259. *The Ionisation of Dinitrogen Tetroxide in Nitric Acid. Evidence from Measurements of Infrared Spectra and Magnetic Susceptibilities.*

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The infrared spectra of solutions of dinitrogen tetroxide in anhydrous nitric acid have been found to contain lines belonging to nitrosonium and nitrate ions. Lines due to non-ionised dinitrogen tetroxide appeared with increasing intensity as the concentration of the solutions was increased. None of the lines expected for non-ionised nitrogen dioxide was observed. Intensity measurements have been interpreted to show that in dilute solutions one nitrate ion is formed per solute molecule, consistent with the ionisation :

$$N_2O_4 \longrightarrow NO^+ + NO_3^-$$

The magnetic susceptibilities of these solutions have been measured and interpreted to confirm the conclusion, reached from the infrared-spectral study, that the extent of the dissociation :

$$N_2O_4 \longrightarrow 2NO_2$$

is very small compared with that of the ionic dissociation.

It has been concluded from Raman-spectral studies that dinitrogen tetroxide in dilute solution in nitric acid is dissociated partly homolytically, but mainly heterolytically :

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

The frequency associated with the nitrosonium ion, obtained for these solutions, is at about 2240 cm.$^{-1}$ and is considerably below the usual value of 2300 cm.$^{-1}$. It was suggested that it is unlikely that the low value is due to a solvent effect, for two main reasons. First, for solutions of nitrosonium hydrogen sulphate and perchlorate in nitric acid peaks were obtained at 2300 cm.$^{-1}$. Secondly, it was shown that for solutions of dinitrogen tetroxide in nitric acid, the frequency is restored to its normal value by the addition of small quantities of sulphuric acid.

Lynn, Mason, and Corcoran [2] have measured optical densities of solutions of dinitrogen tetroxide in nitric acid, with and without addition of potassium nitrate. Their conclusion that the fraction of solute which is ionised in dilute solution (up to 0·06 molal-dinitrogen tetroxide) is 0·7 ± 0·3, shows that the extent of ionisation is considerable, but allows the interpretations that the extent of the homolytic dissociation is comparable or negligible.

One of the main objects of the present work was to obtain information about the relative importance of the heterolytic and homolytic dissociations.

Infrared-spectral Evidence.—The infrared spectrum of a 7 molal *-solution of dinitrogen tetroxide in anhydrous nitric acid is compared with that of the solvent in Fig. 1. Frequencies observed are listed in Table 1, the first column listing those frequencies which belong to the solvent and the second those which are not so attributable. The remaining columns list those infrared active fundamentals, which fall in the region concerned, for the species NO_3^-,[3] N_2O_4,[4] NO_2,[5] and NO^+.

The strong line at 2220 cm.$^{-1}$ is attributed to the nitrosonium ion. The unusually low value for the frequency confirms the results of Goulden and Millen; the value obtained here is even lower than the values obtained by Raman spectroscopy, but the solutions

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* Concentrations of solutions are given as stoicheiometric molality of dinitrogen tetroxide unless otherwise stated.

[1] Goulden and Millen, *J.*, 1950, 2620.

[2] Lynn, Mason, and Corcoran, *J. Phys. Chem.*, 1955, **59**, 238.

[3] Williams and Decherd, *J. Amer. Chem. Soc.*, 1939, **61**, 1382.

[4] Perkins and Wilson, *Phys. Rev.*, 1952, **85**, 755.

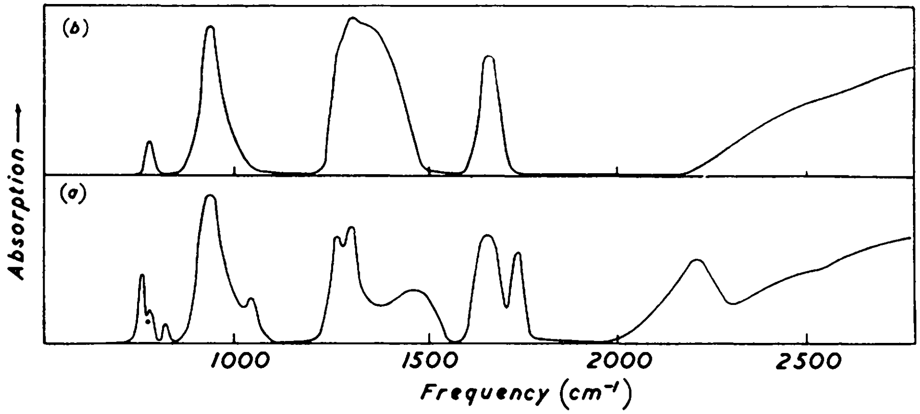
[5] Moore, *J. Opt. Soc. Amer.*, 1953, **43**, 1045.

used in the latter case were more dilute. The presence of nitrate ion is clearly indicated by the strong appearance of the allowed fundamentals, 830 and 1350 cm.$^{-1}$. The line at 1050 cm.$^{-1}$ is also attributed to the nitrate ion, for it was also found in the infrared spectra of solutions of potassium nitrate in nitric acid. This frequency corresponds to the totally symmetric stretching vibration, being well known in the Raman spectrum of the nitrate ion, and is presumably allowed in the infrared spectrum of the solution because of an effective lowering of symmetry by solvation. The remaining lines, apart from those of the solvent, are attributed to undissociated dinitrogen tetroxide, for they correspond well in frequency and relative intensity to the fundamental frequencies in this region, reported by Perkins and Wilson.[4] The infrared spectrum does not provide evidence of non-ionised nitrogen dioxide in these solutions. It may be that the fundamental frequency at about 750 cm.$^{-1}$ is masked by a line due to the tetroxide, and that at about 1320 cm.$^{-1}$ is obscured by a broad band due to the overlap of lines due to nitric acid and nitrate ion, but the fundamental frequency at 1620 cm.$^{-1}$ should serve to identify non-ionised nitrogen dioxide.

TABLE 1. *Frequencies* (*cm.*$^{-1}$).

Belonging to the solvent	Not belonging to the solvent	NO_3^-	N_2O_4	NO_2	NO^+	Belonging to the solvent	Not belonging to the solvent	NO_3^-	N_2O_4	NO_2	NO^+
—	—	675	684	—	—	1300	—	—	—	—	—
—	750	—	748	750	—	—	—	—	—	1323	—
770	—	—	—	—	—	—	1400	1350	—	—	—
—	830	830	—	—	—	—	—	—	—	1616	—
930	—	—	—	—	—	1664	—	—	—	—	—
—	1050	—	—	—	—	—	1750	—	1747	—	—
—	1260	—	1260	—	—	—	2220	—	—	—	2300

FIG. 1. *Comparison of the infrared spectrum of a 7 molal-solution of* (a) *dinitrogen tetroxide in nitric acid with the spectrum of* (b) *the solvent.*



(*The diagram is not intended to compare intensities of bands, since the conditions were not the same for all the bands.*)

The spectra of solutions of other concentrations in the range 2·5 to 12 molal, are similar to that in Fig. 1, except that the dinitrogen tetroxide bands become more prominent at the higher concentrations. An attempt was made to estimate quantitatively, by means of intensity measurements, the fraction of solute which is ionised in these solutions. The optical densities of the line at 830 cm.$^{-1}$ due to nitrate ion and that at 770 cm.$^{-1}$ due to nitric acid were measured for a number of solutions of potassium nitrate in nitric acid. A calibration curve of the ratio of the optical densities of these two lines was used to estimate the concentration of nitrate ion in solutions of dinitrogen tetroxide from the ratio of the optical densities of the same two lines in the spectra of these solutions. The results are shown in Fig. 2, which is a plot, as a function of concentration, of the number of solute molecules required to produce one nitrate ion. The results become inaccurate at the higher concentrations because the intensity measurements are made difficult by the appearance of a dinitrogen tetroxide band at 750 cm.$^{-1}$, and also because of possible loss of solute by evaporation. However, it is clear that as the solutions become more dilute, one nitrate ion is produced per solute molecule. This is consistent with the ionisations :

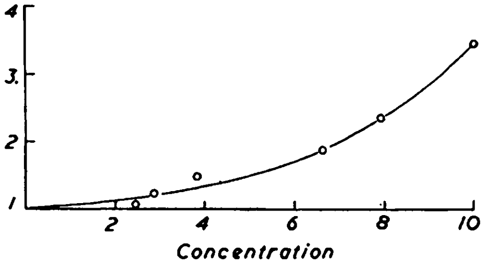
$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

$$N_2O_4 + HNO_3 \rightleftharpoons NO_3^- + HN_2O_4^+$$

The method cannot distinguish between these ionisations, since $HN_2O_4^+$ is analytically equivalent to solvated NO^+. A protonated dinitrogen tetroxide molecule is excluded as the source of the strong line at 2220 cm.$^{-1}$, since this value is too high to be one of the ion's fundamental frequencies.

The results, as can be seen from Fig. 2, confirm the conclusion reached from a study of Raman spectra, that for solutions up to about 1 molal of stoicheiometric dinitrogen tetroxide, the concentration of undissociated tetroxide is small. It is clear too, from the infrared spectra, that solutions up to this concentration do not contain appreciable quantities of nitrogen dioxide, for, first, lines belonging to this molecule were not observed and, secondly, nearly all of the solute is accounted for by the above ionisation.

FIG. 2. *The number* (n) *of dinitrogen tetroxide molecules required to produce one nitrate ion, plotted as a function of concentration* (*stoicheiometric molality*).



The dependence of the frequency of the nitrosonium ion on its environment has been further examined. A 5 molal-solution of dinitrogen tetroxide was examined at a number of temperatures between 20° and —40°. The frequency was found to increase slightly from 2235 cm.$^{-1}$ to 2264 cm.$^{-1}$, with fall in temperature. Finally, the sample was frozen at —185°. The infrared spectrum of the crystals contained a strong line at 2255 cm.$^{-1}$, showing that the ionisation occurs in the solid phase as well as in solution. The nitrosonium ion frequency was measured in the infrared spectra of solid nitrosonium hydrogen sulphate $NO^+HSO_4^-$ and in nitrosonium tetrachloroaluminate NO^+AlCl^{4-}. The values obtained were 2275 cm.$^{-1}$ and 2238 cm.$^{-1}$, respectively.

Among the solutions examined was an 8% w/w solution of nitrosonium hydrogen sulphate in nitric acid. This gave a value of about 2315 cm.$^{-1}$ for the frequency of the nitrosonium ion. The addition of small quantities of sulphuric acid to solutions of dinitrogen tetroxide in nitric acid led to an increase in the frequency of the nitrosonium ion. These results confirm qualitatively the variations in frequency observed in the Raman spectra of these solutions. The present work establishes that the low value of the frequency in the spectra of solutions of dinitrogen tetroxide is not due to an intervention of molecular nitrogen dioxide.

Evidence from Magnetic Susceptibilities of Solutions.—The magnetic susceptibilities of several solutions of dinitrogen tetroxide in nitric acid are recorded in Table 2, together with the susceptibilities of some solutions of potassium nitrate in nitric acid. All the solutions of both solutes are diamagnetic, the susceptibility passing through a maximum in each case. The initial rise in susceptibility presumably reflects the repression by nitrate ion of the self-dissociation of the solvent. The similarity of the susceptibilities for the two solutions shows that the solutions of dinitrogen tetroxide do not contain appreciable amounts of a paramagnetic species. If the assumption is made that the difference between the susceptibilities of the two solutions is due to a paramagnetic contribution from nitrogen dioxide, with one unpaired electron, then it can be calculated that the concentration of nitrogen dioxide does not exceed 0·02 molal in the most concentrated solution examined.

TABLE 2. *Magnetic susceptibilities* (s) *of solutions of dinitrogen tetroxide and potassium nitrate in nitric acid at* 18°.

N_2O_4, molality	*s* per g.	N_2O_4, molality	*s* per g.	KNO_3, molality	*s* per g.
0·815	−0·317	3·511	−0·310	1·041	−0·334
1·173	−0·316	3·672	−0·317	1·571	−0·344
1·455	−0·323	5·827	−0·305	2·338	−0·355
2·107	−0·322	6·813	−0·294	3·740	−0·325
2·614	−0·332			4·587	−0·335
				HNO_3	−0·325

Experimental.—The infrared spectra were recorded with a Hilger D 209 spectrometer, used as a single-beam instrument. For the spectra of solutions in nitric acid, a single drop of the sample was placed between two silver chloride windows and a suitable cell thickness was obtained by clamping the windows together. For the spectra at low temperatures an apparatus similar to that described by Wagner and Hornig[6] was used. In this apparatus the cell is surrounded by a jacket which can be evacuated, or filled with dry nitrogen or air. The cell itself may then be cooled to the appropriate temperature by a freezing mixture, solid carbon dioxide, or liquid nitrogen. A suitable film of nitrosonium hydrogen sulphate was prepared by melting a sample and then allowing it to crystallise. The spectrum of nitrosonium tetrachloroaluminate was observed by using a mull with liquid paraffin.

Magnetic susceptibility measurements were made by the Gouy method, and are probably correct to within about 2%.

Nitric acid was prepared by distillation, at a pressure of about 2 cm. of mercury, from a mixture of 1 part of commercial 97% nitric acid and 3 parts of sulphuric acid. The distillate was collected in a trap cooled in liquid nitrogen. The product was redistilled until a colourless product was obtained.

Dinitrogen tetroxide was prepared by heating "AnalaR" lead nitrate. The product was dried by distillation over phosphoric oxide in a stream of oxygen.

Nitrosonium hydrogen sulphate was prepared by passing sulphur dioxide through nitric acid, and the tetrachloroaluminate by passing nitrosyl chloride through aluminium chloride dissolved in liquid sulphur dioxide.

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[6] Wagner and Hornig, *J. Chem. Phys.*, 1950, **18**, 298.