PHOTOLYSIS OF ASYM-N_2O_4 ($ONONO_2$) ISOLATED IN AN ARGON MATRIX AT 11 K[☆]

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An unstable isomer of dinitrogen tetroxide, $ONONO_2$ (asym-N_2O_4), was photolyzed in an Ar matrix at 11 K at 436 and ≳510 nm. Asym- to sym-N_2O_4 (O_2NNO_2) isomerization was the major process at 436 nm; other products observed where NO, cis-$(NO)_2$, asym-N_2O_3 (O_2NNO) and N_2O_5. Irradiation of asym-N_2O_4 at ≳510 nm induced no reaction.

1. Introduction

In 1959, Fateley, Bent and Crawford [1] reported the existence of an unstable isomer of dinitrogen tetroxide (N_2O_4) having a dinitrosyl nitrate structure ($ONONO_2$) in low-temperature matrices in addition to a stable isomer, O_2N–NO_2 in D_{2h} symmetry (sym-N_2O_4) [2–4]. Further characterization of the infrared [5,6] and Raman [7] spectra of matrix-isolated NO_2–N_2O_4 mixtures has confirmed the presence of this unstable isomer (we call it "asym-N_2O_4" although it was called "iso-N_2O_4" in earlier papers). Formation of $ONONO_2$ in the reaction of cis-$(NO)_2$ with solid oxygen at 13–27 K has also been discussed by Smith and Guillory [8,9].

In a relevant study on N_2O_3, Varetti and Pimentel [10] have revealed that when N_2O_3 is formed from NO and NO_2 in a N_2 matrix it displays the vibrational spectrum of the normal form of N_2O_3, i.e. O_2NNO (asym-N_2O_3) in C_s symmetry as in the gas phase [11, 12]. This molecule was found to be converted to an isomer, ONONO (sym-N_2O_3) by near-infrared irradiation at 20 K and isomerized back to asym-N_2O_3 by irradiation in the ultraviolet region (370–480 nm) [10]. Although part of the photolytic behavior of N_2O_4 isomers in low-temperature matrices has been revealed by Varetti and Pimentel [10] and Smith and Guillory [9] for the purpose of characterization of infrared absorption bands of these species, photochemistry at a specified wavelength has not been studied so far. Since asym-N_2O_4 has never been observed in the gas phase, it would also be interesting to get some insight into the formation mechanism of asym-N_2O_4.

In the present study, the predominant formation of asym-N_2O_4 in an Ar matrix at 11 K has been observed under favorable experimental conditions, and the photochemistry of asym-N_2O_4 has been investigated in the near UV–visible region. The reaction channels of the photolysis of asym-N_2O_4 at 436 nm in an Ar matrix are reported, and the formation dynamics of asym-N_2O_4 are assessed in this Letter.

2. Experimental

A CsI cold plate (25 X 35 mm, 2.0 mm in thickness) was installed on a copper block mounted on a cold head of a commercial cryo-pump system (Cryogenic Technology Inc. model 21). All cold parts of the system are

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enveloped in a cylindrical stainless steel vacuum vessel (102 mm inner diameter and 265 mm long) which can be evacuated by an oil rotary pump with a liquid N_2 trap. The vacuum vessel has a pair of KBr windows through which IR absorption spectra of a sample deposited on the cold surface can be measured. A fused silica window, through which photolytic light is irradiated on the sample, is installed on the vessel perpendicular to the KBr windows. The CsI cold plate is set at 45° to both the KBr and silica windows. The copper block is fitted with a heater to control the temperature of the cold window from 11–100 K within ±1 K accuracy by a Si diode temperature sensor and a temperature control unit (Lakeshore Inc.).

The sample NO_2 (Matheson Co.) was prepared by degassing at liquid N_2 temperature after mixing with ≈1 atm of O_2 to oxidize $NO-N_2O_3$ impurity. Research grade Ar (Teikokusanso Co. Ltd.) was purified by passing through a trap containing molecular sieve cooled at −70 to −90°C. Diluted mixtures of NO_2/Ar(1/50–1/100) were prepared in a 4 ℓ glass bulb and introduced into the vacuum vessel through a stainless steel tubing (1 mm outer diameter). The sample was effusively injected through a single nozzle located at 20 mm from the CsI surface. Flow rates of the sample mixture were varied in the range of 0.08–64 mmol/h and the deposition time ranged from 5 min to 2 h giving a total amount of deposition of 0.2–5 mmol. The stagnation pressure of the gas mixture was varied in the range of 10–760 Torr.

Photolysis was made using a collimated beam (30 mm diameter) from a high-pressure Hg arc lamp (Ushio Electric Co. USH-500D). An interference filter (Nihon Shinku Kogaku Co. IF-437), whose transmission is centered at 437 nm ($\Delta\lambda \approx 20$ nm fwhm), and a glass filter (Corning 3-69) which transmits only $\gtrsim 510$ nm, were used to isolate the 436 nm lines and visible lines of the Hg arc, respectively. A H_2O cell 150 mm in length was used to eliminate infrared radiation of the lamp. The irradiation time was 18 h. During the irradiation, the temperature rise of the cold surface was typically within 1 K.

Infrared spectra were measured by a Fourier transfrom infrared spectrometer (Nicolet FTS-7199) using a liquid N_2 cooled HgCdTe detector. The spectral region covered was 4000–700 cm^{-1} with a resolution of 0.5 cm^{-1}. Typically, 128 scannings were accumulated to obtain a spectrum.

3. Results and discussion

3.1. *Assignments of matrix isolated species*

Absorption bands observed in NO_2/Ar matrices (1/50–1/100) at 11 K were assigned to NO_2, asym- and sym-N_2O_4, NO, cis-$(NO)_2$, and asym-N_2O_3 in comparison with the data reported in the literature [1,5,6, 9,10].

Absorption bands of asym-N_2O_4 are observed at 1827.9 (N=O stretch), 1644.0 (NO_2 asymmetric stretch), 1290.5 (NO_2 symmetric stretch), 903.3 (ON–O stretch) and 786.9 cm^{-1} (NO_2 bend), while those at 1749.2 (NO_2 asymmetric stretch) 1257.0 (NO_2 symmetric stretch) and 745.8 cm^{-1} (NO_2 band) are assigned to sym-N_2O_4. Sym-N_2O_4 displays aggregate bands at 1736 or 1728 cm^{-1} depending upon whether it is formed thermally or photochemically. Agreement of the frequencies observed in the present study and those reported by Fateley et al. [1] both measured in Ar matrices, is in general within 1 cm^{-1}, except for a band at 1257.0 cm^{-1} of sym-N_2O_4 for which the value reported by Fateley et al. [1] is a few cm^{-1} higher. Also, the differences in frequencies between those reported in O_2 [5,8] and observed in Ar are in general minimal, while those in N_2 as reported by Varetti and Pimentel [10] reveal substantial shifts from other values.

3.2. *Preferential isolation of asym-N_2O_4*

In order to prepare a matrix sample suitable for a photochemical study of asym-N_2O_4, the experimental conditions of deposition were varied so as to attain a higher yield ratio of asym-N_2O_4 to sym-N_2O_4. Figs. 1a–1c compare the absorption spectra obtained under different conditions in the range of 1200–1350 cm^{-1}, where bands due to symmetric stretching modes of both asym-N_2O_4 (1291 cm^{-1}) and sym-N_2O_4 (1257 cm^{-1}) can be covered. The effect of the deposition rate is demonstrated in figs. 1a and 1b. It is clearly seen that the reduction of deposition rate from 11 to 0.2 mmol/h significantly favors the formation of asym-N_2O_4 in the matrix. Comparison of deposition with different partial pressures of NO_2 in the gas mixture shows that a higher NO_2 partial pressure gives a higher ratio of sym-N_2O_4 as depicted in figs. 1c and 1d. These results are consistent with the favorable conditions for asym-N_2O_4 formation noted in an earlier paper [1].

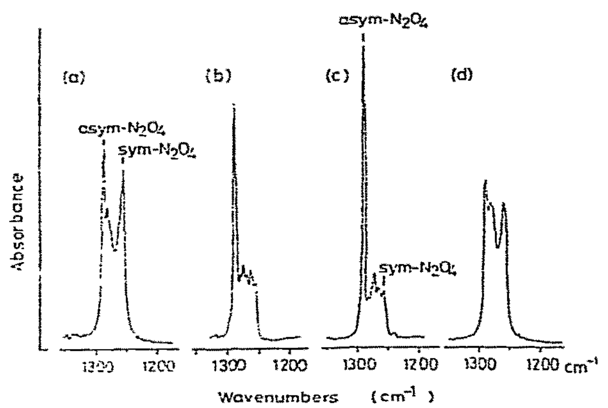

Fig. 1. Dependence of the formation ratio of asym- and sym-N_2O_4 on the flow rate and NO_2/Ar matrix ratio. (a) NO_2/Ar = 1/44, deposition rate 11 mmol/h, P_{NO_2} = 2.1 Torr, P_T = 90 Torr; (b) NO_2/Ar = 1/44, deposition rate 0.2 mmol/h, P_{NO_2} = 2.1 Torr, P_T = 90 Torr; (c) NO_2/Ar = 1/50, deposition rate 0.2 mmol/h, P_{NO_2} = 6.2 Torr, P_T = 310 Torr; (d) NO_2/Ar = 1/18, deposition rate 0.2 mmol/h, P_{NO_2} = 18.0 Torr, P_T = 330 Torr.

Further, increase in stagnation pressure from 90 to 310 Torr tends to give a higher ratio of asym- to sym-N_2O_4, as shown in figs. 1b and 1c. Under the favorable conditions employed in the present work, the peak absorbance ratio of the NO_2 symmetric stretch bands of asym-N_2O_4 and sym-N_2O_4 at 1291 and 1257 cm^{-1} was typically 6 : 1 for the matrices of NO_2/Ar ratios of 1/50–1/100.

It is of great interest that a thermochemically more unstable species (asym-N_2O_4) is formed predominantly by a simple thermal recombination reaction under certain experimental conditions. The above results indicate that asym-N_2O_4 can be isolated more favorably under the conditions that the reaction pair of NO_2 is frozen more rapidly after reaching the cold surface. At a higher partial pressure of NO_2, a larger amount of heat is liberated upon condensation and sym-N_2O_4 should be present already in the gas phase in higher concentration, thus yielding higher relative ratio of sym-N_2O_4 in the matrix. The preferential isolation of asym-N_2O_4 may be explained by dipolar interaction of reacting NO_2 pair. Since NO_2 has a dipole moment of 0.316 D, two approaching NO_2 molecules are subjected to dipole–dipole attraction force which tends to orient the two NO_2 molecules to lie anti-parallel. This would favor the approach of the O atom to the N atom of the reacting pair and fix the molecule in the structure of $ONONO_2$ when frozen rapidly. This approach would also be favored statistically as compared to the N-atom-to-N-atom approach to form sym-N_2O_4.

3.3. Photochemistry at 436 nm

Irradiation at 436 nm was made for the NO_2/Ar (1/55) matrix prepared under the conditions giving asym-N_2O_4 predominantly. Figs. 2a and 2b show the infrared absorption spectra obtained before and after 4 h irradiation, respectively. The difference spectrum obtained by subtracting fig. 2b from 2a is depicted in fig. 2c. The spectrum before the irradiation, shown in fig. 2a, displays the bands due to monomer NO_2 and asym-N_2O_4 with a smaller amount of sym-N_2O_4. After the irradiation, asym-N_2O_4 decreased and sym-N_2O_4 and asym-N_2O_3 increased. Slight increases of NO and cis-$(NO)_2$ are also observed (not shown in fig. 2). Further, new bands appeared at 1704, 1245

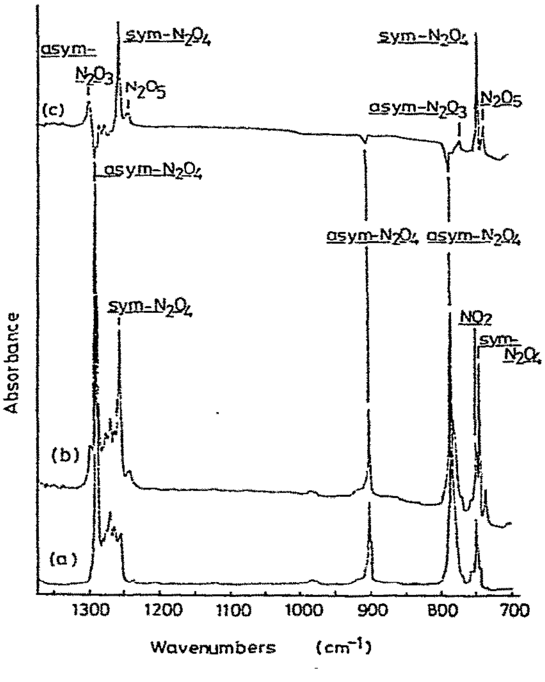

Fig. 2. Infrared spectra of the NO_2–N_2O_4/Ar matrix irradiated at 436 nm. NO_2/Ar = 1/50. (a) Before irradiation, (b) after 4 h irradiation, (c) difference spectrum (b) – (a).

and 737 cm^{-1} after the irradiation. Since the relative intensities of these bands did not change significantly during the irradiation and from run to run, these bands are ascribed to a single species. These bands were also noted by Varetti and Pimentel [10] (at 1704, 1305, 1247 and 739 cm^{-1} in N_2) and Smith and Guillory [9] (at 1704, 1300, 1241 and 736 cm^{-1} in O_2) and ascribed to N_2O_5. In the present study, the N_2O_5 band at $\approx$1300 cm^{-1} would be overlapped by the asym-N_2O_3 band as indicated in fig. 2c. The infrared absorption of the covalent form of N_2O_5 is known to appear at 1752, 1700, 1316, 1248, 737, 719 cm^{-1} in CO_2 [1] and 1742, 1702, 1335, 1245, 853, 732, 712 cm^{-1} in neat N_2O_5 [13]. Though the fundamental frequency of the infrared active ν_3 mode is known to be 1480 cm^{-1} in the gas phase [14], no absorption bands due to NO_3 could be identified in the product spectrum after irradiation.

Fig. 3 shows the change of absorbance of reactants and products as a function of irradiation time. Analysis of the formation curve of sym-N_2O_4 showed that the isomerization reaction follows first-order kinetics.

Under 13 h irradiation in the wavelength range $\gtrsim$510 nm for the asym-N_2O_4 rich matrix prepared from NO_2/Ar(1/70), no decrease in asym-N_2O_4 nor increase in sym-N_2O_4 was observed. The only change observed was the increase of the shoulder of the NO_2 monomer band, which might be due to orientational relaxation of the monomer in the Ar matrix.

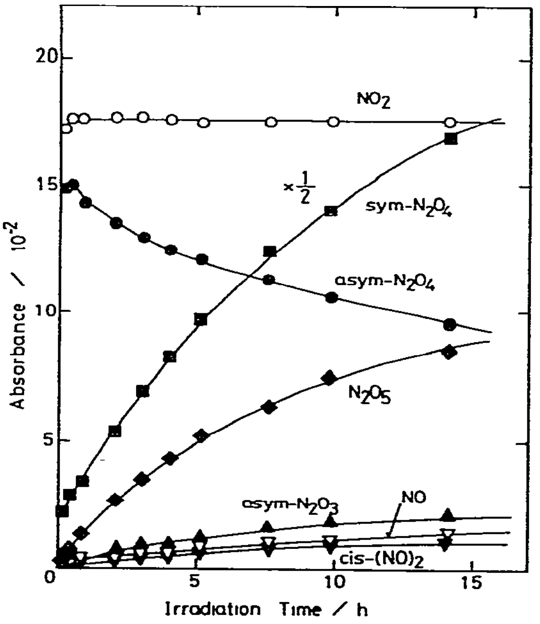

Fig. 3. Change of absorbance of reactants and products in the photolysis of asym-N_2O_4 in Ar matrix at 11 K as a function of irradiation time. NO_2/Ar = 1/50.

Although an electronic absorption spectrum of asym-N_2O_4 has not been known, the tail of near UV absorption bands due to the –ONO moiety should be around 400 nm, wheras sym-N_2O_4 is known to absorb the light with wavelengths shorter than 380 nm [15]. The thermochemical dissociation limit of NO_2 in the gas phase is known to be at 398 nm [16]. Therefore, the irradiation of the NO_2–N_2O_4–Ar mixture at 436 nm should excite both asym-N_2O_4 and NO_2 but the dissociation of the latter species does not occur. Therefore, the photochemical reaction processes

$$\text{asym-}N_2O_4 + h\nu \rightarrow \text{sym-}N_2O_4\ , \qquad (1)$$

$$\rightarrow NO + NO_3\ , \qquad (2)$$

followed by the recombination of NO, NO_2 and NO_3 would be envisioned as a plausible mechanism to explain the observed products, sym-N_2O_4, NO, cis-$(NO)_2$, asym-N_2O_3 and N_2O_5.

As for the major process of asym- to sym-N_2O_4 isomerization, the following three mechanisms may be conceived:

$$\text{asym-}N_2O_4 + h\nu \rightarrow (N_2O_4)^* \rightarrow \text{sym-}N_2O_4\ , \qquad (3)$$

$$\text{asym-}N_2O_4 + h\nu \rightarrow (2NO_2)_{\text{cage}} \rightarrow \text{sym-}N_2O_4\ , \qquad (4)$$

$$\text{asym-}N_2O_4 + NO_2 + h\nu \rightarrow \text{asym-}N_2O_4 + NO_2^*$$

$$\rightarrow (\text{asym-}N_2O_4 + NO_2)_{\text{local melt}}$$

$$\rightarrow \text{sym-}N_2O_4 + NO_2\ . \qquad (5)$$

If the isomerization is induced by the excitation of NO_2 monomer followed by the energy dissipation resulting local heating, the irradiation at $\gtrsim$510 nm can also induce the isomerization since NO_2 absorbs the light of this wavelength range. However, this is not the case, and thus the isomerization mechanism should be either process (3) or (4).

Although processes (3) and (4) cannot be distinguished experimentally in the present study, a process of intramolecular isomerization such as (3) has been suggested in the analogous isomerization reactions of ONONO [10] and ClONO [17] to nitryls (XNO_2) in low-temperature matrices.

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