CHEMISTRY LETTERS, pp. 237-240, 1977. Published by the Chemical Society of Japan

THE COLOR REACTION OF POLYVINYLCARBAZOLE WITH NITROGEN DIOXIDE AND ITS APPLICATION FOR THE DETECTION OF NITROGEN DIOXIDE

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Polyvinylcarbazole reacts selectively with nitrogen dioxide and develops a yellow color. The color producing components are identified to be nitro derivatives of the polymer. A new indicator tube developed as an application of this reaction will be used conveniently for the detection of nitrogen dioxide in the field of industrial hygiene.

In the fields both of industries and of air pollution control, N-containing copolymers have been examined as the specific absorbents for the removal of, and for the detection of nitrogen dioxide and sulfur dioxide in air. For example, a porous crosslinking copolymer of ethylvinyl benzene and divinyl benzene (Porapak Q) is examined as the rapid preferential absorbent of nitrogen dioxide from air[1], and porous crosslinked copolymers of various ethylvinyl pyridine and divinyl benzene[2] and m-aminophenol condensation resins[3] are examined as the specific absorbents for removing NO_2 or SO_2 contamination in an atmosphere. Up to now, however, no information is available on the effect of nitrogen dioxide on polyvinylcarbazole (PVCZ).

In this letter, I wish to report on the selective color reaction of PVCZ with nitrogen dioxide and on the possibility of its application to the detection of nitrogen dioxide in air.

A film of PVCZ (purified by chloroform-acetone) prepared by the evaporation of the PVCZ chloroform solution to dryness, was thin enough (approx. 20-40 μ). The film was exposed to 1 atm N_2 in the presence of NO_2 or of various test gases in a sampling flask about 1.2 ℓ in volume, (see Fig. 1) at room temperature. Test gases were prepared to the desired concentration in the sampling flask by using a McLeod gauge when the pressures were low or a Bourdon tube gauge resistant to NO_2 (Nagano Keiki Seisakusho Ltd, model NKS-GS 35-141) when the pressures were high. As NO_2 reacts with mercury, test gases with high concentrations of NO_2 in N_2 were prepared by repeated dilution in N_2 and the test gas with relatively low concentration of NO_2 in N_2 (approx. 100 ppm) was the product of Takachiho Kagaku Co..

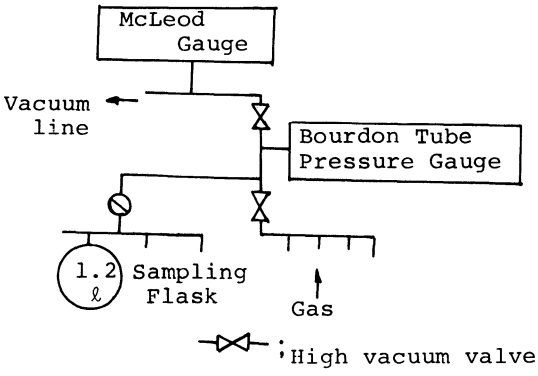

Fig. 1. Apparatus for Preparation of various Concentration of Gases.

Concentrations of NO_2 in N_2 were determined by means of the standard Saltzman procedure[4]. IR and UV spectra of PVCZ films before and after being exposed to various gases were measured with IR spectrometer (Japan Spectroscopic Co., Ltd., model IRA-1 and 2) and UV spectrophotometer (Hitachi, model 124),respectively.

PVCZ films were exposed to various test gases at room temperature. In some cases experiments were performed with the concentrations of test gases both high and low. The effect of the absorbed gases on the color change is shown in Table 1. When the films were exposed to ambients containing NO_2 or SO_2, the films developed a yellow color, more sensitively by NO_2 than by SO_2. After taken out from 1 atm N_2 containing SO_2, the yellow (reacted) films returned completely to the original white films within 10 min. at room temperature.

This shows that the film-SO_2 interaction bond is very weak, so it is considered that the bond would be due to the charge transfer complex between PVCZ and SO_2[5]. The yellow film which absorbed NO_2 was placed in vacuo at 60°C for about 3 hrs and was also left in an atmosphere for over 3 months at room temperature. No change of the color of the film was observed. PVCZ solution in chloroform reacted with NO_2 and formed similar greenish yellow precipitation (precipitation A). The reaction of carbazole solution in chloroform and NO_2 formed also a yellow crystal, but it was a little more soluble.

Table 1 Selective color reaction of PVCZ with nitrogen dioxide at room temperature

Type of gas	Conc. of gas % (exposure time)	ppm (exposure time)	Color change of PVCZ film	
NO	1.3 (3 hrs)	200 (6 hrs)	—	—
NO_2	1.3 (10 min)	157 (6 hrs)	Brownish yellow	Greenish yellow
SO_2	50 (10 min)	250 (6 hrs)	Yellow	—
CO	1.3 (3 hrs)		—	
CO_2	In dry ice		—	
NH_3	1.3 (3 hrs)		—	

To identify the product of PVCZ-NO_2 interaction, after exposing the films to NO_2 (10 torr) for various periods of time, the infrared spectra of the reacted films were measured (Fig. 2). Exposure time increasing, four new bands appeared distinctively at 1520, 1290, 820 and 790 cm^{-1}, and the intensity of the absorbance of PVCZ at two bands, 1320 and 1100 cm^{-1} increased. When PVCZ film was exposed to NO_2 for longer periods of time at lower temperature, the new band appeared at 1110 cm^{-1}. These spectra which should be assigned to PVCZ-NO_2 interaction were compared with the IR spectra of carbazole (commercial reagent),2 or 6-nitrocarbazole[6] and 2,6-dinitrocarbazole[7] prepared according to references. The new bands of PVCZ-NO_2 interaction seem to be similar to the specific spectra observed for mononitro and dinitrocarbazole. Further, PVCZ was nitrated with a mixture of conc. HNO_3 and acetic acid according to the reference[8] and then IR spectra of the nitrated PVCZ were compared with those of PVCZ-NO_2 interactions both of the film and the precipitation A. In the range from 650 to 3400 cm^{-1}, individual bands of both PVCZ-NO_2 interactions coincided quite well to those of the nitrated PVCZ.

The UV spectra of PVCZ-NO_2 films and precitation A dissolved in dimethyl formamide (DMF) are compared with that of the nitrated PVCZ in Fig. 3. Because of high contents of nitro group[8], very small amount of PVCZ-NO_2 film was soluble in DMF.

The film and the precipitation A solution showed an absorption band at 375 nm which assigned to nitro group of the nitrated PVCZ[8]. IR and UV spectra of PVCZ film exposed to 1 atm N_2 containing several hundred ppm of nitrogen dioxide agree also to the results when the pressure of nitrogen dioxide is 10 torr. Therefore, the color component in PVCZ-NO_2 reaction is most likely, nitro derivatives of PVCZ.

From the results of UV and IR measurements, it was found that only nitration of carbazole ring occured. This is an unique result which is different from those on reactions of the other polymers with nitrogen dioxide reported previously —— namely, the main-chain scission reaction[9] has been observed for polystyrene and polyethylene exposed to nitrogen dioxide for long time, dipole-dipole interaction between NO_2 and pyridyl group has been shown for an absorption of nitrogen dioxide by poly (vinylpyridine) resin[2], and the simultaneous oxidation and nitration proceeded on the porous polystyrene-divinyl benzene copolymer exposed to nitrogen dioxide in the presence of oxygen[1].

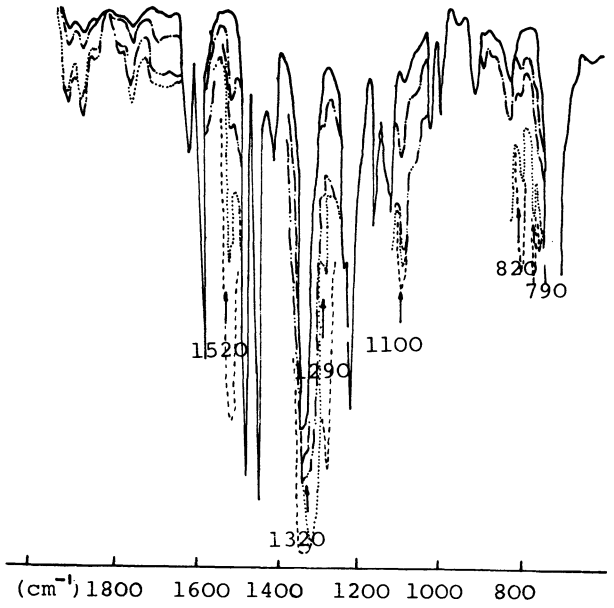

Fig. 2. Infrared Spectra of adsorbed NO_2 on PVCZ film. (——;PVCZ, —·—;PVCZ after being exposed for 2 min., —··—;PVCZ after being exposed for 5 min., ·····;after 30 min. ,------;Precipitation A)

In order to find out if there was any change of the color reaction with atmospheric gases, PVCZ films were exposed repeatedly to the mixture of N_2 plus 1) 6% and 30% water vapor 2) 1.3% and 10% oxygen 3) 10% and 50% carbon dioxide. The PVCZ films exposed to these gases were analysed by infrared spectrography. No additional band to those of PVCZ film was observed in any of these cases. And, three sampling flasks containing 650 ppm of NO_2 plus 4) 20% oxygen 5) 20% carbon dioxide 6) 7% water vapor, were prepared and PVCZ films were placed in the flasks for 1 hr. The gas mixture of NO_2, N_2 and O_2 or CO_2 showed no different result from the mixture of NO_2 and N_2, but PVCZ film exposed to the mixture of NO_2, N_2 and water vapor showed weaker absorption at 1520 cm^{-1} by 30-40%. This result would be due to the decrease of the concentration of NO_2 because of the reaction of NO_2 with water vapor. Therefore, it may be concluded that PVCZ film

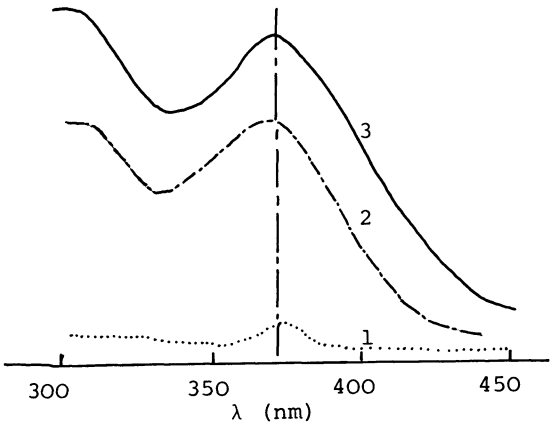

Fig. 3 Spectral Variations of PVCZ film absorbed NO_2(1), Precipitation A(2) and PVCZ nitrated with HNO_3-CH_3COOH Mixture(3).

does not react with any of the test gases.

The color reaction of nitrogen dioxide with the solid polymer has a number of possible application, one of which is the convenient method for the detection of nitrogen dioxide. If the reaction is a surface reaction, its use in length-of stain indicator tubes for the detection of nitrogen dioxide could be considered.

To certify the possibilities of the application of PVCZ-NO_2 interaction to the detection of nitrogen dioxide, following experiments were performed; 97 ppm and 47 ppm of nitrogen dioxide in N_2 were sampled by commercially available Kitagawa type aspirating pump (100 ℓ / 3 min) method through capillaries (1 mm in inside diameter and 100 mm in length), packed with the silicagel beads (35-70 mesh) coated with 0.2 % (w/w) PVCZ (0.1g PVCZ to 50g silicagel beads). The capillaries were stained by the nitrogen dioxide passing through the tube and produced the yellow zone. The mass of nitrogen dioxide fed to the capillary was determined by the Saltzman procedure. Fig. 4 shows the relation between length of the stained zone and amount of the fed NO_2 compared with the result using commercially available Kitagawa type gas detector tube No. 117 (manufactured by Komyo Rikagaku Kogyo,Inc.). The length of the yellow zone is fairly linear to the mass of nitrogen dioxide supporting the hypothesis of the surface reaction. While the length of stain of commercial detector tube (Fig. 4b) is a logarithmic function of the accepted mass. The linear dependence of the length of stain on the mass might be atractive method which can be applied for the precise determination of nitrogen dioxide of relatively high concentrations in industrial hygiene. Further work is required for the optimum evaluation of its applicability.

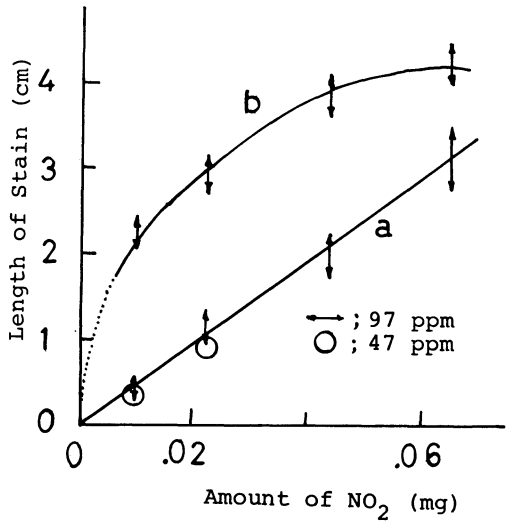

Fig. 4. Length of Stain versus Mass of NO_2. (a; PVCZ, b; Commercial indicator tube)

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(Received December 20, 1976)