On the behaviour of nitrogen oxides in liquefied argon and krypton. Dimerisation of nitric oxide¹

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Abstract

Solutions containing several nitrogen oxide species have been investigated in liquefied argon in the temperature range 84-105 K, and in liquefied krypton in the temperature range 116-150 K, using infrared spectroscopy. The following nitrogen oxide species were characterised in these solutions: NO, *cis*-ONNO, *trans*-ONNO, the asymmetric dimer ONON, asymmetric ONNO₂, symmetric ONONO and N₂O₄ with D_{2h} symmetry. The enthalpy of dimerisation of NO to *cis*-ONNO has been determined in liquefied argon to be -14.3 ± 1 kJ mol⁻¹.

Introduction

Nitrogen oxides $(N_x O_y)$ prove to be an interesting subject in spectroscopic studies, due to the large variety of forms in which they can appear. Some of these forms, however, are very unstable and can only exist at low temperatures, in equilibrium with other nitrogen oxide species. Although infrared spectroscopy of cryogenic solutions is most suitable to study these low temperature equilibria, only little research has been performed in this field. Previous studies of cryogenic solutions of nitrogen oxides were published by Smith et al. [1], who reported on the infrared spectroscopy of solutions of nitric oxide in liquefied krypton at 117 K and in liquefied nitrogen at 76K, and by Holland and Maier [2], who investigated infrared spectra of nitrogen oxides in liquefied xenon in the temperature range 160-220 K, and the isomerisation of dinitrogen trioxide. These authors, however, did not succeed in studying the dimerisation of NO to N_2O_2 more closely.

In this study we report on solutions of nitrogen oxides, formed by the condensation of nitric oxide and nitrogen dioxide in liquefied argon and in liquefied krypton. Different isomers, equilibria and solubilities will be discussed.

Because of the complexity of the equilibria involved it is instructive to review the relevant literature data on the nitrogen oxides investigated in this study. Nitric oxide and dinitrogen dioxide have been widely investigated in the vapour phase [3-6], the liquid phase [1,7] and the solid phase [7-14]. In the vapour phase, to our knowledge, only evidence for the existence of the cis-ONNO isomer has been found. Western et al. [15] determined the structure of this dimer in the vapour phase by molecular beam electric resonance spectrometry. Their results show a plane trapezoidal C_{2v} symmetry with bond lengths $r_{NN} = 2.33$ Å and $r_{\rm NO} = 1.15$ Å, and an angle $\angle ONO = 95^{\circ}$. The high value for the N-N bond length demonstrates the weakness of the dimerisation, so that a low absolute value for the enthalpy of dimerisation of nitric oxide to dinitrogen dioxide must be expected. Menoux et al. [4] reviewed the literature data on the enthalpy of dimerisation of dinitrogen dioxide in

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the vapour phase up to 1983. In their review, the values quoted for the enthalpy of dimerisation range from $-12.0 \text{ kJ mol}^{-1}$ to -9.4 kJ mol^{-1} in the temperature range 90-140 K, and from -6.7 kJ mol^{-1} to -4.5 kJ mol^{-1} at higher temperatures. More recently, binding energies of $8.49 \pm 0.48 \text{ kJ mol}^{-1}$ and $7.64 \pm 0.42 \text{ kJ mol}^{-1}$ have been reported by Hetzler et al. [5] and Howard and McKellar [6], respectively.

Studies of the pure liquid and solid phase of nitric oxide [1,7], provide a complete list of fundamentals, combination bands and overtones due to the nitric oxide dimer. Matrix isolation studies of nitric oxide [10,13] prove the existence of other dinitrogen dioxide species. Guillory and Hunter [13] reported not only on the *cis*-ONNO structure with C_{2v} symmetry, but also on the existence of a *trans*-ONNO structure, and a *cis*-ONNO structure in an unstable configuration. Hawkins and Downs [10] give a list of frequencies due to the *cis*-ONNO structure, the *trans*-ONNO structure and their isotopically substituted molecules in the region between 1900 cm⁻¹ and 1700 cm⁻¹.

Another isomer of dinitrogen dioxide is found when nitric oxide and hydrogen chloride are condensed at 77 K. When such a mixture condenses, a deeply red colored solid is observed. Ohlsen and Laane [16] determined the structure of this unstable isomer as asymmetric ONON (asym-ONON).

At low temperatures, NO mixed with NO₂ produces measurable amounts of dinitrogen trioxide, which can exist as two isomers. One of the isomers is the asymmetric ONNO₂ (asym-N₂O₃), investigated with infrared or Raman spectroscopy in the vapour phase [17], the liquid phase [18] and the solid phase [8,19–22]. The enthalpy of the association of NO and NO₂ to asymmetric dinitrogen trioxide has been determined by a number of authors [23], ranging from about -40 kJ mol^{-1} to -45 kJ mol^{-1} at 25°C.

The other isomer is the unstable symmetric ONONO (sym- N_2O_3). The existence of this isomer has been shown for the solid phase, in the pure solid [19] and in matrices [8,20-22], and

for solutions in liquefied xenon, investigated by Holland and Maier [2]. These authors determined the enthalpy difference between the two isomers using a temperature study. The value calculated was 7.5 kJ mol^{-1} , asym-N₂O₃ being the more stable isomer.

At the freezing point $(-11.2^{\circ}C)$, nitrogen dioxide is known to exist almost completely as the dimer dinitrogen tetroxide. The structure of the symmetric N_2O_4 molecule (O_2NNO_2) shows a D_{2h} symmetry. However, when monomeric NO₂ is condensed at low temperatures, other structures can occur. In the infrared and Raman spectra of solid N_2O_4 in the pure solid [19,24,25] and in matrices [8,11,26-28], bands have been observed due to asymmetric N_2O_4 (ONONO₂), having two possible structures: species D with a cis form and species D' with a trans form. Also evidence has been found of the existence of symmetric N₂O₄ with symmetry D_{2d} . Infrared frequencies of gaseous N_2O_4 are given by Bibart and Ewing [29]. In Fig. 1 the structures of the different nitrogen oxide species, discussed in the introduction, are shown.

Experimental

Nitric oxide was prepared by the reaction of sodium nitrite with ferrous sulphate in the presence of diluted sulphuric acid, as described by Cotton and Wilkinson [30]. The compound was purified using bulb-to-bulb distillations.

The hydrogen chloride used for the formation of the asymmetric dimer ONON was supplied by UCAR and has a stated purity of 99.98%. The argon and krypton liquefied as the solvent were obtained from L'air Liquide and have a stated purity of 99.9999% and 99.995% respectively. These gases were used without further purification.

The spectra were recorded on a Bruker Model IFS 113v Fourier transform spectrometer, equipped with a globar source. In the mid infrared region a Ge/KBr beam splitter and a LN_2 cooled broadband MCT detector were used; in the far infrared region a 6 micron mylar beam splitter and a DTGS

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Fig. 1. Representation of the different nitrogen oxide species discussed in the text.

detector were used. For the survey spectra, 200 scans, recorded at 0.5 cm^{-1} resolution, were averaged, Happ Genzel apodised and Fourier transformed with a zero filling factor of 4. In the temperature studies the resolution was set at 1.0 cm^{-1} , and a zero filling factor of 2 was used in the Fourier transformation.

The set-up used for the experiments in liquefied argon and krypton has been described in more detail in a previous publication [31], so only a brief description will be given here. The set-up consists of two main parts: a pressure manifold, needed for the filling and evacuating of the cell and for monitoring the amount of solute gas used in a particular experiment, and the cell, machined from a massive copper block. The cell is equipped with wedged Si windows, has an optical path length of 40 mm, and is suspended in a vacuum shroud equipped with KBr windows for the mid infrared region and polyethylene windows for the far infrared region.

For comparison, the spectra of solid N_2O_3 and N_2O_4 were obtained by condensing the compound on a CsI window, cooled to liquid nitrogen temperature. The spectra of solid nitric oxide were obtained by depositing the compound on a CsI window cooled to 10 K using a Leybold-Heraeus ROK 10-300 cryo-cooling system.

The nitrogen oxide solutions in liquefied argon and krypton were prepared as follows. Using cold nitrogen vapours, the cell was first cooled to the desired temperature. An isolated part of the filling manifold, with known volume, was filled with the nitrogen oxides, the pressure being monitored by a piezoelectric pressure meter. The nitrogen oxides were then flushed through the manifold into the cell by the condensing noble gas. The turbulence of the condensing solvent was assumed to be sufficient to homogenise the solution.

The vibrational frequencies observed in this study for the different species, and their assignments, are compared with literature values, obtained in different environments, in Tables 1–6. For the sake of clarity these tables have been organised per species.

Discussion

The NO used in the preparation of solutions in liquefied argon was tested for purity by recording

Infrared frequencies^a of asym-ONON

Table 1			
Infrared	freq	uencies ^a	of NO

Literature data L–Xe ^b	This study L–Ar ^c	Assignment ^b
3707	3713 vw	$2\nu_1$
1868	1870 m	ν_1 N=O stretch

^a All frequencies are given in cm⁻¹; s = strong; m = medium, w = weak, v = very. ^b From ref. 2.

^c Completely dissolved (85 K).

its vapour phase mid infrared spectrum immediately prior to use. Therefore it is rather suprising to see the complexity of the mid infrared spectrum of freshly prepared solutions like the one shown in Fig. 2, which was recorded at 85 K. Also, while no bands are expected for the diatomic molecule NO in the far infrared region, several absorption bands are observed for the solutions in the region, which is shown in Fig. 3.

In Fig. 4A the NO stretching region, from 2000 to 1500 cm^{-1} , of a freshly prepared solution is given

Table 2 Infrared frequencies^a of *cis*-ONNO

Literature data Solid ^b	This study L–Ar ^c	Assignment ^b
3738 mw	3728 vw	$2\nu_1 + \nu_4^{d}$ or $2\nu_2 + 2\nu_4^{d}$
3450 mw	3450 vw	$\nu_1 + \nu_2$
1770 vvs	1773 vs	ν_1 -O=N stretch
1685 ms	1687 m	ν_2 -N=O stretch

 $\frac{1685 \text{ ms}}{\text{a All frequencies are given in } \text{cm}^{-1}\text{; } \text{s} = \text{strong.}}$

m = medium, w = weak, v = very.

^b From ref. 16.

Table 3

^c Not dissolved (85 K).

^d Combination band with the ν_4 -O=N-O-bend of asym-ONON.

in detail. The highest transition in this region, at $1870 \,\mathrm{cm}^{-1}$ in agreement with the assignment of Smith et al. [1], must be due to free NO. This transition is relatively broad, indicative of substantial rotational motion of the NO molecule in liquefied argon. Based on the matrix isolation studies by Guillory and Hunter [13] and the studies of solutions in krypton and nitrogen by Smith et al.

Literature data			This study		Assignment ^g		
Solid ^b	Liquid ^b	N ₂ matrix ^c	L-Xe ^d	Solid ^e	L-Ar ^f		
3712 m	3708 m		3707	_	3713 vw	$2\nu_1$	
3596 m	3600 s	_	3594	3592 w	3604 m	$\nu_1 + \nu_2$	
3507 m	3515 m	_	_	_	3524 vw	$2\nu_{5}$	
2038 w	2032 m	-	_	-	2033 vw	$\nu_{2} + \nu_{3}$	
1865 vs	1863 vs	1870	1868	1861 s	1862 s	ν_1 sym N=O stretch	
_	_	1857	_	_	1849 vvw	ν_1 sym N=O stretch of <i>cis</i> -O ¹⁵ NNO	
	_	1851	_	_	1844 vvw	ν_1 sym N=O stretch of <i>cis</i> - ¹⁸ ONNO	
1760 s	1770 vs	1776	1762	1760 vs	1771 vvs	$\nu_{\rm s}$ antisym N=O stretch	
_	_	1756	_	_	1754 vw	ν_{s} antisym N=O stretch of <i>cis</i> -O ¹⁵ NNO	
-	_	1747	_	_	1743 vw	$\nu_{\rm s}$ antisym N=O stretch of cis- ¹⁸ ONNO	
-	262 ^h	_	-	-	256 m	ν_2 sym NNO bend	

^a All frequencies are given in cm^{-1} ; s = strong, m = medium, w = weak, v = very.

^b From ref. 1.

^e Deposited at 10 K, spectrum at 10 K.

^f Completely dissolved (85 K).

^g From refs. 1, 7 and 13.

^hObserved in Raman spectrum of liquid NO [1].

^c From ref. 13.

^d From ref. 2.

Infrared frequencies ^a of asym-N ₂ O ₃					
Literature data			This study		
Solid ^b	N_2 matrix ^c	L-Xe ^d	Solid ^e	L-Kr ^f	
_	_	3626 (1.75)	3701 w	3627 vw	

2900 (1.60)

2072 (0.37)

1828 (52.3)

1625 (49.5)

1294 (39.9)

769 (8.3)

616 (0.26)

2867 w

2125 w

1868 vs

1594 vs

1302 vs

783 m

625 w

2909 vw

2073 vvw

1830 vs

1631 vs

1297 vs

770 m

Table 4

^a All frequencies are given in cm^{-1} ; s = strong, m = medium, w = weak, v = very.

^b From ref. 8.

1867

1596

1303

788

^c From ref. 20. The relative integrated absorbances are given in parentheses.

^d From ref. 2.

^e Deposited at 77 K, spectrum at 77 K.

1840 (0.49)

1630 (1.07)

1303 (0.73)

776 (0.23)

^fCompletely dissolved (140 K).

^g Not dissolved (85 K).

^h From ref. 21.

ⁱ Combination band with the ν_6 N–N stretch of asym-N₂O₃.

[1], the maxima at 1862 cm^{-1} and 1771 cm^{-1} must be assigned to cis-ONNO. On the low frequency side of the absorption band at 1771 cm^{-1} weak absorption bands are observed at $1737 \,\mathrm{cm}^{-1}$ and

 $1716 \,\mathrm{cm}^{-1}$. These bands are very broad, which shows that they are presumably due to undissolved species. The frequencies of these bands match those reported by Givan and Loewenschuss

Table 5

Infrared frequencies^a of sym-N₂O₃

Literature data			This study			Assignment ^h	
Solid ^b	Solid ^b N ₂ matrix ^c L–Xe ^d		Solid ^e L-Kr ^f		L-Ar ^g		
_	_		-		3388 vvw	2 _{ν6}	
_	_	-	-	-	2132 vw	?	
1677 ms	1690 (0.38)	1687 s	1680 m	1691 vvw	1692 vvs	ν_6 antisym N=O stretch	
_	1674	-	_	_	1674 vvw	ν_6 antisym N=O stretch O ¹⁵ NONO	
_	1661 (0.025)	_	-	_	1664 w	ν_1 sym N=O stretch	
964 s	969 (0.050)	(965)	966 m	-	970 vw	ν_2 sym N–O stretch	
699 m	704	-	704 w	_	708 mw	ν_8 antisym O=N-O bend	
_	387 (0.12)	-	-	-	386 vs	ν_3 NON bend	
_	366 (0.34)	375 s	-		360 s	ν_{4} sym O=N-O bend	

^a All frequencies are given in cm^{-1} ; s = strong, m = medium, w = weak, v = very.

^b From ref. 19.

^c From ref. 20. The relative integrated absorbances are given in parentheses.

^e Deposited at 77 K, spectrum at 77 K.

^f Completely dissolved (120 K).

^g Completely dissolved (85 K).

^h From ref. 32.

Assignment^h

 $2\nu_1$

 $\nu_2 + \nu_3$ $\nu_1 + \nu_6$

 ν_1 N=O stretch

 ν_2 antisym NO₂ stretch

 $\nu_8 \text{ NO}_2$ wag out of plane

 ν_3 sym NO₂ stretch

 ν_4 NO₂ deformation

L-Ar^g 3716 w

2866 w

2132 w

1874 s

1595 s

1306 s

785 m

623 w

^d From ref. 2.

Literature data			This study			Assignment ^h	
Solid ^b	O ₂ matrix ^c	L-Xe ^d	Solid ^e L-Kr ^f L-A		L-Ar ^g		
2958 m	_	2954 (2.3)	2961 w	2961 w	2964 vvw	$\nu_s + \nu_{11}^{i}$	
2628 ^j m	_	2617 (1.15)	2626 vw	2623 vw	2626 vvw	$\nu_1 + \nu_{11}$	
$\frac{1760 \text{ vs}}{1735 \text{ vs}}$	$\left\{ {1750^k \atop {1735^i}} \right\}$	1742 (98.4)	1756 vs 1734 vvs	1747 vs	$\frac{1761 \text{ m}}{1737 \text{ s}}$	ν_9 antisym NO ₂ stretch (B_{2u})	
-	-	1724	1722 s	1729 m	1716 w	$\nu_6 + \nu_{11}^{m}$	
1256 vs	1261	1251 (59.7)	1253 vs	1255 vs	1256 s	ν_{11} sym NO ₂ stretch (B_{3u})	
^{756 vs} 738 vs }	$\frac{755^{k}}{746^{1}}$	743 (35.6)	^{755 s} 739 vs }	746 vs	$\left. \begin{array}{c} 752 \ m \\ 741 \ m \end{array} \right\}$	ν_{12} antisym NO ₂ deformation (B_{3u})	

Table 6		
Infrared	frequencies ^a	of N_2O_4

^a All frequencies are given in cm^{-1} ; s = strong, m = medium, w = weak, v = very.

^b From ref. 33.

^c From ref. 27.

^d From ref. 2. The relative integrated absorbances are given in parentheses.

^e Deposited at 77 K, spectrum at 77 K.

^rCompletely dissolved (140 K).

^g Not dissolved (85 K).

^h From refs. 2 and 29.

ⁱ Combination band with the ν_5 NO₂ antisymmetric stretch (B_{1g}).

^j In ref. 33 assigned as $2\nu_7 + \nu_{11}$.

^k Amorphous O₂ lattice mode.

In amorphous O_2 .

^m Combination band with the ν_6 NO₂ rock (B_{1g}).



Fig. 2. The mid infrared spectrum (4000-400 cm⁻¹) obtained by condensation of NO in liquefied argon at 85 K.



Fig. 3. The far infrared spectrum $(450-150 \text{ cm}^{-1})$ obtained by condensation of NO in liquefied argon at 85 K.

[25] for solid N_2O_4 and the absorption bands are therefore assigned to this solid, which must be suspended in the solution. Comparison with matrix isolation experiments [20–22] and with solutions in liquefied xenon [2] shows that the absorption bands at 1692 cm⁻¹ and 1664 cm⁻¹ are due to sym-N₂O₃. The sharpness of these absorption bands indicated that this species is dissolved in the liquefied argon. Finally, the absorption band at 1595 cm⁻¹, in agreement with the results of Hisatsune et al. [19] has to be assigned to the asymmetric form of N₂O₃, which, as the solid N₂O₄, must be suspended in the solution.

On top of the bands identified above, both the solid asym- N_2O_3 and solid N_2O_4 show other bands in this region, which are obscured in Fig. 4A by the bands due to NO and (NO)₂, and which will be identified below.

We assume that one of the reasons for the presence of the different N_xO_y species after condensation of NO in liquefied argon is oxidation by molecular oxygen adsorbed on the stainless steel walls of the filling manifold or by the oxide layer typical of the stainless steel surface. Another reason for the formation of other nitrogen oxides may be the disproportionation of NO, catalysed by the metal surface of the filling manifold. This disproportionation transforms NO in N₂O and NO₂. This is confirmed by the observation for some solutions of a weak absorption band at 2220 cm⁻¹, due to N₂O [34]. While this band in all cases is weak, the predominant process appears to be the oxidation reaction.

In order to check the hypothesis of the oxidation of NO in the stainless steel manifold, the solution in the infrared cell, after the recording of initial spectra, was distilled through the stainless steel manifold into a separate stainless steel cylinder attached to the manifold, and redistilled back into the cell. When this procedure was repeated a couple of times, it was observed that in the infrared spectrum of the solution all absorption bands due to free NO and the dimer N₂O₂ had disappeared. The NO stretching region for the final solution is shown in Fig. 4B (2000-1500 cm⁻¹) and in Fig. 5 (4000- 400 cm^{-1}). Using the assignments discussed above, it is clear that only the bands due to solid N_2O_4 , solid asym-N₂O₃ and some dissolved sym-N₂O₃ are present in the spectrum. In Fig. 4B the broad band at $1874 \,\mathrm{cm}^{-1}$, which can be seen as a faint shoulder on the absorption band due to monomer NO in Fig. 4A, is due to solid asymmetric N₂O₃



Fig. 4. The N=O stretching region of a solution of nitrogen oxides in liquefied argon at 85 K. A, freshly prepared solution; B, after several redistillations of the solution; C, the spectrum obtained by subtraction of the rescaled spectrum 4B from spectrum 4A.

[19], and the weak, broad band at 1761, all but obscured by the 1770 cm^{-1} in Fig. 4A, is due to solid N₂O₄ [25]. During the distillation process, the cell was never heated above -150° C. This temperature is far below the melting point of

asym- N_2O_3 (-100.7°C) and also far below the melting point of N_2O_4 (-11.2°C). Therefore, the N_2O_3 and N_2O_4 will remain in the cell during the distillation procedure. The turbulence in the cell due to the recondensation of the solution will



Fig. 5. The mid infrared spectrum of NO in liquefied argon at 85K after complete oxidation of NO.

cause the deposits of sym- N_2O_3 to go back into the solution and will cause the deposits of asym-N₂O₃ and N₂O₄ to form a new suspension, giving rise to the spectrum in Fig. 4B. During the distillation of the solution into the stainless steel cylinder some of the remaining NO will be oxidised to NO_2 , which will either condense in the stainless steel cylinder as the dimer N_2O_4 or will associate with a free NO molecule to form N₂O₃. This cylinder, during redistillation of the solution into the infrared cell, was kept at low temperatures, so that the N_2O_3 and N_2O_4 present in the cylinder was not transferred back into the cell. Therefore it is not really surprising to see that after the distillation process, the relative intensities of the bands due to solid N₂O₄ and solid asym- N_2O_3 have hardly changed.

In order to get a clear view of the different nitrogen oxide species observed in this study, the different structures will be discussed separately.

The equilibrium between NO and (NO)₂

As observed above, in a freshly prepared solution of NO in liquefied argon, both NO and at least the cis dimer $(NO)_2$ are present. When the temperature of the solution increases, the intensities of the bands due to the dimer decrease, while that due to the monomer increases. When the temperature of the solution is lowered again, opposite changes in the relative intensities occur. This shows that in the solutions an equilibrium is established that can be described as

 $2NO \rightleftharpoons (NO)_2$

In order to establish the enthalpy of dimerisation involved, absorption bands due to the monomer and the dimer must be quantified. It is obvious from Fig. 4A that this quantification is obstructed by the presence of bands due to solid asym- N_2O_3 and solid N_2O_4 . However, using the spectra of the redistilled solution, from which all bands due to NO and $(NO)_2$ have disappeared, the disturbance could be accounted for. To this end, the spectrum of the redistilled solution was rescaled so that the intensity of the band at $1595 \,\mathrm{cm}^{-1}$ matches the intensity of this band observed in the spectrum of the freshly prepared solution. Subsequently, the rescaled spectrum was subtracted from that of the freshly prepared solution. This procedure is illustrated in Fig. 4C, where the result of the subtraction of the spectrum in Fig. 4B from that in Fig. 4A is given. As can be seen, in the region around $1595 \,\mathrm{cm}^{-1}$ the resultant baseline is completely flat. Also, in the region of the other absorption band of asym-N₂O₃, around $1874 \,\mathrm{cm}^{-1}$, no indication of a mismatch of the intensities is present. As there is no obvious relation between the relative amounts of solid N_2O_4 and solid asym-N₂O₃, it is remarkable to see that also in the region of the absorption bands of solid N_2O_4 , around $1750 \,\mathrm{cm}^{-1}$, the baseline in Fig. 4C is wellbehaving, proving that the bands due to solid N₂O₄ have been quantitatively subtracted. It must immediately be admitted, though, that the bands due to solid N_2O_4 are substantially weaker than those of solid asym-N₂O₃, so that minor mismatches will be difficult to detect. All in all, the equal amounts of solid N2O4 and solid asym- N_2O_3 suspended in the solutions before and after the redistillation must be a fortuitous consequence of the way the redistillation, described above, was performed. It can be seen in Fig. 4C that the bands due to the dissolved sym-N₂O₃, at 1692 and $1664 \,\mathrm{cm}^{-1}$, have not been completely matched. Especially near $1692 \,\mathrm{cm}^{-1}$ the baseline shows that not only is the integrated intensity slightly mismatched, but also that the contour of the band in both experiments is not completely identical. It will be shown below that the bands due to sym- N_2O_3 are quite temperature sensitive, and therefore the behaviour of the baseline in Fig. 4C shows that the temperatures at which the spectra in Figs. 4A and 4B were recorded were not quite identical. Fortunately, these bands occur outside the region in which NO and (NO)₂ absorb, so that this mismatch does not disturb the quantification of the $NO/(NO)_2$ equilibrium. In the subtracted spectrum, on the low frequency side of the band 1771 cm⁻¹, two weak, sharp bands are visible, at 1754 and at $1743 \,\mathrm{cm}^{-1}$. Careful comparison of the spectra in Figs. 4A and 4B shows these are genuine absorption bands and not artefacts due to the subtraction. Their relative intensity being of the correct order of magnitude, they are assigned to the natural isotopes O¹⁵NNO and ¹⁸ONNO respectively.

The above procedure was repeated using spectra

recorded at 10 different temperatures, ranging from 84.3 to 93.4 K. Five of the resultant subtractions are shown in Fig. 6. The changes in the relative intensities clearly illustrate the temperature dependence described above.

The cis-NO dimer at most can show two NO stretches, one at 1862 cm^{-1} , and the other at 1771 cm^{-1} . However, even when the low frequency isotopic side bands mentioned above are neglected. the band at 1771 cm^{-1} is clearly complex, which is especially clear at the lowest temperatures. With decreasing temperature, the full width at half height of the band at 1771 cm^{-1} increases. This is in contradiction with the expected thermal behaviour of the band, and it shows that at lower temperatures a second component starts to emerge. This doublet structure of the 1771 cm^{-1} complex can be clearly seen in the spectrum recorded at the lowest temperature, Fig. 6A. It is rather difficult to assign also the second component to cis-(NO)₂, and therefore we prefer to assign it to a different species. The obvious candidate is trans-(NO)₂, that has been reported to show a band near 1771 cm^{-1} [13]. The other N=O stretch of this dimer being infrared inactive for symmetry reasons, the absence in the experimental spectra of a second N-O stretching band due to this species does not contradict the assignment. A band profile analysis of this region of the spectrum recorded at the lowest temperature shows that both components are quite narrow, suggesting that the trans dimer is also dissolved in the liquefied argon. At this stage it is not clear whether the observed profile at the lowest temperature is due to a rapid growing in of the band due to $trans-(NO)_2$ or due to a different solvent sensitivity of the two components of the doublet, causing their high temperature accidental degeneracy to be lifted at lower temperatures. As the trans dimer has been reported to be less stable than the cis dimer, we prefer the former explanation. Indirect evidence supporting this will be reported below.

At all temperatures, on the high frequency side of the band at $1771 \,\mathrm{cm}^{-1}$ a broad, weak shoulder is present. The broadness of this band shows that



Fig. 6. The spectrum of the $NO/(NO)_2$ equilibrium at each temperature was obtained by subtracting the rescaled spectrum obtained from a redistilled solution from the spectrum of a freshly prepared solution. The temperatures used were: A, 84.3 K; B, 86.6 K; C, 87.7 K; D, 91.1 K, E, 93.4 K.



Fig. 7. The mid infrared spectrum (4000-400 cm⁻¹) obtained by co-condensing NO and HCl in liquefied argon at 85 K.

most likely it is due to a solid suspended in the solution. Its frequency is very close to that of the asymmetric dimer, ONON [16]. As stated in the introduction, this dimer has been reported by Ohlsen and Laane [16] to form only in the presence of some Lewis acids such as HCl. Although for the experiments shown in Fig. 6 no HCl was added to the mixture, the cell used in the experiments had been used numerous times to study mixtures containing HCl. Therefore, it is not impossible that traces of HCl adsorbed to the cell walls catalysed the formation of the ONON dimer.

In order to find supporting evidence for this assignment, in a separate experiment a gaseous mixture containing comparable amounts of NO and HCl was condensed in liquefied argon at 85 K. The resulting spectrum is shown in Fig. 7. The presence of NO and *cis*-(NO)₂ is deduced from the bands at 1870 and 1862 cm⁻¹, but now near 1773 cm^{-1} a very broad, very intense absorption band is present. This band cannot be due to *cis*-(NO)₂ alone, and, therefore, it is believed to be also due to the asymmetric dimer. This is supported by the presence, in the spectrum in Fig. 7, of weak broad bands at 3728, 3450 and 1687 cm⁻¹, which have not been observed in the experiments without

added HCl, and which have been assigned by Ohlsen and Laane [16] to the asymmetric dimer as well. Their broadness suggests the asymmetric dimer is in suspension and is not dissolved, showing the insolubility of this species in liquefied argon. These observations evidently support our assignment of the weak, broad shoulder at 1773 cm^{-1} in the spectra shown in Fig. 7, to undissolved asymmetric dimer.

The spectra shown in Fig. 6 only contain contributions due to monomer and dimer NO, and can be used to obtain the enthalpy of dimerisation. This requires knowledge of the integrated intensities of the band due to the monomer and of a band due to the dimer. It is clear from Fig. 6 that this at least for the monomer is not straightforward. In order to resolve the monomer band at 1870 from the cis- $(NO)_2$ band at 1862 cm^{-1} , a band profile analysis with Gauss/Lorentz sum functions, using a twoband combination, was initially attempted. However, due to the rotational structure on the monomer contour it was found impossible to obtain a reliable resolution. Therefore, a trial-and-error procedure was adopted, the success of which is due to the much higher FWHH of the monomer band compared to that of the dimer band. In this

frequency of the dimer absorption. Subsequently,

the parameters for the dimer band were systemati-



Fig. 8. The procedure of the integration of the contributions due to NO and N_2O_2 in the temperature study of the NO/ N_2O_2 equilibrium. The subsequent steps are explained in the text. procedure, in a first step the least squares optimised doublet approximation for the region for the 1925– 1800 cm⁻¹ region was calculated. Then, the calculated dimer contribution was subtracted from the experimental spectrum, and the resulting difference profile inspected for anomalies in the vicinity of the

ference spectrum. The procedure is illustrated in

Fig. 8. The top trace is the spectrum shown in

Fig. 6B. By cutting the spectrum at 1810 cm^{-1} , the complex absorption near 1771 is isolated and can be integrated numerically. This part is shown in Fig. 8B. Figs. 8C and 8D then show the resolved contributions due to dimer and monomer, respectively. Inspection of Fig. 8D now clearly reveals the presence of a P and R branch in the monomer absorption, confirming the relatively free rotation of the species in liquefied argon.

Using the equations

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 = -RT \ln K$$
$$K = \frac{[(\text{NO})_2]}{[\text{NO}]^2} = A \frac{I_{(\text{NO})_2}}{(I_{\text{NO}})^2}$$

the enthalpy of dimerisation was obtained from the slope of the Van't Hoff plot obtained by plotting $\ln(I_{(NO)_2}/(I_{NO})^2)$ against 1/T. In total, three Van't Hoff plots were constructed, always using the monomer intensity obtained as described above, but using three different series of $I_{(NO)_2}$. In the first, the integrated intensity of the absorption complex around 1771 cm^{-1} was used. In the second, the intensity of ν_1 , the 1862 cm⁻¹ dimer band, was employed. The third one was constructed using the integrated intensity of the $\nu_1 + \nu_5$ combination band of the two NO stretches in cis-(NO)₂ at 3604 cm⁻¹. The intensity behaviour of this band as a function of temperature is shown in Fig. 9. In this figure, trace A corresponds to the lowest temperature, 86.5 K, while trace F was obtained at the highest temperature, 102.4 K. It is clear that this band is not overlapped by nearby transitions, and hence it can be numerically integrated straightforwardly. For the present band, this was done in the region shown in Fig. 9, i.e. between 3625 and $3585 \,\mathrm{cm}^{-1}$.

In Fig. 10 the Van't Hoff plots are displayed. All three show a satisfactory linearity, with, however, a slightly different slope. The use of the 1771 cm⁻¹ complex leads to an enthalpy of dimerisation equal to $-11.6 \pm 0.3 \text{ kJ mol}^{-1}$, while using ν_1 the value obtained is $-15.3 \pm 0.3 \text{ kJ mol}^{-1}$. Finally, the use of the $\nu_1 + \nu_5$ intensities leads to a ΔH_0 of $-13.4 \pm 0.3 \text{ kJ mol}^{-1}$.



Fig. 9. The $\nu_1 + \nu_5$ combination band of *cis*-ONNO in liquefied argon as a function of temperature. From top to bottom the temperatures are: A, 86.5 K; B, 88.7 K; C, 91.1 K; D, 93.2 K; E, 97.7 K; F, 102.4 K.

Because there is no indication that the measured intensities of the NO monomer band and of the ν_1 and $\nu_1 + \nu_5$ bands of *cis*-(NO)₂ are influenced by the presence of bands due to other compounds, it is disturbing to find that the dimerisation enthalpies determined using these intensities are significantly different. The obvious reasons for this are the successive manipulations of the experimental data necessary to obtain the intensities for monomer NO and for ν_1 of *cis*-(NO)₂. These manipulations, unfortunately, could not be avoided for the present experimental environment, and, therefore the intensities obtained here must be regarded as the best data available to date. If the error is



ABSORBANCE Α в С D Е 1706 1653 ⊽/cm-1

Fig. 10. Van't Hoff plots used to calculate the enthalpy of dimerisation of NO to N_2O_2 . As intensities the integrated absorbances of the $\nu_1 + \nu_5$ combination band of *cis*-ONNO (top), the ν_5 antisymmetric N=O stretch of *cis*-ONNO (middle) and the ν_1 symmetric N=O stretch of *cis*-ONNO (bottom), combined, in each case, with the integrated intensity of the monomer NO stretching, were used.

mainly due to the inaccurate resolution of the ν_1 of *cis*-(NO)₂ from the monomer intensity, an underor overestimation of the monomer intensity is accompanied by an error in the opposite direction for the intensity of ν_1 of *cis*-(NO)₂. This of course

Fig. 11. The disappearance of the absorption bands of sym- N_2O_3 in liquefied argon as a function of the temperature. From top to bottom the temperatures are: A, 84.4 K; B, 86.6 K; C, 87.7 K; D, 91.1 K; E, 93.4 K.

negatively influences the ΔH_0 calculated from these data. Due to exactly the same experimental limitations, however, even if the intensities of $\nu_1 + \nu_5$ of *cis*-(NO)₂ were obtained with high accuracy, because of the use of the same monomer NO intensities, the ΔH_0 calculated using $\nu_1 + \nu_5$ will also be affected. Therefore, we propose as the value for the dimerisation enthalpy the average of the values obtained using ν_1 and $\nu_1 + \nu_5$ of *cis*-(NO)₂. This leads to a ΔH_0 equal to



Fig. 12. The mid infrared spectrum (4000-400 cm⁻¹) of a solution of N_2O_3 and N_2O_4 in liquefied krypton at 141 K.

 $-14.3 \pm 1 \text{ kJ mol}^{-1}$. The error limits on this value were chosen so as to include within the limits of error the two values used in the averaging.

Finally the ΔH_0 calculated using the intensities of ν_5 of cis-(NO)₂, $-11.6 \pm 0.3 \text{ kJ mol}^{-1}$ is again significantly lower than the other experimental values. This, in our opinion, reflects the presence in the ν_5 complex of a band due to the less stable *trans*-(NO)₂, in agreement with the conclusion drawn above.

From the survey presented by Menoux et al. [4], it is clear that the ΔH_0 for dimerisation in the vapour phase is rather temperature sensitive, which for Van der Waals molecules is not unexpected [35]. The experimental value obtained in a temperature interval closest to the interval used in this study, is the one reported by Dinerman and Ewing [3], and equals $-10.2 \text{ kJ mol}^{-1}$. Its absolute value is significantly lower than the one obtained in this study. There are two possible reasons for this. In our opinion, the smaller part of the difference is due to the lower temperatures used in this study (84.3–93.4 K). The major contribution, however, must be due to the fact that the present value was obtained in solution. The dipole moment of cis- $(NO)_2$ is approximately twice as high as that of NO itself, so that the dimer will be stabilised slightly more in liquefied argon than the monomer, while this extra stabilisation is absent in the vapour phase.

The behaviour of N_2O_3

It was observed above that in the spectra of solutions in liquefied argon both asym-N₂O₃ and sym- N_2O_3 are observed, the former as insoluble crystallites dispersed in the solution, and the latter dissolved in the liquid argon. Upon increasing the temperature of the solution, the bands due to sym- N_2O_3 very rapidly decrease in relative intensity. This is shown in Fig. 11, where the stretching bands due to this species as recorded in a temperature study are given. All spectra in this figure are shown with the same absorbance scale, with the temperature varying from 84.4 K for the top spectrum to 93.4 K for the bottom spectrum. It can be seen that in the mere 10 K covered in this study the bands all but disappear. The intensity decrease of the bands due to sym- N_2O_3 was accompanied by an intensity increase of the band due to NO. This is partly caused by the dissociation of N₂O₃, but will



Fig. 13. Spectrum of a mixture of asym- N_2O_3 and N_2O_4 in liquefied krypton. A, Spectrum recorded at 116 K; B, Spectrum recorded at 141 K; C, Spectrum recorded at 150 K.

definitely also be partly due to the dissociation of the dimer. When the temperature of the solution was lowered again, the bands due to $sym-N_2O_3$ reappeared.

The rapid intensity decrease of the bands due to $sym-N_2O_3$ can be interpreted as reflecting, through

the Van't Hoff isochore, the relatively high enthalpy of formation of this species from NO and NO₂. This interpretation implies the existence of an equilibrium between sym-N₂O₃ and its decomposition products NO and NO₂. However, during this study no bands due to NO₂ were detected. This shows that at any time of the experiment the concentration of this species was very low, much lower than what has to be expected from the intensity decrease of the bands of sym-N₂O₃. The reason for this is the very low solubility of the dimer to which the NO₂ set free by the dissociation of sym-N₂O₃ will dimerise. For the observed behaviour upon heating the solution to be an equilibrium phenomenon, sym-N₂O₃ has to be in equilibrium with the precipitated N₂O₄. Although it is generally felt that equilibria in which a solid compound is involved are slow in being established, the rapid reappearance of the sym-N₂O₃ bands upon cooling of the solution suggests that the dissolution of solid N₂O₄ occurs quite rapidly.

In liquefied krypton, due to the higher temperatures at which the solutions are investigated, practically no sym- N_2O_3 was detected in the spectra (Fig. 12). At the lowest temperatures for these solutions the broad bands near 1875 and $1595 \,\mathrm{cm}^{-1}$ due to undissolved asym-N₂O₃ are accompanied by much sharper bands, at 1830 and 1631 cm^{-1} . These can be seen in Fig. 13A, recorded at 116K. These new bands, as suggested by their position and sharpness, are assigned to dissolved asym-N₂O₃. In Fig. 13B, showing the spectrum recorded at 141 K, the bands due to undissolved asym- N_2O_3 have completely disappeared, showing that the species is completely dissolved, which is reflected by the much higher intensities of the 1830 and $1631 \,\mathrm{cm}^{-1}$ bands. When the solution is kept at this temperature for a prolonged time, these bands are observed to slowly decrease in intensity. This shows that at that temperature the decomposition equilibrium of asym-N₂O₃ establishes itself relatively slowly. Finally, in Fig. 13C the spectrum of the solution recorded at 150 K is shown. The intensities of the asym-N₂O₃ bands now is substantially lower, from which can be inferred that also the stability of asym-N₂O₃ is critically dependent on the temperature.

In liquefied krypton, in contrast with the liquefied argon solutions, only two bands due to N_2O_4 , at 1747 and 1729 cm⁻¹, are observed. In spite of the increased temperature, these bands are narrower than their counterparts in liquefied argon. These observations show that in liquefied krypton also the N_2O_4 has dissolved.

From Fig. 13A to 13C, the intensity of the N_2O_4 bands increases. This must be due to the decomposition of asym- N_2O_3 , followed by the dimerisation of the NO_2 formed. Upon recooling of the solution the intensity of the asym- N_2O_3 bands was found to increase. However, at the time scale used in the experiment they did not reach their original intensity. This is thought to be due to the loss of NO upon heating the solution, with the diffusion, upon recooling, of NO back into the solution being a very slow process.

Because of the observed kinetic effect on the intensities of the bands due to $asym-N_2O_3$ at intermediate temperatures, and because of problems with measuring the intensity of the NO band, no attempts to thermodynamically quantify the dissociation equilibrium of $asym-N_2O_3$ were undertaken.

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