Dinitrogen Trioxide. Part XIII.[1] Hydration of Gaseous Dinitrogen Trioxide and a Reinvestigation of its Dissociation

By **Alan J. Vosper**, Department of Chemistry, Portsmouth Polytechnic, Burnaby Road, Portsmouth PO1 3QL

The hydration and dissociation of gaseous N_2O_3 have been studied using an improved spectrophotometric method. The influence of the partial pressure of NO_2 and H_2O on the various equilibrium constants is considered. The possible existence of additional nitrogen oxides and the stability of gaseous HNO_2 is discussed.

NITROUS ACID is an intermediate in many gas-phase reactions involving nitrogen oxides and is of considerable interest in atmospheric chemistry. A knowledge of its stability is therefore important. When NO, NO_2, and H_2O are mixed, equilibria (1)—(4) are known to be

$$N_2O_4 \rightleftharpoons 2NO_2,\ K_1 = p_2^2/p_4 \quad (1)$$

$$N_2O_3 \rightleftharpoons NO + NO_2,\ K_2 = p_1p_2/p_3 \quad (2)$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2,\ K_3 = p_{HNO_2}^2/p_3p_{H_2O} \quad (3)$$

$$3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O,\ K_4 = p_1^2p_{HNO_3}p_{H_2O}/p_{HNO_2}^3 \quad (4)$$

established. Alternatively, (2) and (3) can be combined giving (5). The symbols p_1, p_2, p_3, and p_4 represent the

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O,\ K_5 = p_1p_2p_{H_2O}/p_{HNO_2}^2 \quad (5)$$

partial pressure of NO, NO_2, N_2O_3, and N_2O_4, in agreement with previous nomenclature. In fact, HNO_2 consists of an equilibrium mixture of *cis* and *trans* isomers due to restricted rotation about the central bond.[2] In the present work it was not possible to distinguish between these isomers so that p_{HNO_2} represents the sum of their partial pressures.

The stability of gaseous HNO_2 is at present somewhat uncertain. Previous measurements [3,4] of K_5, although not in good agreement, seemed to define the stability of this molecule. However, more recently a study of the reaction of NO with H_2O_2 revealed a higher concentration of HNO_2 at 550 K than would be expected from extrapolating the equilibrium data.[5] The molar absorption coefficients for gaseous HNO_2 calculated from recent data [6] surprisingly exceeded the corresponding values in aqueous solution by a factor of three. Since the concentration of HNO_2 in the gas was calculated using experimental values of K_5, this might suggest that the actual concentration of HNO_2 was larger than the calculated value. It has recently been reported that the apparent stability of low concentrations of HNO_2 vapour was much larger than expected from the equilibrium studies.[7] In view of these results it was decided to reinvestigate this system using an improved experimental method.

The dissociation of N_2O_3 [equation (2)] was reported in Part I of this series.[8] At a given temperature the values of K_2 determined by different authors [8-11] are not in good agreement and they appear to vary significantly with p_2.[8-10] Reliable values of K_2 were required to calculate K_3. Because of this, the dissociation of N_2O_3 was reinvestigated using the same equipment and method as for the hydration studies but omitting the water.

EXPERIMENTAL

The preparation and purification of chemicals, and all physical measurements, were made in an all-glass high-vacuum system fitted with greaseless stopcocks and joints. Commercial samples of N_2O_4 were purified as described previously.[8] Commercial samples of NO were used initially but were found to contain traces of N_2O and NO_2. In later experiments the NO was generated by adding sulphuric acid to an aqueous solution containing nitrite and iodide. In each case the gas was carefully purified by chemical means and fractional distillation of the liquid.[8] The final product condensed to a colourless liquid and i.r. and u.v. spectroscopy gave no evidence for higher oxides. Trace amounts ($<0.1\%$) of N_2O remained but these would not affect the results. The water was doubly distilled and outgassed several times under high vacuum.

The reaction vessel was fitted with optical windows and was contained within a thermostatted compartment in the

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optical system of a modified Unicam SP 500 spectrophotometer.[12] An appropriate pressure of nitrogen(IV) oxides was admitted into the vessel and p_2 was determined spectrophotometrically as previously described.[13] The H_2O and NO were premixed by blending suitable volumes of dry and water-saturated NO from two gas burettes. The partial pressure of water was checked by determining the dew point; *i.e.* a portion of the gas was slowly cooled until moisture was deposited on a small mirror. The moist NO was then admitted to the reaction vessel, and the total pressure set to a convenient value between 30 and 300 kN m^{-2}. After allowing sufficient time for complete mixing and the establishment of thermal and chemical equilibrium, p_2 was redetermined and the total pressure was measured by balancing it against a mercury manometer using an all-glass spiral gauge as a null instrument. Temperatures were measured using calibrated mercury-in-glass thermometers.

Calculation of Results.—The experiments involved simultaneous measurement of the total pressure and p_2 for known mixtures of NO, NO_2, and H_2O. The value for p_2 was obtained spectrophotometrically and high precision is required if reliable equilibrium constants are to be obtained. The present measurements are believed to be more accurate than previous work for the following reasons.

Measurements were made at a number of different wavelengths (usually ten) between 450 and 550 nm which corresponded to local maxima or minima, since NO_2 shows a well defined fine structure in its visible spectrum.[14] Previous workers either employed measurements at a single wavelength or polychromatic radiation. Corrections were applied for the variation of the molar absorption coefficient of NO_2 with temperature and pressure. The latter correction assumed that the other gases (mainly NO) had a similar effect to N_2 or O_2, but in fact the correction was negligible except at the highest pressures. A correction was also applied for the absorption of radiation by N_2O_3 using the known spectrum of this molecule.[15] This was small in the 450—550 nm region, but became more important at longer wavelengths and very significant at shorter wavelengths. Because of this and the possible photodecomposition of NO_2,[6] measurements below 450 nm were avoided. Several cells with different nominal path lengths were used and in each case absorption measurements were made using known partial pressures of NO_2. Thus the absorption of radiation could be directly related to p_2 and a knowledge of the actual cell path length was not required. In practice, quite small values of p_2 (down to *ca.* 0.2 kN m^{-2}) could be measured.

Since the calculation of the equilibrium constants was very similar to the previous methods[3,4,11] it will not be described in detail. It depends on a material balance for NO, NO_2, and H_2O (if present) as well as a knowledge of p_2 and the total pressure. Values of the equilibrium constants K_1 and K_4 are required. The former were taken from the literature[13] and the latter were calculated using standard thermochemical data.[16] It was then possible to obtain the partial pressures of all the components and hence calculate the relevant equilibrium constants. Under the experimental conditions, p_{HNO_3} was extremely small. It should be stressed that the validity of the calculations depends on the absence of appreciable concentrations of any species other than those appearing in equations (1)—(5).

RESULTS AND DISCUSSION

(a) *The* NO–NO_2 *System.*—Measurements were made with p_1 and p_2 in the ranges 30—300 and 0.2—6.0 kN m^{-2} respectively. For a given value of p_1 (*ca.* 100 kN m^{-2}), K_2 showed little systematic variation with p_2 except at the highest pressures when it appeared to decrease with increasing p_2 (Figure 1). This condition corresponded to the highest experimental error so that the effect might be spurious. Previous authors, working at higher p_2 values and using a vapour-density method, reported[8-10] a steady decrease in K_2 with increasing p_2. The effect was initially attributed to the non-ideality of the gases,[10] but deviations from ideality should be small for all the components. An alternative explanation is that some other molecular species might be present. Although N_2O_2 can exist in the gas phase[17] at low temperatures and/or high pressures, calculations showed that its concentration was negligible under the conditions of the present or previous experiments.

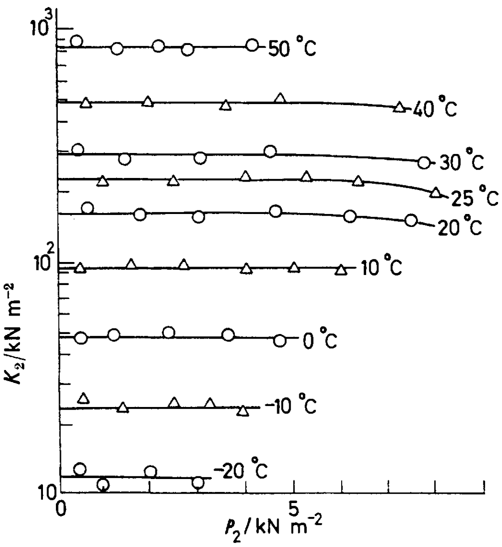

FIGURE 1 Variation of K_2 with p_2 at various temperatures

It is known[10] that K_1 also apparently decreases with increasing p_2. It has been recently suggested[18] that this could be due to the additional equilibrium (6).

$$N_3O_6 \rightleftharpoons 3NO_2,\ K_6 = p_2{}^3/p_{N_3O_6} \qquad (6)$$

There is mass-spectroscopic evidence for N_3O_6 and higher polymers in molecular beams produced by an ultrasonic nozzle,[18] but no direct evidence for its presence in the gas under normal conditions. Similarly, the apparent variation of K_2 with p_2 could be explained by an additional equilibrium such as (7). If molecular species

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such as N_3O_5 or N_3O_6 are present, the present calculations need revising. However, because the measurements

$$N_3O_5 \rightleftharpoons 2NO_2 + NO,\ K_7 = p_1p_2^2/p_{N_3O_5} \quad (7)$$

employ relatively low p_2 values, the dissociation of such species should be extensive.

A careful study of the i.r. and u.v. spectra of both NO_2 and $NO-NO_2$ mixtures was made in order to test for the presence of additional species. For the former system all the i.r. and u.v. bands had intensities which were either proportional to p_2 (due to NO_2) or to p_2^2 (due to N_2O_4). No bands were observed whose intensity was proportional to p_2^3 as required for N_3O_6. The presence of an isobiestic region near 320 nm suggested only NO_2 and N_2O_4 were present in high concentration. For the $NO-NO_2$ system additional i.r. bands were present whose intensity was proportional to both p_1 and p_2. These are attributed to N_2O_3. No bands were found which could be assigned to N_3O_5 or some other new species. The u.v. spectra were less informative, showing a weak band in the visible region and a very strong band in the u.v., both due to N_2O_3. The phase diagram for the $N_2O_3-N_2O_4$ system [19] gave no evidence for any intermediate compound such as N_3O_5. Thus the evidence, although not completely conclusive, does not favour the existence of appreciable concentrations of other species such as N_3O_5 or N_3O_6.

It seems more likely that the variation of K_1 and K_2 with p_2 is due to the adsorption of polar NO_2 on the walls of the vessel as previously suggested.[8] In agreement with this, it appears that the observation of these effects depends on the experimental method used. Vapour-density measurements [8-10] result in K_1 or K_2 depending markedly on p_2, whereas a velocity of sound method [20] and the spectrophotometric method [13] do not show this variation. In fact the values of K_1 and K_2 at a given temperature as determined by vapour-density measurements are in agreement with other methods provided the former are extrapolated to zero pressure.

At each temperature an average value of K_2 was calculated, weighting each result in accordance with its estimated error. Three results which differed from the mean by more than three standard deviations were neglected (two of these involved a high p_2 value). A plot of $\log_{10} K_2$ against $1/T$ was linear (Figure 3). The mean values of $\Delta H^\ominus$ and $\Delta S^\ominus$ were calculated using the method of least squares. The results are compared with previous values in Table 1. The use of a higher-order polynomial was not justified since $\Delta H^\ominus$ and $\Delta S^\ominus$ did not change significantly over the experimental temperature range. The results were combined with standard thermodynamic data [16] for NO and NO_2 to obtain the data for N_2O_3 given in Table 2.

A number of thermodynamic calculations for N_2O_3 have been reported. The most recent set [21] uses accurate rotational constants and gives results in good agreement with this work, but unfortunately the lower-frequency fundamentals for this molecule are not known with certainty [22] and these dominate the vibrational contributions at normal temperatures. Calculations using the most recent assignment of the fundamental frequencies do not give a value for $\Delta S^\ominus$ in good agreement with this work (Table 1). It seems possible that the low-frequency fundamentals are incorrect. In particular it is suggested that ν_7 (an in-plane rocking mode) probably occurs at a higher wavenumber than 160 cm⁻¹. The corresponding vibrational mode in N_2O_4 was estimated to occur at 270 cm⁻¹.[23] If it occurred at a similar position in N_2O_3 the agreement between the calculated and experimental values of $\Delta S^\ominus$ would be satisfactory.

TABLE 1

Thermodynamic data obtained from the various equilibrium constants

Equilibrium constant	Temperature range/K	$\Delta H^\ominus$/kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}	Ref.
K_2	253—323	41.17 ± 0.33	144.3 ± 1.0	*a*
	298—318	46.8	162.8	10
	278—318	40.6 ± 0.6	142.3 ± 2.2	8
	243—283	44.1	154.4	11
		40.9	142.4	21
			136.4	*c*
K_3	283—323	1.9 ± 1.2	17.3 ± 4.0	*a*
K_5	283—323	39.3 ± 0.9	127.0 ± 3.0	*a*
	293—353	37.9 ± 1.3	125.1 ± 5.4	3
			131.2	*d*

[a] This work. [b] Obtained by recalculating the original data of ref. 8. Drs. T. Ishida and W. Spindel are thanked for making this information available. [c] Calculated using the vibrational assignments given in ref. 22. [d] Calculated value.

TABLE 2

Some thermodynamic functions of N_2O_3 and HNO_2 at 298.15 K

Species	$\Delta G_f^\ominus$/ kJ mol^{-1}	$\Delta H_f^\ominus$/ kJ mol^{-1}	$S^\ominus$/ J K^{-1} mol^{-1}	Source
N_2O_3	139.7	82.3	306.3	From K_2
	139.3	82.5	308.4	Ref. 21
			314.2	*a*
HNO_2 (equilibrium mixture)	−46.1	−78.8	256.2	From K_5
			254.4	*b*
HNO_2 (*cis*)			248.0	*b*
(*trans*)			249.0	*b*

[a] Calculated using the vibrational assignments given in ref. 22. [b] Calculation.

(b) *The* $NO-NO_2-H_2O$ *System.*—The experimental results were less satisfactory for this system. The spectrophotometric determination of p_2 was more difficult in the presence of water vapour which appeared to cause minor modifications of the visible spectrum of NO_2. This could indicate some weak interaction between the two molecules.

The experimental results showed a greater scatter and the equilibrium constant K_5 appeared to show a definite variation with p_2 (Figure 2). It is difficult to be certain

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whether this effect is real or is due to some systematic error in the measurements. The experimental values of K_5 were therefore extrapolated to zero pressure before calculating the thermodynamic data. The variation of K_5 with p_{H_2O} was more difficult to study since the range of values of the latter are limited. At low pressure the experimental errors are high and the equilibrium was rather slowly established, while at high pressures deposition of water on the walls of the vessel can occur. Because of these restrictions no measurements were made below 283 K. The results suggested that K_5 decreased with increasing p_{H_2O}. This could be due to some extra stability of HNO_2 in the presence of water, *e.g.* due to hydrogen bonding.

Because of the high values of p_1, the disproportionation of HNO_2 [equation (4)] was not important. I.r. spectroscopy gave little evidence for HNO_3, although a small correction was made for its presence using calculated values for K_4.

A plot of $\log_{10} K_5$ (using the values extrapolated to zero pressure) against $1/T$ gave a linear relation (Figure 3). Calculations indicated that the variation of $\Delta H^\ominus$ and $\Delta S^\ominus$ with temperature is greater in this case (*ca.* 1% over the experimental temperature range), but the experimental uncertainty in these quantities is also greater. The integrated van't Hoff equation was therefore used and the mean values of $\Delta H^\ominus$ and $\Delta S^\ominus$ are given in Table 1. The results are in fair agreement with a previous study[3] considering the experimental errors, and the values of K_5 are in moderate agreement with previous results near room temperature.[4]

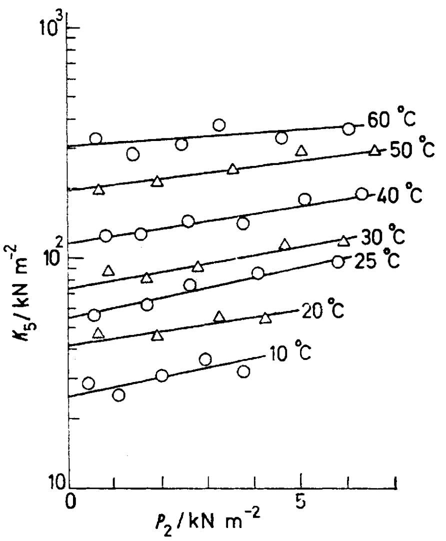

FIGURE 2 Variation of K_5 with p_2 at various temperatures

The entropies of *cis*- and *trans*-HNO_2 have been recalculated using reliable values for the rotational constants.[24] The relative amounts of the two isomers in the equilibrium mixture were calculated assuming that the *trans* isomer was more stable by 2.09 kJ mol^{-1}.[16] The entropy of the equilibrium mixture was thus obtained (Table 2) as well as values of $\Delta S^\ominus$ for reactions (3) and (5) (Table 1). The calculated values of $\Delta S^\ominus$ agree moderately well with those obtained from the equilibrium constants, allowing for the various sources of error. It should be stressed that the calculations do depend on the correct assignment of the fundamentals of *cis*- and *trans*-HNO_2.[25] Combining the present experimental results with standard thermodynamic data,[16] the results obtained for the *cis–trans*-equilibrium mixture of HNO_2 are given in Table 2.

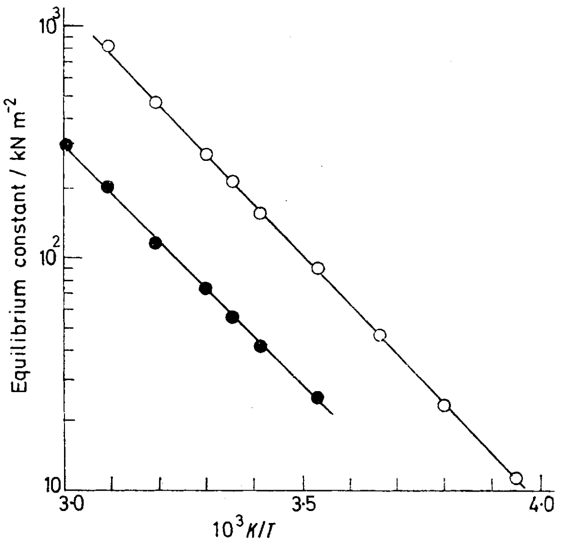

FIGURE 3 Variation of K_2 (○) and K_5 (●) with $1/T$

For the NO–NO_2 system, equilibria (1) and (2) are established within microseconds at room temperature.[26] By contrast, for the NO–NO_2–H_2O system, equilibria (3) and (5) are established more slowly.[27] Therefore the high stability of HNO_2 under certain experimental conditions may be due to kinetic rather than thermodynamic factors. There is considerable kinetic evidence that the reaction proceeds *via* a heterogeneous mechanism. Thus the rate equation may be written as $d[HNO_2]/dt = k[N_2O_3][H_2O]^n$ where n is *ca.* 2 and k depends on the surface to volume ratio.[27] It seems probable that a favourable transition state is not achieved in the gas phase, but reaction can occur at the walls in adsorbed water layers. For the reverse reaction it is necessary for two molecules of HNO_2 to be at the reaction site if the product is N_2O_3. It appears that the anomalous stability of HNO_2 in the gas phase under certain experimental conditions is primarily due to kinetic factors.

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