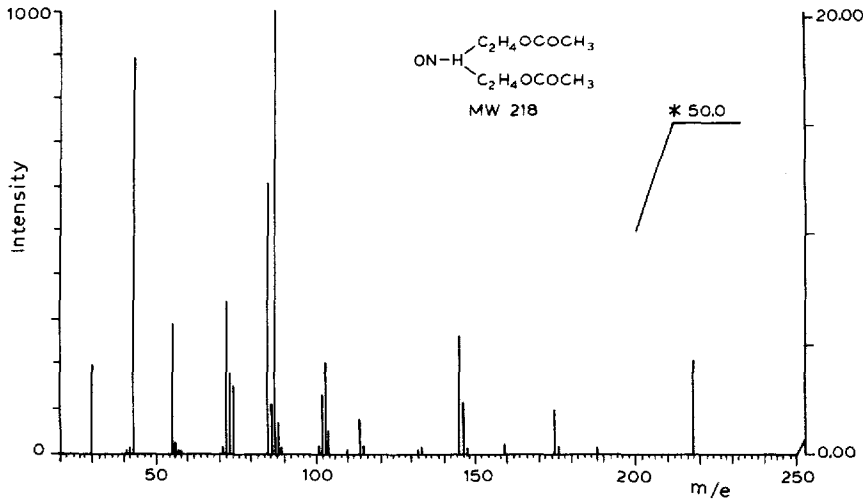


Fig. 6. Mass spectrum of NDEA (acetyl derivative).

elimination of CH_3CO and elimination of CH_3CO and NO at *m/e* 218, 175 and 145, respectively. The spectrum has a fragment ion at *m/e* 103 ($M - CH_2^+ = OH$) caused by α-cleavage of the alkyl chains characteristic of nitrosoamines and a fragment ion at *m/e* 72 (*m/e* 103 − HNO) caused by the subsequent elimination of HNO. A fragment ion at *m/e* 30, probably attributable to NO, was also observed. Peak A was thus confirmed as the diacetylated derivative of NDEA.

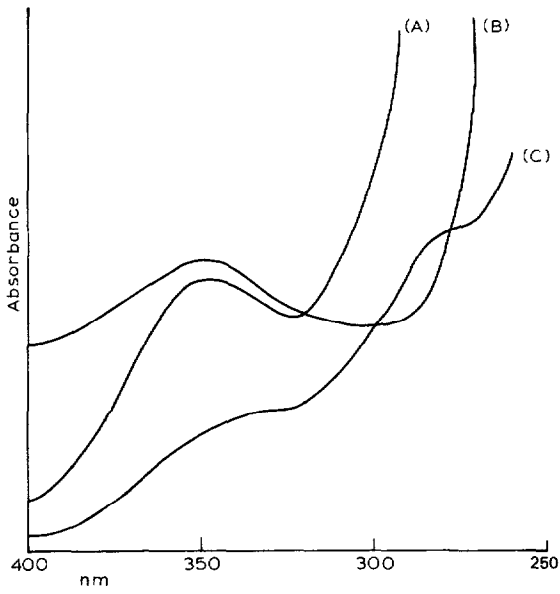


Fig. 7. UV absorption spectrum of (A) N-nitrosodiethanolamine, (B) N-nitrosodiethylamine and (C) reaction product.

UV spectroscopic analysis

The reaction product of TEA with NO_2 was extracted with dichloromethane, which was distilled off in a stream of nitrogen under reduced pressure. The residue was dissolved in 10 ml of ethanol to use for UV spectroscopic analysis. NDEA and separately synthesized NDEA were also treated in a similar way. The λ_{max} values obtained were NDEA 350 nm, N-nitrosodiethylamine 350 nm and the dichloromethane extracted solution 350 and 285 nm. From these results and Fig. 7 it can be seen that both of these substances exhibited an absorption at 350 nm, probably attributable to NO.

Qualitative analysis of the nitroso group by the Liebermann reaction

Although the presence of the nitroso group was confirmed from the above results to some degree, the Liebermann nitroso reaction was carried out to identify the nitroso compound. A 2-ml volume of the chloroform extract was distilled in a stream of nitrogen under reduced pressure to remove the solvent, 0.05 g of phenol was added to the residue and the mixture was heated for 30 sec. After the residue had been cooled, 1 ml of concentrated sulphuric acid was added to it, which turned it dark green. The sulphuric acid solution was poured into 30–50 ml of cold water, to which 3% sodium hydroxide solution was added to make it alkaline. It assumed a dark green colour. The NDEA synthesized separately and the N-nitrosodiethylamine developed a dark green colour similar to the dichloromethane extract. Sodium nitrite gave a dark blue colour. The nitroso compound produced by the reaction of TEA and NO_2 was thus confirmed as an N-nitroso compound.

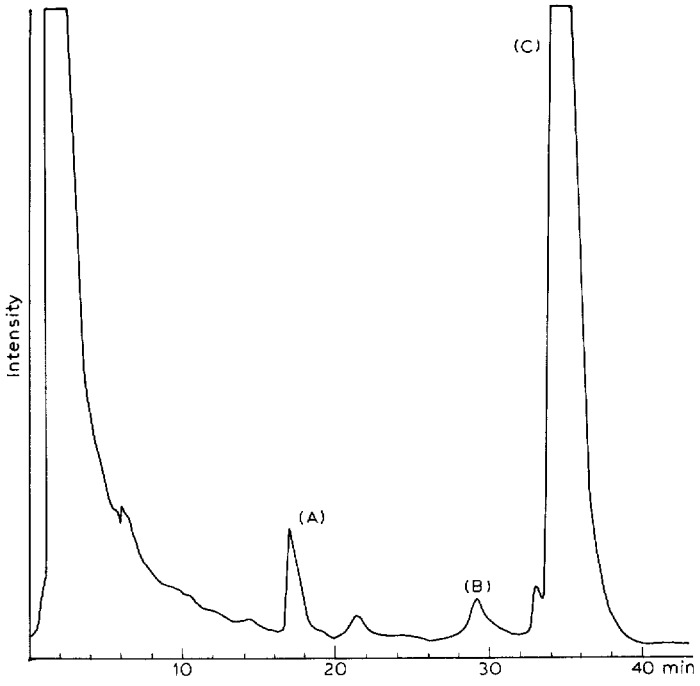


Fig. 8. Gas chromatogram obtained after air sampling. A, NDEA; B, DEA; C, TEA.

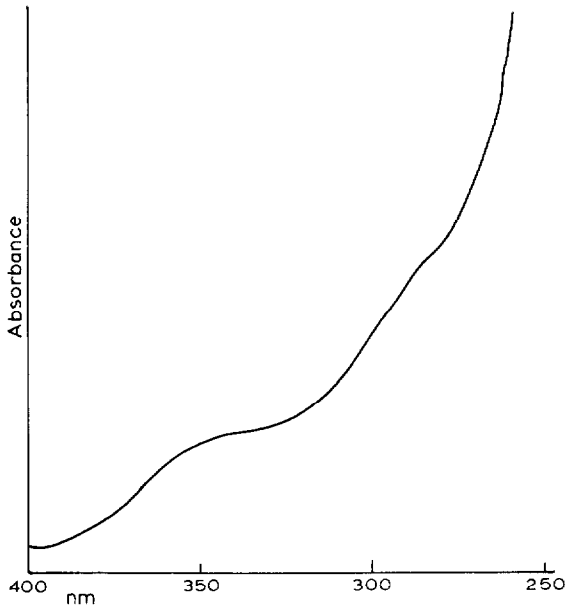


Fig. 9. UV absorption spectra obtained after air sampling.

Qualitative analysis of the product from absorption of NO_2 in air

Fig. 8 shows the gas chromatogram of the acetylated derivative, treated in the above way, of the contents of the TEA plate exposed to NO_2 in air for 3–5 days. These results are in good agreement with those in Fig. 4, which shows the presence of peaks of the acetylated derivatives of NDEA and DEA. Fig. 9 shows the UV absorption spectrum of the dichloromethane extract of the plate contents. It has a peak at 350 nm similar to the absorption wavelength of NO in Fig. 7. These results confirm qualitatively that NO_2 in air was absorbed into TEA in the form of an N-nitroso compound.

CONCLUSION

The results of this study suggested the presence of a product identical with that obtained by exposing NO_2 in air to the TEA plate. The product was qualitatively confirmed to be NDEA. However, the presence of other products was expected and NDEA was regarded as one of the products. Although it is generally determined by using a thermal energy analyser, high-performance liquid chromatography or GC with an electron-capture detector, GC with a flame-ionization detector is also suitable.

ACKNOWLEDGEMENTS

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