401. *Dinitrogen Trioxide. Part IV.*[1] *Composition of the Vapour in Equilibrium with Liquid Mixtures of Nitrogen Dioxide and Nitric Oxide.*

By I. R. Beattie and A. J. Vosper.

A study has been made of the vapour composition above liquid mixtures of nitrogen dioxide and nitric oxide. The vapour in equilibrium with a liquid containing equimolar amounts of nitrogen dioxide and nitric oxide is almost exclusively nitric oxide. The visible and near-ultraviolet spectra of some oxides of nitrogen in the gas phase and in solution are discussed. An all-glass circulating pump is described.

In a previous paper[1] we reported the vapour pressure of liquid mixtures of nitric oxide and nitrogen dioxide. Although our results were generally in agreement with those of earlier workers,[2,3] the agreement with the data of Purcell and Cheesman[4] was poor. The British paper[4] contains the only available data on the composition of the gas in equilibrium with liquid mixtures of nitric oxide and nitrogen dioxide. We have re-investigated this system.

Experimental

Preparation of Reagents.—The preparation of nitric oxide and nitrogen dioxide has been described previously.[5]

Apparatus.—Most of the work was carried out in an all-glass apparatus in the absence of grease. In two experiments a greaseless diaphragm tap was included in the system. The liquid mixture of nitric oxide and nitrogen dioxide was contained in a cryoscope[6] which was connected to a spiral gauge used as a null-point instrument in the measurement of vapour pressures. The cryoscope was also connected to a pumping system for circulating the gases over the liquid mixture of nitrogen oxides and through an optical cell.

Fig. 1 shows the pump which was operated by means of three independent electromagnets acting on steel inserts. This pump was useful down to pressures of a few millimetres. The two valves were ground-glass ball-and-socket joints, while the plunger and barrel were obtained from a " Summit " interchangeable hypodermic syringe of 20 c.c. capacity. The glass of the syringe had a coefficient of linear expansion close to that of " Pyrex," so that direct sealing was possible. The pump would not operate in the presence of liquids as these caused sticking of the ball and socket valves.

Analysis of the Gases.—This was carried out at several different wavelengths in the range 4000—6000 Å, with a " Unicam " S.P. 500 ultraviolet spectrometer. The spectrometer was modified in that the cell compartment was replaced by a thermostatically controlled tank with plain " Pyrex " windows. Movement of the 5 cm. gas cell into or out of the light beam, for comparison with the reference cell, was accomplished by means of long inlet tubes connected to glass springs.

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[1] Part III, Beattie and Vosper, *J.*, 1960, 4799.

[2] Whittaker, Sprague, Skolnik, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 4794.

[3] Baume and Robert, *Compt. rend.*, 1919, **169**, 970.

[4] Purcell and Cheesman, *J.*, 1932, 826.

[5] Beattie and Bell, *J.*, 1957, 1281.

[6] Beattie, Bell, and Vosper, *J.*, 1960, 4796.

Spectrum of Nitrogen Dioxide.—We observed the spectrum of pure nitrogen dioxide by using a cell temperature of 135°, at which the vapour pressure of dinitrogen tetroxide would be negligible.

DISCUSSION

The analysis of a mixture of nitric oxide, nitrogen dioxide, dinitrogen tetroxide, and dinitrogen trioxide by ultraviolet spectroscopy is simplified by the fact that nitric oxide is transparent above 2300 Å at normal pressures,[7] while dinitrogen tetroxide is transparent above 4000 Å.[8] The position with regard to dinitrogen trioxide is rather obscure. Early workers [9] found a band system in the 3000—4000 Å region which was initially attributed to dinitrogen trioxide. However, it was subsequently suggested that this spectrum was due either to selective enhancement of certain bands of the nitrogen dioxide molecule, or more probably to the presence of nitrous acid which would result if the reacting gases were not perfectly dry.[10] Although there has been some support for the enhancement theory,[11] D'Or and Tarte [12] have shown that " dry " gas mixtures of nitric oxide and nitrogen dioxide show only a trace of this banded system unless the apparatus has been baked out under a high vacuum, when a continuous absorption appears below 3000 Å. This work has been supported [13] by a study of the isotopic shift effect for the band system, where H_2O or D_2O was used with a mixture of nitric oxide and nitrogen dioxide. Melvin and Wulf [10] note that " the absorption in the red or orange that leads to the blue colour of liquid N_2O_3 has not yet been observed " in the gas.

FIG. 1. *The all-glass circulating pump.*

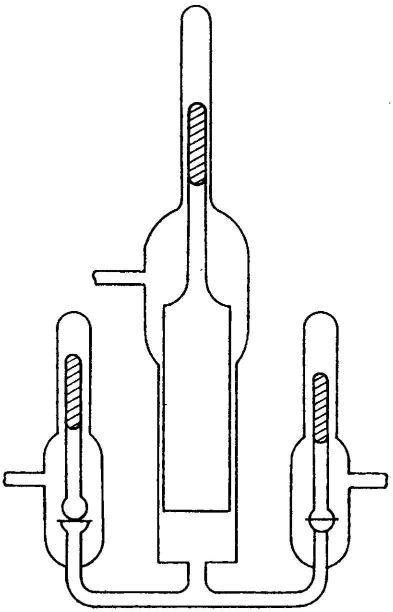
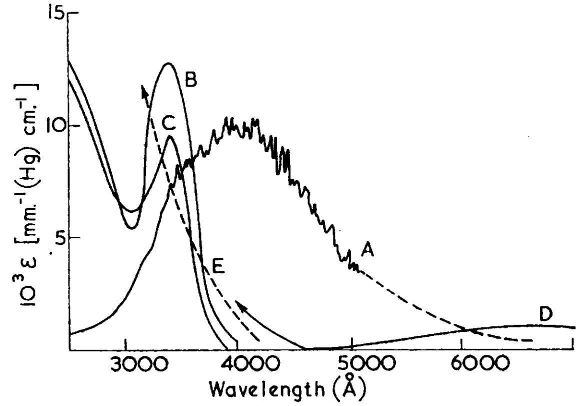


FIG. 2. *The spectrum of certain oxides of nitrogen in the gas phase and in solution*: A, *nitrogen dioxide*; B, *dinitrogen tetroxide in cyclohexane*; C, *dinitrogen tetroxide in the gas phase*; D, *dinitrogen trioxide in toluene at* −80°; E, *dinitrogen trioxide in the gas phase.* (The curve from the lower arrow head increases rapidly to >130.)



The spectrum of dinitrogen trioxide in several solvents [14] has shown the presence of a

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[7] Jenkins, Barten, and Mulliken, *Phys. Rev.*, 1927, **30**, 150.
[8] Hall and Blacet, *J. Chem. Phys.*, 1952, **20**, 1745.
[9] Melvin and Wulf, *Phys. Rev.*, 1931, **38**, 2294.
[10] Melvin and Wulf, *J. Chem. Phys.*, 1935, **3**, 755.
[11] Newitt and Outridge, *J. Chem. Phys.*, 1938, **6**, 752.
[12] D'Or and Tarte, *Bull. Soc. roy. Sci. Liège*, 1951, 685; *Bull. Soc. chim. belges*, 1950, **59**, 365.
[13] Porter, *J. Chem. Phys.*, 1951, **19**, 1278.
[14] Mason, *J.*, 1959, 1288, and references therein.

weak absorption maximum at about 7000 Å and an intense absorption, similar to that in the gas phase, below 3500 Å. Fig. 2 shows the spectrum of several nitrogen oxides in the gas phase in the region 3000—7000 Å. Whittaker *et al.*[15] have suggested that nitrogen dioxide has the same spectrum (and extinction coefficients) in solution as in the gas phase. Addison and Sheldon[16] have measured the absorption spectrum of dinitrogen tetroxide in several solvents. In non-co-ordinating solvents the spectrum is very similar to that in the gas phase. It is reasonable to suppose that the spectrum of dinitrogen trioxide in the gas phase will be similar to that of a solution of dinitrogen trioxide. If we assume that dinitrogen trioxide is fully associated in toluene at −80° it is possible to calculate extinction coefficients. This has been done, and the results are shown in Fig. 2.

Kaufmann and Kelso,[17] while studying the thermal decomposition of nitric oxide, observed the spectra of two mixtures initially containing the same quantities of nitrogen(IV) oxide, but in one case containing an excess of nitric oxide to one atmosphere total pressure and in the other an excess of oxygen to the same total pressure. If no dinitrogen trioxide were formed the two spectra would be identical. By using the given spectra, plus the equilibrium constants for the dissociation of dinitrogen tetroxide[18] and dinitrogen trioxide,[5] it is possible to calculate approximately the extinction coefficients of dinitrogen trioxide in the range 3500—4000 Å. These results are included in Fig. 2, where it is clear that the gas-phase spectrum shows resemblances to that obtained in solution.

The intensity of the band around 7000 Å for solutions of dinitrogen trioxide is low, even at its maximum. In view of the small quantities of dinitrogen trioxide usually found in equilibrium mixtures of nitrogen oxides at room temperature this compound is not likely to be important in the analysis of the gases in the visible region. However, for relatively high pressures of nitric oxide the amount of dinitrogen trioxide may become comparable with the amount of nitrogen dioxide, and in the region of 7000 Å could cause quite erroneous analytical results if not allowed for. Our analyses, carried out at several different wavelengths above 4000 Å, showed no trend with wavelength. We assume that the combination of low extinction coefficient and low concentration of dinitrogen trioxide enables us to ignore the presence of the gas.

The results of examination of the vapour-phase composition are shown in the Table and take the form of a liquid composition, a vapour pressure, and a gas composition. These three variables are not necessarily simply related. Inspection of the Table shows that the composition of the gas x_g (where x refers to composition in terms of NO_x) is almost independent of the particular combination of pressure and composition of the liquid x_l, *for any given sample in our apparatus.* In view of the fact that each sample was studied in a closed system, the total composition for any given sample is constant. It is therefore possible to construct a graph such as that shown in Fig. 3, where values of the liquid composition (interpolated to a pressure of either 20 or 50 cm.) are plotted atainst the gas composition. It is not easy to assess the errors in the gas-phase composition, but systematic errors are not likely to occur except in so far as equilibrium-constant data are used for the calculations. The length of the horizontal lines indicates the spread of our analytical figures for the gas phase at any given total composition. The error in x_l is at most $\pm 0{\cdot}002$. The line drawn on the graph is the mean of our results and agrees in a satisfactory manner with the results obtained from the data of Purcell and Cheesman[4] (at 76 cm.).

It appears from these results that the composition of the vapour above liquid mixtures of nitric oxide and nitrogen dioxide is nearly independent of temperature for a particular liquid composition. Further, the vapour above " pure " dinitrogen trioxide is almost exclusively nitric oxide. These results, taken together with the vapour-pressure and

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[15] Whittaker, *J. Chem. Phys.*, 1956, **24**, 780; Steese and Whittaker, *ibid.*, p. 776.

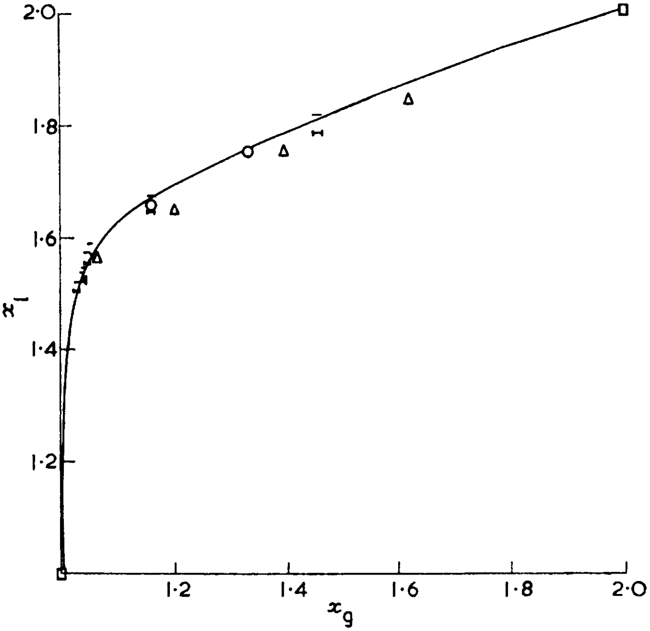
[16] Addison and Sheldon, *J.*, 1958, 3142.

[17] Kaufmann and Kelso, *J. Chem. Phys.*, 1955, **23**, 1702.

[18] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

magnetic results[1] on this system, support the suggestion that nitric oxide has a low physical solubility in dinitrogen trioxide.

FIG. 3. *The composition of the vapour, x_g, against the composition of the liquid, x_l, for mixtures of nitric oxide and nitrogen dioxide.*



|——| 20 cm. pressure. —— 50 cm. pressure. ○ Two points with diaphragm taps (see Table).
△ Data from Purcell and Cheesman. □ Pure nitric oxide or pure nitrogen(IV) dioxide.

Our results for the extinction coefficients of nitrogen dioxide (obtained at 135°) are in good agreement with those of earlier workers for lower temperatures, where equilibrium-constant data are necessary.

Vapour pressure, liquid composition, and gas composition for mixtures of nitrogen dioxide and nitric oxide.

Sample	x_l	Pressure (mm.)	x_g
1	1·747 *	76·5 *	1·335 *
2	1·656 *	23·9 *	1·160 *
3	1·785	91·0	1·477
	1·792	182·7	1·461
	1·803	339·3	1·446
	1·816	495·8	1·451
4	1·644	27·4	1·160
	1·654	179·8	1·163
	1·663	338·2	1·159
	1·676	552·6	1·163
5	1·560	17·3	1·056
	1·564	88·7	1·057
	1·572	229·0	1·053
	1·589	478·7	1·051
6	1·544	41·0	1·054
	1·551	143·4	1·049
	1·559	275·3	1·045
	1·570	477·1	1·043
7	1·528	75·9	1·045
	1·532	229·0	1·041
	1·538	376·2	1·040
	1·551	562·4	1·040
8	1·521	187·4	1·047
	1·532	399·7	1·036
	1·537	479·4	1·038
9	1·502	112·2	1·032
	1·506	209·4	1·028
	1·513	352·0	1·030
	1·521	527·7	1·028
	1·527	636·0	1·025

* Apparatus contained a greaseless diaphragm tap.

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KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

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