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Reaction of Alcohol with NO_2 on a Cleaned Glass Surface

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Formation of alkyl nitrite from alcohol and NO_2 was very fast on a Pyrex glass surface cleaned with chromic acid mixture. The reaction was practically zero order with respect to alcohol and second order with respect to NO_2. The rate constant was $(1.7\pm0.08) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} for methyl nitrite formation and the apparent activation energy was -53.5 kJ mol^{-1}.

Recently, alcohol has attracted attention as a clean alternative fuel and the emission of unburned alcohol from the combustion process is estimated to increase in urban areas. Therefore, it seems to be the pressing need to elucidate the behavior of alcohols in ambient air. It is well known that alcohol reacts with NO_2 to form alkyl nitrite according to the reaction (1).[1]

$$ROH + 2\ NO_2 \longrightarrow RONO + HNO_3 \qquad (1)$$

Alkyl nitrite is important in photochemical smog formation since it accelerates ozone formation by providing OH radical on UV irradiation.[2] The reaction (1) has been reported to be very slow.[3,4] However, we found that the reaction was influenced by the surface of the reaction vessel and it became very fast on the glass surface which was cleaned with chromic acid mixture.

Definite amounts of methyl alcohol and NO_2 were taken into an evacuated reaction vessel and the vessel was filled up with air to obtain the mixture of methyl alcohol at 500 ppb and NO_2 at 200 ppm on a volume/volume basis, respectively. The vessel was allowed to stand at room temperature in the dark and methyl nitrite produced in the reaction mixture was determined with the lapse of time by gas chromatography with a column packed with 10% tricresyl phosphate coated on Chromosorb W-AW-DMCS and an electron capture detector. The results are

shown in Fig. 1. The formation of methyl nitrite was extremely slow in a Teflon bag and also slow in a Pyrex glass bottle the inner surface of which had been cleaned with phosphoric acid, but tremendously fast in a Pyrex glass bottle the inner surface of which had been cleaned with chromic acid mixture. The same result was obtained with a quartz bottle. The cleaning was carried out as follows. The reaction vessel was filled with chromic acid mixture and allowed to stand for 1 h. The mixture was drained out and the vessel was rinsed successively with tap and deionized water until chromium could not be detected. The vessel was dried at 100 °C for 3 h. The absence of chromium on the cleaned surface was confirmed by atomic absorption spectrometry on the solution obtained by dissolving the surface of the Pyrex glass thus rinsed. Curve 1 gave a termolecular rate constant

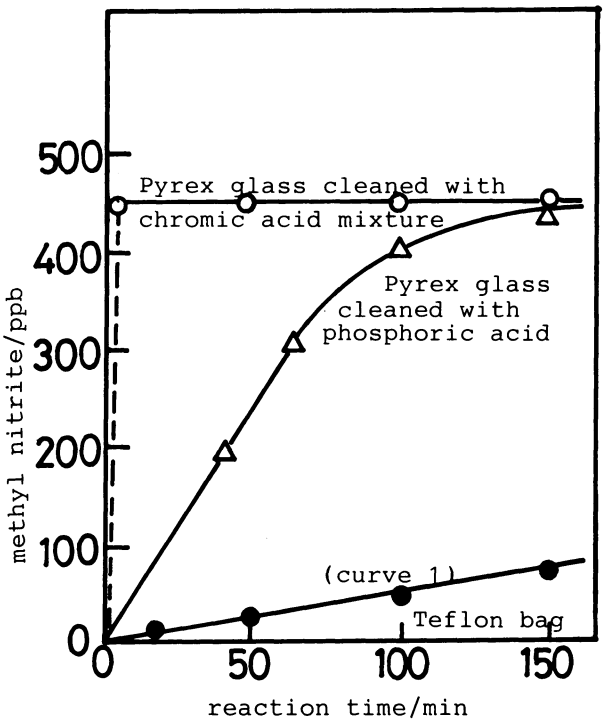

Fig. 1. Time profile of the formation of methyl nitrite.

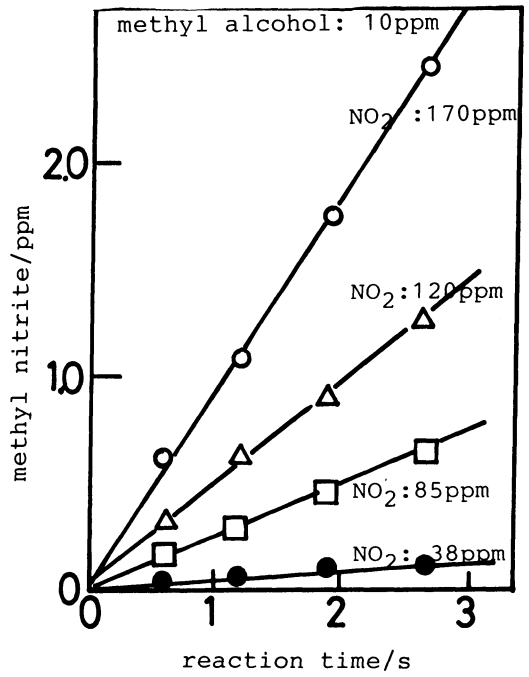

Fig. 2. Formation of methyl nitrite in the heterogeneous reaction.

of $(0.98\pm0.08) \times 10^{-36}$ cm^6 $molecule^{-2}$ s^{-1} for methyl nitrite formation at 25 °C and this value is in good agreement with those reported by Niki et al. ($(0.57\pm0.06) \times 10^{-36}$ cm^6 $molecule^{-2}$ s^{-1}).[5] The rate constant on the Pyrex glass surface cleaned with chromic acid mixture was determined by flow method. An air stream containing 10 ppm of methyl alcohol was mixed with an air stream containing various concentration of NO_2 and the mixture was passed through a Pyrex glass tube the inner surface of

which had been cleaned with chromic acid mixture. Samples were withdrawn at several sites along the tube and analyzed for methyl nitrite. The results are shown in Fig. 2. The rate depended on the 0.12 power of methyl alcohol concentration and on the 1.88 power of NO_2 concentration. These dependency may suggest that the rate determining step is the reaction of two molecules of nitrogen dioxide on the glass surface. The second order rate constants at 25 °C were determined to be $((1.7\pm0.08) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) on a Pyrex glass and $((1.5\pm0.07) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) on a quartz which was known to be inactive for the formation of alkyl nitrite.[6] And this value is more than 20 times larger than that of heterogeneous reaction of methyl alcohol with NO_2 on SUS reported by Takagi et al.[6] The Arrhenius plot based on the data in temperature range from 0 °C to 50 °C gave the apparent activation energy of -53.5 kJ mol^{-1}. This value is in fairly good agreement with the value -67 kJ mol^{-1} reported by Fairlie et al. [7]

When the cleaned surface of the Pyrex glass tube was exposed to air containing 100 ppm of ammonia, the formation reaction of methyl nitrite was retarded as shown in Fig. 3. This result suggests that the formation of alkyl nitrite takes place on the acidic sites of cleaned surface of Pyrex glass.

The formation of alkyl nitrite was quantitative with respect to the concentration of methyl, ethyl, isopropyl, n-propyl, isobutyl, t-butyl, and n-butyl alcohols in the presence of excess NO_2. This quantitative relationship can be used for the determination of these alcohols in the gas phase at ppb level and the study in this aspect is now in progress.

In conclusion, the formation of alkyl nitrite from alcohol and NO_2 is very fast via a heterogeneous pathway and, therefore, its formation in ambient air from exhaust emission from vehicles fueled with methyl alcohol may not be precluded as suggested by Jonsson and Bertilsson[3] on the basis

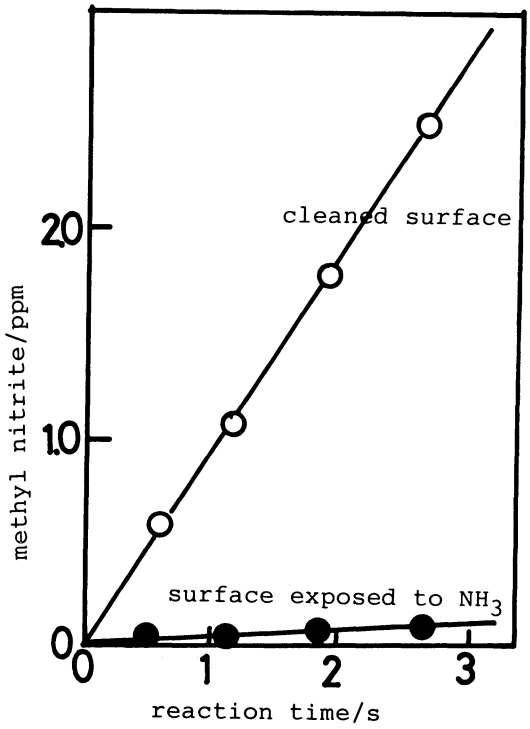

Fig. 3. Deactivation of Pyrex glass surface with ammonia.

of homogeneous reaction rate. A fast heterogeneous reaction might take place on particulates on which SO_2, sulfuric acid, NO_2, or nitric acid is adsorbed.

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