CHEMISTRY LETTERS, pp. 1367-1370, 1978. Published by the Chemical Society of Japan

GAS PHASE REACTION OF N_2O_5 WITH PROPYLENE

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Products of gas phase reaction of N_2O_5 with propylene in air were analyzed using a long-path Fourier transform infrared spectrometer and a GC-EI and CI mass spectrometer. The major products was propylene glycol 1,2-dinitrate (PGDN), and other products were acetaldehyde, propylene oxide, NO_2, and HNO_3. Formation of PGDN observed previously in the photooxidation of the propylene-nitrogen oxides-air system was attributed to the reaction of N_2O_5 with propylene.

Recently, propylene glycol 1,2-dinitrate (PGDN)(1,2-propanediol dinitrate) was identified as a photooxidation product in the propylene-nitrogen oxides-air system.[1)] Since the reaction system constitutes a basic model of photochemical air pollution, and PGDN is known[2,3)] to be a very toxic compound, this result is of great significance, not only from the view of atmospheric chemistry, but also from that of the toxicology of photochemical smog. In order to elucidate the formation mechanism of PGDN in the photooxidation system, a thermal reaction of N_2O_5 with propylene was examined in this study, with the expectation that this reaction system might result in the formation of PGDN.

In spite of the atmospheric importance, less attention has been paid to the gas phase reaction of N_2O_5 with olefins than to the liquid phase.[4-6)] Niki et al.[7,8)] have studied the gas phase kinetics of N_2O_5 - olefin systems, and deduced rate constants for the reactions of NO_3 with olefins. However, the reaction products remain unidentified.

In this study, the gas phase reaction of N_2O_5 with propylene in dry air has been studied using an evacuable smog chamber[9,10)] (1450 mm in diameter, 3500 mm in length and 6065 dm^3 in volume) or a 3 dm^3 Pyrex reactor. The smog chamber is equipped with a long-path Fourier transform infrared spectometer (LP-FTIR, Block Engineering Co., FTS-496S). The path length and spectral resolution used in this study were 221.5 m and 2 cm^{-1}, respectively.

An authentic sample of PGDN was synthesized according to the method employed

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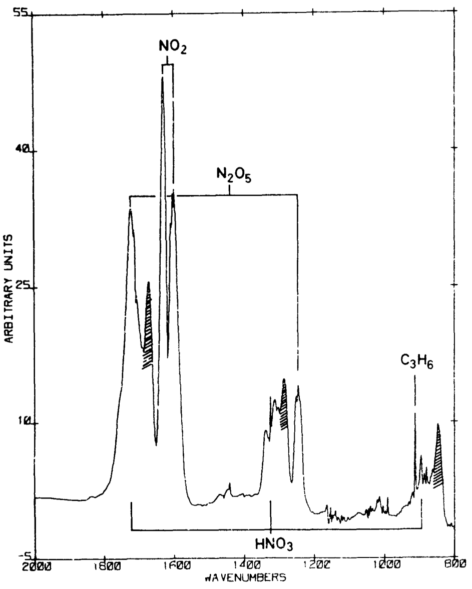

Fig.1 Fourier transform infrared spectrum of the reaction mixture of N_2O_5 and propylene in air. Hatched bands are due to a product which are asigned to PGDN.

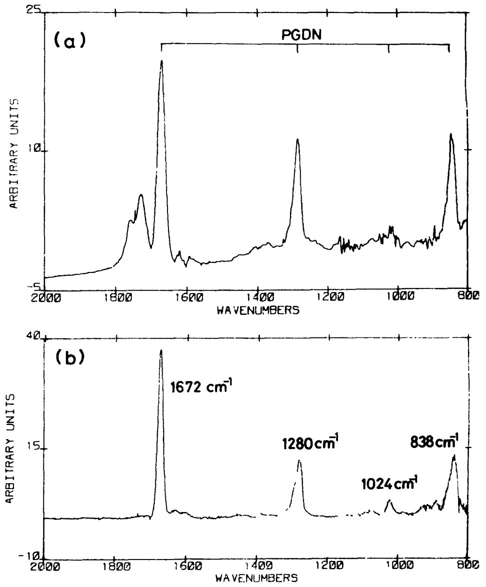

Fig.2 Comparison of (a) the product spectrum, and (b) standard spectrum of an authentic sample of PGDN.

by Crater.[11] Propylene glycol was nitrated by a mixed acid. The separated raw product was washed several times with a dilute aqueous sodium bicarbonate solution and water. After drying over sodium sulfate, the product was fractionally distilled by the trap-to-trap method under vacuum using liquid nitrogen as a coolant, since the normal distillation method is dangerous for such a polynitrate. The medium fraction of the distillation was identified as PGDN by NMR and IR. The wave numbers of the IR absorption bands of the synthesized PGDN in neat liquid agreed well with values found in the literature.[12]

Figure 1 shows the IR absorption spectrum of the reaction mixture when 2 ppm each of N_2O_5 and propylene in air were mixed for 20 min in the smog chamber. In addition to the absorption bands due to reactants, N_2O_5 and propylene, and products, NO_2 and HNO_3, three unidentified bands are observed as shown by the hatching in Fig.1. When the standard spectra of N_2O_5, propylene, NO_2, and HNO_3 are subtracted from Fig.1, a product spectrum of unidentified compounds is obtained as shown in Fig.2(a). For comparison, Fig.2(b) presents the gas phase IR absorption spectrum of the authentic sample of PGDN. To our knowledge the IR spectrum of PGDN in gas phase has not been reported, and differs appreciably from that in neat liquid. Comparison of the spectra indicates that three prominent peaks at about 1670, 1280, and 840 cm^{-1} in the product spectrum can be assigned to the anti-symmetric NO_2 stretch, symmetric NO_2 stretch, and N-O stretch of PGDN. The peak at around 1750 cm^{-1} in the product spectrum may be ascribed to acetaldehyde and other minor unidentified carbonyl products, judging from GC studies described below.

In order to identify the products conclusively, the reaction of 300 ppm each of N_2O_5 and propylene in air was carried out by using the Pyrex reactor. The reaction mixture was sampled by a 10 cm^3 gas-tight syringe, and injected into a GC

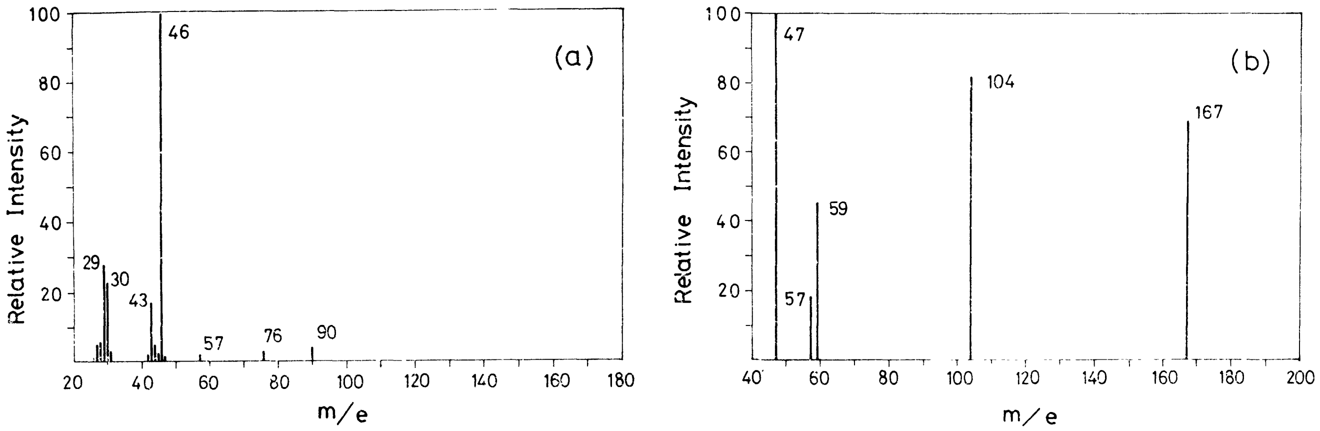

Fig.3 Mass spectra of a product, PGDN obtained by
(a) electron ionization (EI) (b) chemical ionization (CI)

and GCMS. The columns used were (A) Porapak Q, stainless column (3 mm x 2 m) at 90°C, and (B) SE-30 5% on Shimalite, stainless column (3 mm x 2 m) at 120°C. From GC analysis, several reaction products were observed. Two were volatile, being detected by the former column, and others were much less volatile, being detected by the latter column. GC-mass spectrometry with electron impact ionization (GC-EIMS) indicates that the volatile products were acetaldehyde and propylene oxide. Judging from the FID-GC chromatogram, the major product was one of the less volatile products, which has the EI mass spectrum shown in Fig.3(a). The intense peak at mass number 46 indicates NO_2^+ produced by fragmentation, suggesting that this product corresponds to the nitrate observed by the IR spectrometry. According to Fraser[13)], however, parent peaks of organic nitrates are generally difficult to observe as far as electron impact is employed as a method of ionization. Therefore, GC-chemical ionization mass spectometry(GC-CIMS) was carried out. In this case, the highest mass number is expected to appear at M +1. The CI mass spectrum of the product obtained using methane as reagent gas is shown in Fig.3(b). The highest mass number observed was 167, thus suggesting the molecular weight of 166.

From the mass spectrometric results, the product is deduced to be propylene glycol 1,2-dinitrate ($CH_3CH(ONO_2)-CH_2(ONO_2)$). This compound has a molecular weight of 166, and mass peaks at 90 ($CH_3CH(ONO_2)^+$) and 76 ($CH_2ONO_2^+$) observed in EI-MS are easily expected from the molecular structure. To conclude the identification, the results were compared with those for the authentic sample of PGDN. The GC retention time and both of EI and CI mass spectrum of PGDN were in complete agreement with those of the major product obtained in the reaction of N_2O_5 with propylene. As far as we know, CI mass pattern of PGDN has not been reported, and EI mass pattern reported by Fraser[13)] did not show M/e at 90, which was clearly observed in Fig.3(a). Other less volatile products were not identified conclusively, but one of the products was tentatively assigned as 1-formylethyl nitrate ($CH_3CH(ONO_2)-CHO$) from GC-MS study.

Figure 4 shows the yields of the products, when the initial concentration of N_2O_5 was varied. The yields were obtained by GC analysis after they reached steady values. The sensitivity calibration of PGDN for the FID-GC was made using benzene solution of the authentic sample. Formation ratio of PGDN, acetaldehyde, and propylene oxide is nearly independent of the N_2O_5 concentration under the experimental conditions. Thus, PGDN is apparently a major product of the gas phase reaction of N_2O_5 with propylene. Although formation of glycol dinitrate was noted in early studies[4,5] of liquid phase N_2O_5-olefin reaction, the identity of the products was inconclusive. In a later work[6], the N_2O_5-propylene reaction in an inert solvent such as methylene chloride, etc., was found to give 1-nitro-2-propyl nitrate (27%) and a mixture of nitro-olefins (16%). Apparently more studies are necessary to establish the reaction mechanism of N_2O_5-olefin reactions both in gas and liquid phases.

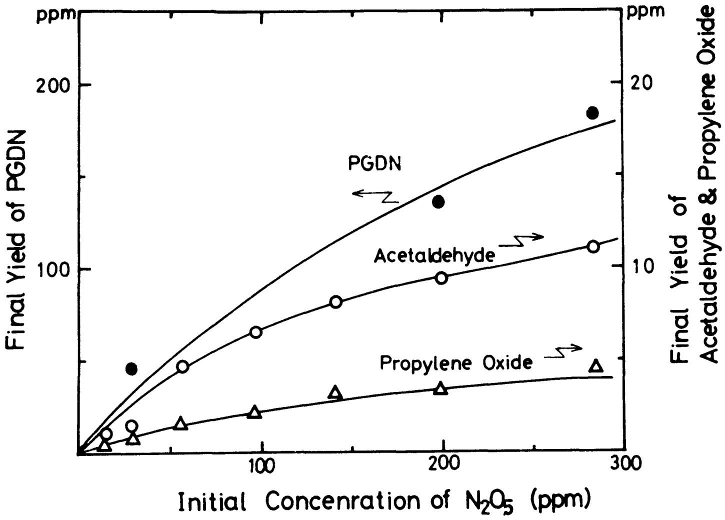

Fig.4 Yields of products vs initial concentration of N_2O_5. Initial concentration of propylene is 283 ppm.

In the photooxidation reaction of propylene-nitrogen oxides-air system formation of N_2O_5 has been observed,[14] which would be due to the reactions

$$O_3 + NO_2 \longrightarrow NO_3 + O_2 \qquad NO_3 + NO_2 \rightleftharpoons N_2O_5$$

From the experimental results of this study, PGDN observed in the photooxidation system[1], is most probably formed by the reaction of propylene with N_2O_5, or NO_3 which is equilibrated with the former. Due to the importance of the reaction from the viewpoint of photochemical air pollution, the reaction mechanisms of N_2O_5-olefin reactions are being studied in our laboratory.

Acknowledgement The authors wish to express their thanks to Mr. H. Takagi in our Institute for his operation of the GCMS, and Prof. S. Suzuki and Dr. O. Koga in the University of Chiba for the use of their GC-CIMS.

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(Received October 4, 1978)