147. *Electrical Conductances of Solutions in Nitric Acid. Part III.* Solutions of Dinitrogen Tetroxide.*

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Electrical conductances and transport numbers are reported for solutions of dinitrogen tetroxide in nitric acid. The electrical conductances are comparable with those of alkali-metal nitrates in nitric acid. The transport measurements are interpreted in terms of the cathode process $NO_2^+ + e \longrightarrow NO_2$ and the reverse process at the anode. It is concluded that dinitrogen tetroxide is almost completely ionised in dilute solutions in nitric acid.

THREE modes of ionisation of dinitrogen tetroxide in dilute solution are known: in water NO_2^- and NO_3^- are produced, in strong acids such as sulphuric acid NO^+ and NO_2^+ are formed, and under other conditions the intermediate ionisation leads to NO^+ and NO_3^-. The present study extends previous Raman [1] and infrared spectroscopic studies [2] of the last type of ionisation in nitric acid as solvent, by investigating the electrical conductance and transport properties of these solutions.

EXPERIMENTAL

Materials.—Nitric acid was prepared as described in Part I.[3] Dinitrogen tetroxide was prepared by dropping fuming nitric acid on potassium nitrite, passing the gases through phosphoric oxide tubes, and condensing the product in a trap cooled in alcohol–solid carbon dioxide. The condensate was purified by re-distillation in a stream of oxygen and condensed as a white solid at $-80°$. Solutions were prepared by distillation into the acid in a current of oxygen.

Electrical Measurements.—Conductances were determined at $-10°$ as described in Part I, and are recorded in Table 1. In the transport-number determinations solutions were electrolysed in a Hittorf apparatus modified as illustrated in Fig. 1 to prevent the loss, by subsequent migration, of NO_2^+ formed in the anode compartment. In order to avoid contamination of the solution the taps for isolating the compartments were left unlubricated but sealed with solution. The phosphoric oxide tubes and the stoppers covering the taps prevented the entry of water vapour during electrolysis. Depending on the solution concentration, $1—5 \times 10^{-3}$ F, as measured by a copper coulometer in series, was passed through the cell, the quantity of electricity being corrected for inaccuracies inherent in this type of coulometer (Part II). After electrolysis the contents of the compartments were analysed for stoicheiometric NO_2 as described in Part II.

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* Part II, *J.*, 1958, 2248.

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

[2] Millen and Watson, *J.*, 1957, 1369.

[3] Lee and Millen, *J.*, 1956, 4463.

The migration of the nitrosonium ion together with the cathode process $NO_2^+ + e \longrightarrow NO_2$, which was discussed in Part II, results in a net gain of $(1 + 2t_{NO^+})$ moles of stoicheiometric NO_2 per Faraday. Transport numbers calculated on this basis are listed in Table 2. Evaluation of transport numbers from the change in the anode compartment on the basis of the reverse electrode reaction $NO_2 \longrightarrow NO_2^+ + e$ gave slightly lower values. This difference almost certainly arises from a slight intervention of the anode reaction $NO_3^- \longrightarrow NO_2^+ + \frac{1}{2}O_2 + 2e$, the usual anode process in the electrolysis of solutions of nitrates in nitric acid as established in Part II. The contribution of this process becomes more pronounced as the concentration of dinitrogen tetroxide decreases.

FIG. 1. *Transport apparatus.*

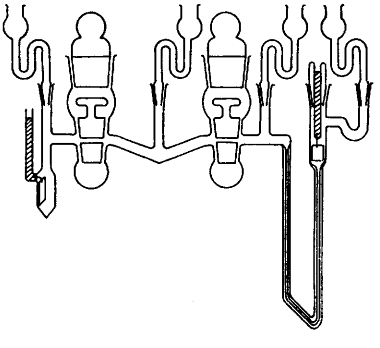
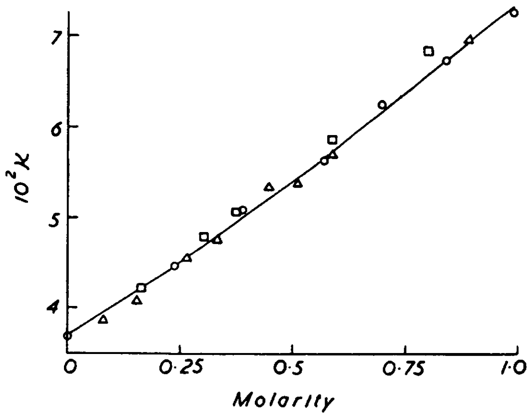


FIG. 2. *Comparison of conductances of dinitrogen tetroxide and of ammonium and potassium nitrates.*



○, N_2O_4; △, KNO_3; □, NH_4NO_3.

TABLE 1. *Specific conductances and densities of solutions of dinitrogen tetroxide in nitric acid.* $T = -10{\cdot}02°$.

N_2O_4(M)	0·0699	0·2400	0·3874	0·5694	0·6970	0·8422	0·9725	1·208	1·869
$10^4\kappa$ (ohm^{-1})	365·0	446·3	509·1	565·5	626·1	674·6	730·2	812·2	996·0
d_4^{-10}	1·5645	1·5685	1·5715	1·5752	1·5785	1·5819	1·5849	1·5911	

TABLE 2. *Transport numbers of the nitrosonium ion in solutions of dinitrogen tetroxide in nitric acid.*

$T = -10°$.	N_2O_4 (M)	0·1442	0·2793	0·3728	0·4136	0·5152	0·5808	0·7016	1·577
	t_{NO^+}	0·047	0·077	0·115	0·131	0·176	0·160	0·237	0·377
	l_{NO^+}	13·1	12·7	15·3	16·2	19·0	16·0	21·2	—
$T = 20°$.	N_2O_4 (M)	0·0497	0·110	0·181	0·379	0·420	0·831	1·242	1·535
	t_{NO^+}	0·053	0·093	0·138	0·193	0·197	0·282	0·302	0·326

DISCUSSION

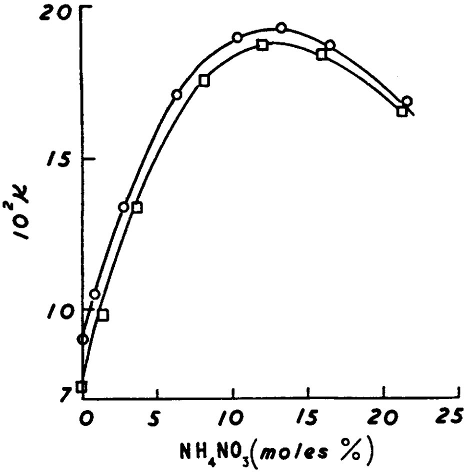
Fig. 2 shows that the specific conductance of a solution of dinitrogen tetroxide is entirely comparable with that of potassium or ammonium nitrates in nitric acid over the whole range of concentration investigated. If it is accepted that alkali-metal nitrates are completely ionised in these solutions, it is difficult to avoid the conclusion that dinitrogen tetroxide must be very largely ionised. The high conductance cannot arise from a large ionic mobility of the nitrosonium ion, for the data in Table 2 show that over most of the concentration range the transport numbers of the nitrosonium ion are slightly smaller than those given in Part II for the alkali-metal ions in nitric acid solution. The transport numbers of Table 2 are not as accurate as those of the alkali-metal ions, particularly for the dilute solutions. Here they are small because of the large contribution to the conductance by the ions formed by solvent self-dissociation, and so are sensitive to errors arising from unavoidable small losses of the tetroxide by vaporisation during electrolysis. Although the mobilities of the ions show some scatter, and increase with increasing concentration, the values are all within the range 17 $\pm$ 4 ohm^{-1}, showing that the mobility of the nitrosonium ion cannot be significantly greater than the mobilities of sodium, potassium, or ammonium ions. Thus the results are well understood in terms of the nearly complete ionisation $N_2O_4 \longrightarrow NO^+ + NO_3^-$. They could scarcely be accounted for by any type of ionisation which provides less than one nitrate ion per molecule of dinitrogen tetroxide. The possibility of an incomplete ionisation which provides more than one nitrate ion per dinitrogen tetroxide molecule, *e.g.*,

$$N_2O_4 \rightleftharpoons 2NO_2;\ NO_2 + HNO_3 \longrightarrow HNO_2^+ + NO_3^-$$

is excluded by the observed magnetic susceptibilities of the solutions.[2]

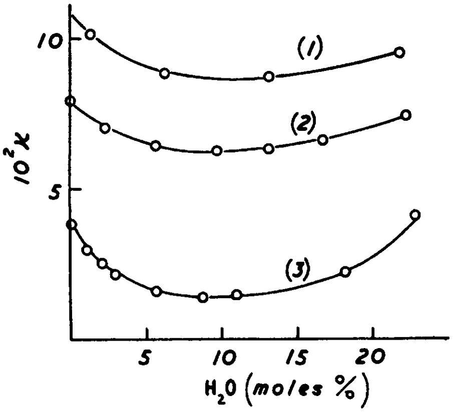
The sensitivity of the ionisation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ to repression by added nitrate ion provides in principle a method for determining the strength of dinitrogen tetroxide as an electrolyte in these solutions. Some evidence in this direction may be obtained from the conductivity study by Taylor *et al.*,[4] whose results can be used to find the increment in conductance produced by a given amount of the tetroxide in solutions containing varying quantities of ammonium nitrate. If the tetroxide were a strong electrolyte, the increment would be expected to be independent of the amount of added nitrate ion, within the limits of the approximation of concentration-independent ionic mobilities. The increment varies little over the range 0—6 moles % of added nitrate ion for an approximately 0·85M-solution of dinitrogen tetroxide.

FIG. 3. *Effect on conductances of adding ammonium nitrate.*



O, 3·2 moles % of N_2O_4 in HNO_3; □, 3·48 moles % of N_2O_5 in HNO_3.

FIG. 4. *Effect on conductances of adding water.*



(1) 5·4% (w/w) of N_2O_4 in HNO_3; (2) 4·4% (w/w) of N_2O_4 in HNO_3; (3) HNO_3 solvent.

We may compare the effect of adding ammonium nitrate to solutions of similar concentrations of dinitrogen tetroxide and pentoxide. The curves of Fig. 3 apply to solutions of these oxides in nitric acid, initially at 3·2 and 3·48 moles %, respectively. These concentrations will change as ammonium nitrate is added to the system, and it is not possible, in the absence of density data for the resulting solutions, to calculate concentrations after each addition of ammonium nitrate; the variation is not expected to be large, however. The decrease in κ with increasing concentration of ammonium nitrate, observed at the higher concentrations, is almost certainly a viscosity effect, such as has been previously found in very concentrated solutions;[5] the important point is that the

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[4] Taylor, Baker, and Lyne, *Canad. J. Chem.*, 1951, **29**, 452.
[5] Berl and Saenger, *Monatsh.*, 1929, **54**, 1036.

two curves run closely parallel. It is unlikely that nitronium nitrate is incompletely ionised in these solutions, and so there is no evidence from conductivity measurements of any marked repression of the ionisation of dinitrogen tetroxide, in 3 moles % solution, by up to six-fold increase in nitrate-ion concentration.

The effect of addition of water on the conductances of solutions of the tetroxide in nitric acid may also be calculated from the data of Taylor *et al.*[6] Fig. 4 shows that the increase in conductance produced by a given amount of tetroxide is approximately independent of the amount of water present in the solvent, up to about 20 moles % of water, indicating that dinitrogen tetroxide is largely ionised in these aqueous nitric acid solutions. The same limitations as mentioned previously apply to the calculation of the concentrations. The rather slower initial decrease in conductance on addition of water to the solutions, as compared with the pure acid, probably arises because of the partial repression of the solvent ionisation due to the nitrate ion produced by the tetroxide already added. For solvents containing more than about 20 moles % of water the increment in conductance due to added tetroxide falls off, but the rapidly increasing concentration of $H_3O^+NO_3^-$ makes interpretation difficult in this region.

Although the evidence indicates that the dinitrogen tetroxide is a strong electrolyte in nitric acid solution, it is clear from the yellow colour of these solutions that ionisation cannot be complete. The solutions have an absorption with a molar extinction coefficient, calculated on the basis of stoicheiometric tetroxide, of the order of 10 at 4400 Å, and of the order of 100 at 4000 Å. The absorption was followed into the ultraviolet region but no maximum could be observed. This is attributed to the overlap of bands due to NO_2 and possibly N_2O_4, with maxima at approximately 4000 Å and 3400 Å respectively as observed in the gas phase,[7] with a band centred at about 3000 Å due to the nitrate ion,[8] followed by the absorption of the solvent itself. Since there is no absorption maximum, the measurements cannot be used to determine the concentration of undissociated NO_2, for quantitative estimates obtained from values on the rising side of an absorption band are subject to large uncertainties by a shift in the position of the absorption band in passing from the gas to solution.

A comparison of relative intensities at a number of wavelengths on the side of the absorption band has been made for various concentrations. Typical results of optical-density ratios obtained for successive dilutions of an approximately 0·8M-solution are given below. The optical densities of these solutions were measured at room temperature by a Unicam spectrophotometer, glass-stoppered cells being used. Readings were taken for each solution at a number of wavelengths, since the sensitivity at any given wavelength varies with the concentration.

Dilution factor	1	2	3	4
λ (Å)	Ratio of optical densities			
4700	1	0·546	0·306	0·200
4800	1	0·552	0·325	0·225
4900	1	0·562	0·354	0·214

Dilution factor	1	2	3	4
λ (Å)	Ratio of optical densities			
5000	1	0·582	0·345	0·235
5100	1	0·650	0·345	0·232

The volatility of dinitrogen tetroxide is a complicating factor in these experiments, but within the accuracy of measurements made on the side of an absorption band, it appears that Beer's law is obeyed, supporting previous work [9] on this system. This indicates that the concentration of NO_2 is directly proportional to the stoicheiometric concentration over this range. This is the result to be expected for the operation of the equilibria:

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

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[6] Taylor, Lyne, and Follows, *Canad. J. Chem.*, 1951, **29**, 439.
[7] Hall and Blacet, *J. Chem. Physics*, 1952, **20**, 1745.
[8] Morton and Riding, *Proc. Roy. Soc.*, 1926, *A*, **113**, 717.
[9] Lynn, Mason, and Corcoran, *J. Phys. Chem.*, 1955, **59**, 238.

if the concentration of the species N_2O_4 is small. The concentration of the species NO_2 has already been shown to be small by magnetic-susceptibility measurements.[2]

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