Photochemistry of dinitrogen pentaoxide in low-temperature matrices

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A combination of matrix isolation and FTIR spectroscopy has been employed to investigate the low-temperature photochemistry (4.2 K) of dinitrogen pentaoxide. UV photolysis of the matrix isolated precursor (MR = 1/1000) at $\lambda > 230$ nm resulted in the photoreduction of N_2O_5 to N_2O *via* N_2O_3 as an intermediate. Both, *asym*- and *sym*-N_2O_3 were formed in argon matrices, whereas in solid nitrogen only *asym*-N_2O_3 was produced. Little or no evidence for the formation of isomeric forms of N_2O_4 was found. Possible photochemical pathways are discussed.

N_2O_5 plays a crucial role as a temporary reservoir for catalytically active nitrogen oxide radicals in the atmosphere.[1] It has strong absorption cross-sections in the near UV and therefore dissociates efficiently upon solar irradiation during daytime.[2,3] Laboratory studies have shown that gas-phase photolysis proceeds mainly *via* the following two primary pathways:

$$N_2O_5 + h\nu \rightarrow NO_3 + NO_2 \qquad (1a)$$

$$\rightarrow NO_3 + NO + O(^3P) \qquad (1b)$$

Although it is generally accepted that the quantum yield for the production of NO_3 is approximately unity at all wavelengths, the exact mechanism of N_2O_5 photolysis is still the subject of a continuing debate.[4–7] Channel (1*b*) has been proposed by Ravishankara *et al.*[14] as their results showed an increase in $O(^3P)$ + NO yield at wavelengths shorter than 290 nm. However, Oh *et al.*[5] account for the formation of NO and $O(^3P)$ by an excited NO_2^* intermediate as follows:

$$N_2O_5 + h\nu \rightarrow NO_3 + NO_2^* \qquad (1a')$$

$$NO_2^* \rightarrow NO + O(^3P) \qquad (2a)$$

$$\rightarrow NO_2 + h\nu' \qquad (2b)$$

This scheme is supported by the emission of 'photolysis-induced fluorescence' (PIF) from an excited NO_2^* photofragment, which has also been detected by Nelson *et al.*[8]

A large number of matrix photolysis studies of lower nitrogen oxides[9–15] and the related atmospheric reservoirs, nitric acid[16–18] and chlorine nitrate,[19,20] have been carried out. Most of these systems display rich secondary photochemistry owing to the existence of the so-called matrix cage effect: primary photofragments may not escape this cage thus increasing the likelihood of recombination processes. For example, in the case of nitric acid, spectroscopic evidence for the HOONO, peroxynitrite, isomer was obtained.[16–18] Previously, this species had only been predicted by theoretical calculations.[21,22] Computational evidence also exists for the ClOONO[21,22] and ONOONO peroxy isomers[23] of chlorine nitrate and dinitrogen tetraoxide, respectively. In the light of these findings the question arises whether a peroxy isomer of N_2O_5, $ONOONO_2$, could also exist in the inert environment provided by a low-temperature matrix.

To our knowledge matrix photolysis studies of N_2O_5 have not been reported previously. Therefore, in this paper we present novel results related to the mechanism of N_2O_5 photolysis in a low-temperature matrix.

Experimental

The experimental arrangement comprises a closed cycle helium system (Heliplex, Model CS-308) optically coupled to an FTIR spectrometer (Digilab FTS-40) as detailed elsewhere.[18] The deposition cold window consists of a highly polished caesium iodide disk which was routinely cooled to 4.2 K. IR absorption spectra of matrices were recorded using a liquid-nitrogen-cooled HgCdTe detector. Typically, single beam spectra were taken at 1 cm^{-1} resolution, boxcar apodised, and computed from the co-addition of 1024 interferograms.

N_2O_5 was synthesised by repeatedly reacting ozone with nitrogen dioxide (BDH, stated purity 99.5%) in a stream of zero-grade oxygen (BOC).[24] The final product was trapped at 195 K, degassed and stored at 77 K. The matrix gases argon (99.999%) and nitrogen (99.999%) were purchased from Messer Griesheim and used without further purification. To prevent decomposition of the reactive guest molecule, gas mixtures were prepared in 2 dm^3 darkened, preconditioned glass bulbs using standard manometric procedures and kept at 77 K until immediately prior to deposition. Furthermore, a specially designed, all-glass pulsing manifold was used and the CsI window routinely coated with a prelayer of the inert matrix gas. Matrices were photolysed through a Spectrosil-B window using a 1000 W xenon lamp (Oriel) for irradiation at $\lambda > 230$ nm or a low-pressure mercury arc lamp flushed with compressed air for photolysis at 253.7 nm.

Results

IR spectrum of matrix-isolated N_2O_5

IR spectra of matrix-isolated N_2O_5 (MR = 1/1000) at 4.2 K are shown in Fig. 1. The absorptions attributed to N_2O_5 in

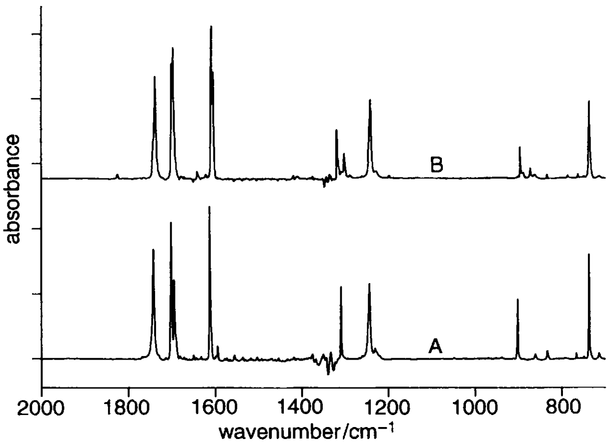

Fig. 1 IR spectra of matrix-isolated N_2O_5 (MR = 1/1000) in A, nitrogen and B, argon

J. Chem. Soc., Faraday Trans., 1996, **92**(13), 2347–2351

nitrogen (1742.3, 1701.4, 1336.8, 1243.5, 861.0 and 736.9 cm^{-1}), trace A, and in argon matrices (1737.6, 1699.4, 1333.2, 1240.9, 861.4 and 735.0 cm^{-1}), trace B, are in good agreement with data published in the literature.[25–27] The vibrational assignments are summarised in Table 1..

Deposition of N_2O_5 was accompanied by some degree of thermal and heterogeneous decomposition, despite the precautions mentioned above. Absorptions due to nitrogen dioxide (at 1612.5 cm^{-1} in nitrogen and 1608.0/1603.5 cm^{-1} in argon matrices) were observed, but little or no N_2O_4 was apparent.[9] Also, because of the low concentrations of N_2O_5 used throughout the series of matrix experiments, the formation of nitric acid could not entirely be prevented. The absorptions of nitric acid observed in nitrogen (1694.6, 1309.5, 901.3 and 766.3 cm^{-1}) and argon (1696.3, 1318.4, 1301.3, 895.3 and 764.9 cm^{-1}) presumably result from the heterogeneous wall reaction of N_2O_5 with residual water. However, in our experimental system $HONO_2$ does not complicate the interpretation of the N_2O_5 photolysis results because of its much slower rate of decomposition at wavelengths longer than 230 nm.[18]

Photolysis of N_2O_5 in solid matrices

Fig. 2 A, shows an absorbance difference spectrum of N_2O_5 in nitrogen (MR = 1/1000) after 60 min of photolysis with the unfiltered output of a xenon lamp ($\lambda > 230$ nm). Negative peaks denote the loss of the precursor molecules, whereas positive absorption bands show the formation of photolysis products. The band positions, intensities and assignments are listed in Table 2. N_2O and monomeric NO were readily identified by their strong absorptions at 2231.0 and 1871.6 cm^{-1}, respectively. Furthermore, a weak feature at 1771.4 cm^{-1} due to *cis*-$(NO)_2$ was also produced.[28] The set of bands at 1836.2, 1628.2, 1300.2 and 773.1 cm^{-1} was attributed to a single species, A, as the bands exhibited the same kinetic behaviour. The relevant time–absorbance profiles are shown in Fig. 3.

Table 1 Vibrational assignment of solid N_2O_5

normal mode	wavenumber/cm^{-1} in N_2[a]	in Ar[a]	in CO_2[b]	neat[c]	neat[d]
B_1, $\nu_{as}(NO_2)$	1742.3	1737.6	1752	1742	1764
A_1, $\nu_{as}(NO_2)$	1701.4	1699.4	1700	1702	1705
B_1, $\nu_s(NO_2)$	1336.8	1333.2	1316	1335	1340
A_1, $\nu_s(NO_2)$	1243.5	1240.9	1248	1245	1258
B_1, $\nu_{as}(NON)$	833.0	833.3		853	864
A_1, $\delta(NO_2)$	736.9	735.0	737	732	760

[a] This work; [b] ref. 26; [c] ref. 27; [d] ref. 25.

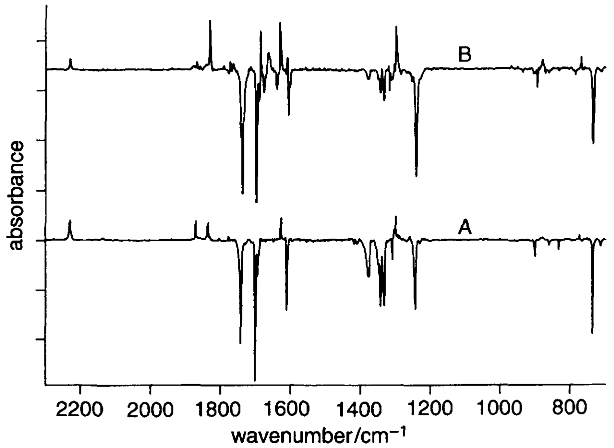

Fig. 2 Absorbance difference spectra of A, an N_2O_5–N_2 matrix (MR = 1/1000) and B, an N_2O_5–Ar matrix (MR = 1/1000) after 60 min photolysis at $\lambda > 230$ nm

Table 2 Wavenumbers (cm^{-1}) of absorption lines of an N_2O_5–N_2 matrix (MR = 1/1000) and N_2O_5–Ar matrix (MR = 1/1000) after 60 min photolysis at $\lambda > 230$ nm

N_2 matrix	Ar matrix	assignment
2231.0 vs	2230.9 m	N_2O
1871.6 vs	1868.5 w	NO
	1859.1 w	*cis*-$(NO)_2$
1836.2 vs	1830.0 vs	A
1771.4 w	1773.3 w	*cis*-$(NO)_2$
	1764.9 w	*cis*-$(NO)_2$
	1685.9 vs	B
	1663.4 m	
1628.2 vs	1630.0 vs	A
1300.2 vs	1298.0 vs	A
1294.5 w		N_2O
	968.4 vw	B
	878.9 m	
773.1 w	769.2 m	A

The experiment was repeated under identical conditions using an argon matrix. Fig. 2 B shows the IR spectrum of an N_2O_5–Ar matrix (MR = 1/1000) after 60 min photolysis at $\lambda > 230$ nm. The IR absorptions and assignments of the photoproducts are included in Table 2. An absorption due to N_2O (2230.9 cm^{-1}) was observed but little NO (1868.5 cm^{-1}) and *cis*-$(NO)_2$ (1859.1 and 1773.3 cm^{-1}) were formed. Species A was found to absorb at 1830.0, 1630.0, 1298.0 and 769.2 cm^{-1}. A pair of bands at 1685.9 and 968.4 cm^{-1} which exhibit identical kinetic behaviour was attributed to species B.

Identification of compounds A and B

An assignment of species A to the peroxy isomer of dinitrogen pentoxide ($ONOONO_2$) can be ruled out since no absorptions were observed in the O—O stretching region (800–1100 cm^{-1}) and the nitrate asymmetric stretching region (1300–1450 cm^{-1}). However, as the bands (1830.0, 1630.0, 1298.0 and 769.2 cm^{-1}) fall into the N=O stretching, asymmetric NO_2 stretching, symmetric NO_2 stretching, and NO_2 bending region of dinitrogen oxides, respectively, two other likely candidates have to be considered: *asym*-N_2O_3 (O=N—NO_2) and *asym*-N_2O_4 (O=N—ONO_2). Both oxides are known to

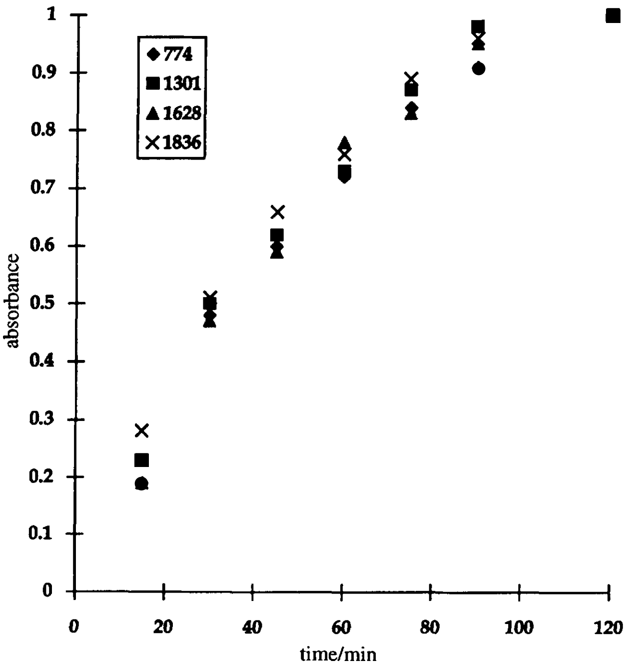

Fig. 3 Normalised kinetic profiles of the absorption bands due to compound A (1836, 1628, 1301 and 774 cm^{-1}) in solid nitrogen

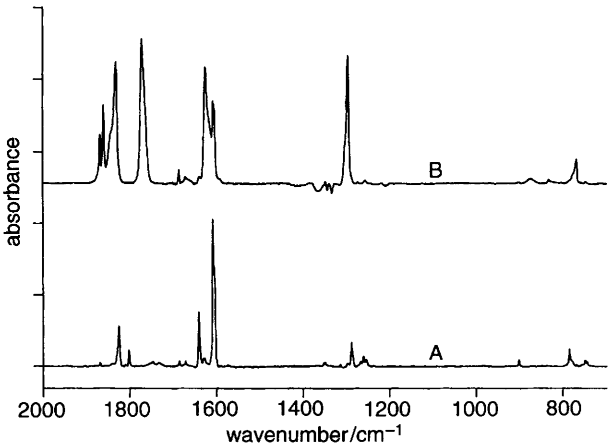

Fig. 4 IR spectra of A, an NO_2–Ar matrix (MR = 1/50) and B, an NO_2–NO–Ar matrix (MR = 1/4/50)

absorb within 15 cm^{-1} of each other because of their similar structure. Both compounds have been the subject of extensive research in the past, but the reported band positions appear to vary significantly with the experimental conditions.[28] In the present experiments, to ensure a correct assignment for A and B, *asym*-N_2O_4 and *asym*-N_2O_3 were synthesised directly *via* deposition of NO_2–Ar and NO_2–NO–Ar gas mixtures, respectively.

The spectrum recorded after deposition of an NO_2–Ar matrix (MR = 1/50) at 4.2 K is shown in Fig. 4 A. The wavenumbers of the matrix absorbers are listed in Table 3. Owing to the absence of NO the absorption bands at 1824.8, 1640.1, 1288.1 and 784.6 cm^{-1} may be attributed, with little doubt, to *asym*-N_2O_4. It is evident that the peak positions of *asym*-N_2O_4 only correspond poorly to those observed for species A (1830.0, 1630.0, 1298.0 and 769.2 cm^{-1}); the average shift being *ca.* 10 cm^{-1}.

The reference spectrum of *asym*-N_2O_3, as produced in an NO_2–NO–Ar matrix (MR = 1/4/50) at 4.2 K, is shown in Fig. 4 B. The use of excess NO over NO_2 minimises the formation of N_2O_4 in favour of N_2O_3. Table 3 lists the band positions and assignments of the absorptions produced in this experiment. Matrix-isolated NO (1867.9 cm^{-1}), *cis*-$(NO)_2$ (1859.5 and 1772.2 cm^{-1}) and NO_2 (1606.4 cm^{-1}) were readily identified. Little *asym*-N_2O_4 (1639.4 cm^{-1}) was observed. The remaining absorption bands at 1830.5, 1625.0, 1295.8 and 769.9 cm^{-1} were therefore assigned to *asym*-N_2O_3. They are in good agreement with the bands observed for species A (1830.0, 1630.1, 1298.0 and 769.2 cm^{-1}) as the discrepancy is typically less than 2 cm^{-1}. Only for the relatively broad, asymmetric NO_2 stretch was a slightly larger shift (5 cm^{-1}) observed which is likely to arise from the low probability of isolation in the concentrated NO_2–NO–Ar matrix (MR = 1/4/50).

Table 3 IR absorptions (cm^{-1}) of an NO_2–Ar (MR = 1/50) and an NO_2–NO–Ar(MR = 1/4/50) matrix

NO_2–Ar	NO_2–NO–Ar	assignment
1868.1 w	1867.9 m	NO
	1859.5 s	*cis*-$(NO)_2$
	1830.5 vs	*asym*-N_2O_3
1824.8 s		*asym*-N_2O_4
1801.5 m		
	1772.2 vs	*cis*-$(NO)_2$
1746.7 w		*sym*-N_2O_4
	1685.6 w	*sym*-N_2O_3
	1670.8 w	
1640.1 s	1639.4 w	*asym*-N_2O_4
	1625.0 vs	*asym*-N_2O_3
1607.8 vs	1606.4 s	NO_2
	1295.8 vs	*asym*-N_2O_3
1288.1 m		*asym*-N_2O_4
1260.0 w		*sym*-N_2O_4
901.0 w		*sym*-N_2O_4
784.6 m		*asym*-N_2O_4
	769.0 m	*asym*-N_2O_3
748.0 m	747.0 vw	NO_2
743.3 vw		*sym*-N_2O_4

Species B was assigned to *sym*-N_2O_3, the thermodynamically less stable isomer of *asym*-N_2O_3, as the bands at 1685.9 and 968.4 cm^{-1} agree well with the data published in the literature.[13,15] A summary of the vibrational frequencies and assignments of the two isomers of N_2O_3 is presented in Tables 4 and 5.

Discussion

Formation of N_2O_3

The stabilisation of N_2O_3 in a matrix upon N_2O_5 photolysis may most easily be understood in terms of a third photolytic channel (1*c*), the formation of NO + NO_2 + O_2, followed by cage recombination of NO + NO_2 to generate N_2O_3.

$$N_2O_5 + h\nu \rightarrow NO_2 + NO + O_2 \qquad (1c)$$

$$NO_2 + NO \rightarrow N_2O_3 \qquad (3)$$

Such a mechanism would correspond well to that observed upon matrix photolysis of chlorine nitrate.[19,20] The secondary product, ClNO, is thought to be formed by cage recombination of Cl and NO, generated by pathway (4).

$$ClONO_2 + h\nu \rightarrow Cl + NO + O_2 \qquad (4)$$

$$Cl + NO \rightarrow ClNO \qquad (5)$$

However, despite the resemblance to the photolytic pattern of $ClONO_2$, direct formation of NO_2 and NO from N_2O_5 photolysis sharply contrasts with the observation that NO_3 is produced with a quantum yield near unity in the gas phase. The formation of NO_3 as a transient intermediate is a distinct possibility as it can only be detected by UV–VIS spectroscopy. Channel (1*a*) represents the most likely route for NO_3 formation. NO_3 has a strong absorption cross section in the visible between 570 and 670 nm[29] and its photolysis will therefore compete with recombination (6*a*) or decomposition (6*b*).

$$N_2O_5 + h\nu \rightarrow NO_3 + NO_2 \qquad (1a)$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad (6a)$$

$$\rightarrow NO_2 + NO + O_2 \qquad (6b)$$

Table 4 Vibrational assignment of *asym*-N_2O_3

	wavenumber/cm^{-1}		
normal mode	Ar matrix[a]	N_2 matrix[a]	N_2 matrix[b]
A′, ν(N=O)	1830.0	1836.2	1839.7
A′, $\nu_{as}(NO_2)$	1630.0	1628.2	1630.4
A′, $\nu_s(NO_2)$	1298.0	1300.2	1302.5
A′, $\delta(NO_2)$	777.1	773.1	775.7

[a] This work; [b] ref. 15.

Table 5 Vibrational assignment of *sym*-N_2O_3

	wavenumber/cm^{-1}		
normal mode	Ar matrix[a]	N_2 matrix[b]	NO matrix[c]
B_2, ν(N=O)	1685.9	1689.7	1687
A_1, ν_s(N—O)	968.4	969.4	975

[a] This work; [b] ref. 15; [c] ref. 13.

Reaction (6*a*) simply regenerates the parent molecule leading to an apparent inhibition of photolysis. Reaction (6*b*) is strongly temperature dependent and hence likely to play a much less important role at 4.2 K than photolysis of NO_3 itself.[30] Specifically, NO_3 may photolyse *via* channel (7*a*) or (7*b*).

$$NO_3 + h\nu \rightarrow NO + O_2 \qquad (7a)$$

$$\rightarrow NO_2 + O \qquad (7b)$$

Channel (7*b*) is thought to occur with a quantum yield near unity, but rapid reaction of the mobile O atom with one of the NO_2 molecules in the matrix cage may also produce NO plus O_2.

$$NO_2 + O \rightarrow NO + O_2 \qquad (8)$$

Recombination of NO and NO_2 would then inevitably lead to the formation of N_2O_3.

It is interesting to speculate on why *sym*-N_2O_3 as well as *asym*-N_2O_3 is formed in argon but not in nitrogen matrices. No significant increase of *sym*-N_2O_3 at the expense of *asym*-N_2O_3 was observed upon IR irradiation with the IR source over the timescale of the experiment, so that the photoinduced isomerisation reported previously can be ruled out.[15] However, an additional process, intramolecular elimination of O_2 from N_2O_5 through an additional primary photolysis channel may be envisaged: in this the formation of *sym*-N_2O_3 would be favoured as it would require less structural rearrangement due to the maintenance of the central N—O—N bridge.

$$N_2O_5 + h\nu \rightarrow sym\text{-}N_2O_3 + O_2 \qquad (1d)$$

Nitrogen, as a polarisable matrix material, is likely to interact significantly more with a polar guest compound than inert, closed-shell argon. An interaction of the π-electrons of N_2 with the oxygen atoms of N_2O_5 might be important. (It has been suggested to occur in $HONO_2$–N_2 matrices.[31]) The result of the complexation would be to prevent intramolecular decomposition. Alternatively, upon N_2O_5 photolysis, heteronuclear union of the photofragments NO_2 and NO with N_2 may occur thereby imposing steric constraints on the recombination process. This effect could lead to preferential N—N bond formation and hence *asym*-N_2O_3.

Secondary processes

N_2O was observed in both argon and nitrogen matrices. Its linear kinetic profile in argon, shown in Fig. 5, implies that it is a stable end product. At the same time N_2O_3 displays a strongly curved profile and decreases upon prolonged irradiation indicating that it is an intermediate in the chemical process. In argon matrices therefore the secondary photolysis of N_2O_3 can be regarded as the most likely process for the formation of N_2O.

$$asym\text{-}N_2O_3 + h\nu \rightarrow N_2O + O_2 \qquad (9)$$

The formation of $N_2O + O_2$ is likely to result from the photodissociation of *asym*-N_2O_3 rather than *sym*-N_2O_3 as the central N—N bond can be maintained during the photolytic process. Previous matrix studies have failed to report this photolytic pathway, presumably because irradiation employed at $\lambda > 350$ nm only breaks the weaker N—N bond or causes intramolecular isomerisation.[13,15] However, similar preferential cleavage of the stronger N—O bond over the weaker N—N bond has been observed for *cis*-$(NO)_2$ which produces $N_2O + O(^3P)$ upon photolysis at $220 < \lambda/\text{nm} < 320$.[12]

$$cis\text{-}ON{-}NO + h\nu \rightarrow ON{-}N + O(^3P) \qquad (10)$$

Note, that N_2O was not observed upon irradiation of N_2O_5 with a low-pressure mercury arc lamp at 253.7 nm.

Considerably more N_2O was formed in nitrogen matrices than in solid argon. This is likely to arise from the additional photolysis of nitrogen dioxide, which is present as an impurity. NO_2 can dissociate to yield $NO + O(^1D)$ upon photolysis at $\lambda < 244$ nm and the excited oxygen atoms may be scavenged by the matrix to form N_2O.[10]

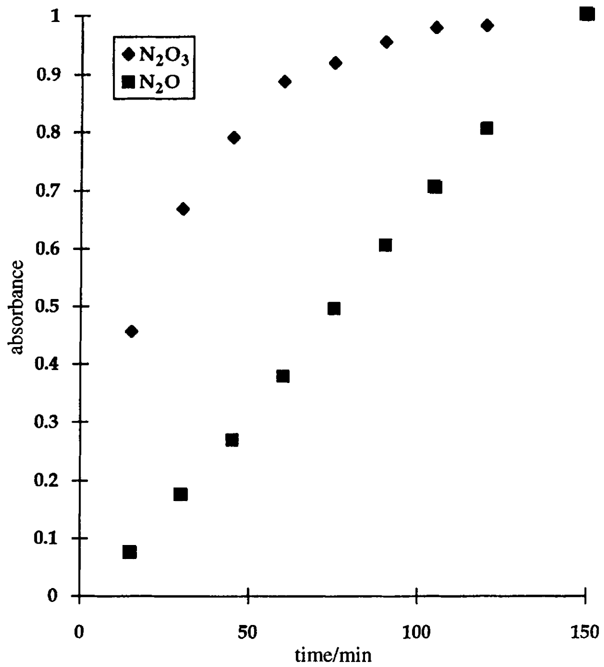

Fig. 5 Normalised kinetic profiles of N_2O_3 (1830 cm^{-1}) and N_2O (2231 cm^{-1}) in solid argon

$$NO_2 + h\nu \rightarrow NO + O(^1D) \qquad (11)$$

$$N_2 + O(^1D) \rightarrow N_2O \qquad (12)$$

Although the direct formation of $O(^1D)$ from N_2O_5 photolysis at wavelengths shorter than 275 nm is also a thermodynamic possibility it can be ruled out since the likely byproduct, *asym*-N_2O_4, is not observed.

Conclusion

The photolysis of matrix-isolated N_2O_5 at $\lambda > 230$ nm predominantly forms N_2O_3, presumably *via* intramolecular O_2 elimination or recombination of NO and NO_2 in the matrix cage. The photofragment NO may be generated either directly from N_2O_5 photolysis or indirectly *via* decomposition of NO_3. Secondary photolysis of N_2O_3 yields N_2O, which appears to be the stable end product.

Our results demonstrate, further, that it is unlikely that 2 NO_2 molecules are formed from N_2O_5 photolysis in the same matrix cage since neither *sym*- nor *asym*-N_2O_4 was detected. Also, we have found no evidence for the existence of the potential peroxy isomer of dinitrogen pentoxide, $ONOONO_2$.

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Paper 6/00373G; *Received* 17*th January*, 1996