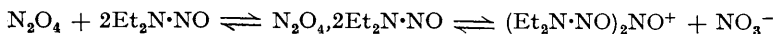


254. *The Liquid Dinitrogen Tetroxide Solvent System. Part XI.* Compound Formation and Ionic Species in Solutions of Diethylnitrosamine in Liquid Dinitrogen Tetroxide.*

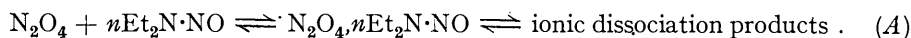
By C. C. ADDISON and C. P. CONDUIT.

The physical and chemical properties of solutions of diethylnitrosamine in liquid dinitrogen tetroxide are interpreted on the basis of the equilibria



Electrical conductivity and viscosity measurements, over the temperature range -33° to $+16^\circ$, show that only the 1 : 2-compound is formed, and that the only effect of temperature change is to adjust the position of the equilibrium. The nature of the cation is deduced from colorimetric measurements and absorption spectra. Anodic oxidation of diethylnitrosamine during electrolysis of these solutions is related to the reaction of dinitrogen pentoxide, and of nitronium pyrosulphate, with diethylnitrosamine. A method for the determination of the latter is described.

THERMAL and conductometric measurements, described in Part VI (*J.*, 1951, 1303), showed that the equilibria in mixtures of diethylnitrosamine and liquid dinitrogen tetroxide may be represented as follows :

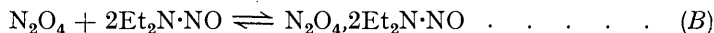


Freezing-point data indicated the existence of the compound $\text{N}_2\text{O}_4, 2\text{Et}_2\text{N}\cdot\text{NO}$ (m. p. -37.5°) only, but heat-evolution curves suggested that at higher temperatures compounds involving other molecular ratios might exist. If such a variation occurred, there should be a corresponding shift with temperature, in the composition of the mixture at which electrical conductivity was a maximum. In order to compare the results at different temperatures, it was necessary to correct for the changing viscosity of the solutions. The viscosities of the mixtures, in themselves, give valuable information on compound formation in the system.

Viscosity of Mixtures.—The relation between kinematic viscosity and nitrosamine concentration is shown in Fig. 1 for several temperatures in the range $+16^\circ$ to -33° . The viscosity isotherms were constructed from the results of temperature-viscosity curves obtained for a series of mixtures in the range 39—100 mol. % of diethylnitrosamine. The isotherms for the lower temperatures terminate sharply at the composition at which the mixture solidified. The kinematic viscosity ν for liquid dinitrogen tetroxide was calculated from the data of Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, A, 397) and of Pascal and Garnier (*Bull. Soc. chim.*, 1919, **15**, 309). Values of ν (in centistokes) for pure diethylnitrosamine are given in the following table :

Temperature	-33.0°	-26.9°	-20.7°	-14.4°	-7.9°	-1.5°	4.5°	11.5°	19.0°
Kinematic viscosity	3.61	3.07	2.65	2.31	2.02	1.82	1.62	1.47	1.28

At -33° the viscosity passes through a pronounced maximum (Fig. 1) with changing concentration, and the peak of the curve occurs at a composition equivalent to the compound, $\text{N}_2\text{O}_4, 2\text{Et}_2\text{N}\cdot\text{NO}$. With increasing temperature the maximum becomes less pronounced, until at 16° it is scarcely perceptible. However, throughout the full temperature range the position of the maximum on the concentration axis remains constant. These results are readily explained on the assumption that only one compound, *viz.*, $\text{N}_2\text{O}_4, 2\text{Et}_2\text{N}\cdot\text{NO}$, is present in the mixture, and that this compound is thermally unstable, so that the equilibrium



is displaced towards the left-hand side with increasing temperature.

* Part X, *J.*, 1951, 2843.

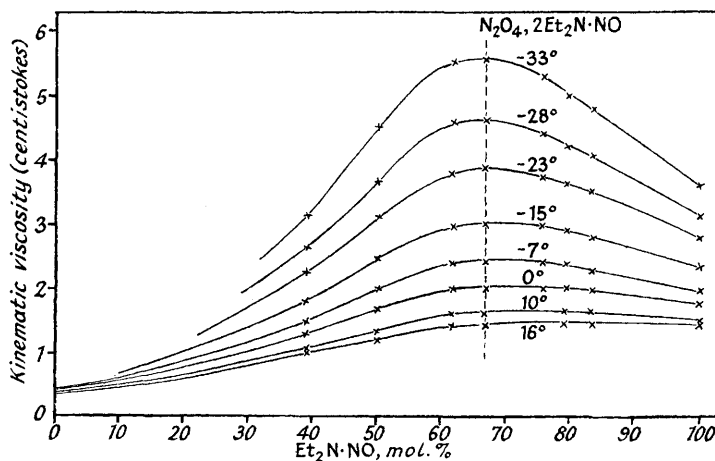
Electrical Conductivity of Mixtures.—Specific conductivities have been measured over a temperature range for mixtures of four different compositions and are recorded in columns (a) of Table 1. In each case, there is a linear relationship between κ and the temperature.

TABLE 1.*

Et ₂ N·NO, mol. % ...	40.0		50.6		61.6		72.2	
Temp.	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
10°	2.620	2.83	2.490	3.39	2.660	4.25	2.165	3.48
0	2.350	3.08	2.155	3.64	2.285	4.56	1.840	3.68
-7	2.165	3.32	1.925	3.87	2.025	4.85	1.610	3.88
-15	1.945	3.64	1.655	4.12	1.715	5.10	1.355	4.08
-23	1.735	4.04	1.390	4.36	1.410	5.34	1.120	4.27
-28	1.600	4.34	1.225	4.55	1.210	5.55	0.975	4.41
-33	1.465	4.79	1.055	4.83	1.020	5.61	0.830	4.52

* (a) = Specific conductivity $\kappa \times 10^{-4}$ ohm⁻¹ cm.⁻¹; (b) = "corrected" conductivity $\kappa\eta/d \times 10^{-6}$.

FIG. 1.



The temperature coefficients of specific conductivity are as follows :

Et ₂ N·NO, mol. %	40	50.6	61.6	72.2
Temp. coeff. $\times 10^{-4}$ (ohm ⁻¹ cm. ⁻¹ /degree)	0.0269	0.0334	0.0380	0.0312

It is of interest that the temperature coefficients pass through a maximum in the region of the composition N₂O₄·2Et₂N·NO.

Allowance has been made for the variation in viscosity with temperature by the calculation of "corrected" conductivity values which are given in columns (b) of Table 1. Whereas the specific conductivity values have a positive temperature coefficient at all concentrations, the corrected conductivity shows a negative coefficient, and it is the corrected values which are to be related to changes in the position of the equilibrium with temperature. Neither liquid dinitrogen tetroxide nor diethylnitrosamine has an appreciable conductivity alone, and the relatively high electrical conductivity of the mixture arises from ionic dissociation of the compound N₂O₄·2Et₂N·NO. The viscosity measurements above suggest that this compound is thermally unstable; increase in temperature will therefore reduce the proportion of compound (and the ionic concentration) in the system. This effect leads directly to a negative temperature coefficient for the corrected conductivity.

Conductivity Isotherms.—The above conclusions were confirmed by the preparation of conductivity isotherms at three widely separated temperatures (shown as full curves in Fig. 2). As temperature decreases, the maximum becomes less pronounced. At 16° and 0° the maximum occurs at the 1 : 2 mol. ratio, but at -23° the curve is flattened to such an extent that it is not possible, from the specific conductivity measurements, to determine the position of the maximum. The same three isotherms, corrected for viscosity, are shown in

Fig. 2 by broken curves. The maxima on the corrected conductivity curves are equally pronounced at all three temperatures, and each maximum occurs at the 1 : 2 mol. ratio. In agreement with measurements on solutions of fixed composition (Table 1), the specific conductivities show a positive temperature coefficient throughout the concentration range studied, whereas the corrected conductivities decrease with increasing temperature. On comparison of the shapes of the full and the broken curves, it becomes clear that the flattening of the peak in the specific conductivity curves, which occurs progressively as temperature is decreased, arises from the increasing viscosity of the mixtures.

Since, on a formal analogy with other solvent systems, diethylnitrosamine represents a "free base" in the liquid dinitrogen tetroxide solvent system (Part V, *J.*, 1951, 1298), it was important to identify as far as possible the ionic species present in these solutions. As a preliminary to this investigation, the direct current-voltage relationship has been

determined for several concentrations. Ohm's law is obeyed throughout the voltage range employed, and at all concentrations, so it appears improbable that there is any change in the nature of the ionic species and/or electrode processes with changing concentration.

Solutions were electrolysed at -10° in an H-shaped cell containing about 30 g. of solution, and fitted with bright platinum electrodes. In a typical experiment, using 30% diethylnitrosamine solution, a potential difference of 220 v applied to the cell ($R = 4.35 \times 10^4$ ohms) gave rise to a current of about 5 milliamp. The following effects (which are independent of concentration) were observed:

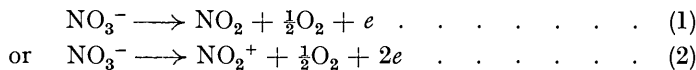
Cathode. After several minutes, the liquid in the immediate vicinity of the electrode became green; after one hour the liquid in the cathode limb developed the brown colour characteristic of dilute solutions of dinitrogen trioxide in the tetroxide.

These effects indicate the liberation of nitric oxide, which is presumed to arise from the discharge of a nitrosonium (NO^+) ion.

Anode. No visible effects occurred at this electrode.

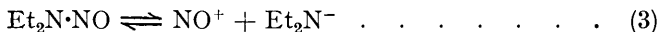
The following modes of ionisation are to be considered in the light of these electrode effects.

(a) The nitrosonium ion may result from the ionisation of the N_2O_4 molecule: $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$. The nitrate ion so formed might be expected to discharge at the anode as follows:

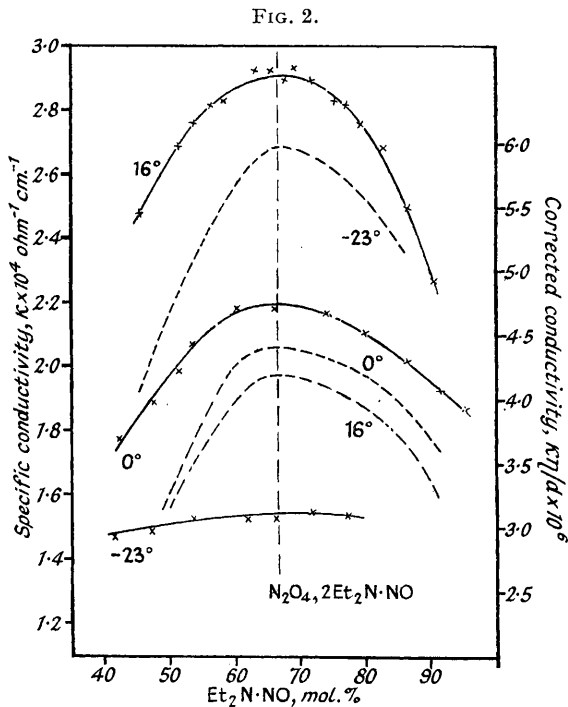
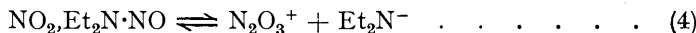


The nitrosamine acts as a depolariser to prevent evolution of oxygen gas.

(b) The nitrosonium ion may result from the fission of the N-N bond in diethylnitrosamine, either directly



or, if we write the compound $\text{N}_2\text{O}_4, 2\text{Et}_2\text{N}\cdot\text{NO}$ in the form $\text{NO}_2, \text{Et}_2\text{N}\cdot\text{NO}$, by the ionisation



Goulden, Ingold, and Millen (*Nature*, 1950, **165**, 565) have shown by spectroscopic measurements that the nitronium ion may form a molecular complex $N_2O_3^+$ with nitrogen dioxide. Little is known of the diethylamine ion Et_2N^- , but it is reasonable to consider its existence since the unsubstituted amine ion NH_2^- is a common feature in reactions in liquid ammonia. Considering ionisation (4), discharge of $N_2O_3^+$ ions at the cathode would give rise to dinitrogen trioxide, as observed; electrolysis would result in the decomposition of one g.-mol. of diethylnitrosamine per Faraday.

Electrolytic Oxidation.—In view of the chemical reaction which takes place between diethylnitrosamine and liquid dinitrogen tetroxide on long standing (Part VI, *loc. cit.*), it is necessary to complete electrolytic experiments in a short time. In order to increase the proportional change in the concentration of the nitrosamine taking place during electrolysis, the small capacity cell shown in Fig. 3 was employed. The diethylnitrosamine was determined before and after electrolysis, and the results are collected in Table 2.

TABLE 2.

Composition of original solution, g. :		Faradays passed ($\times 10^{-4}$)	$Et_2N \cdot NO$ decomposed, (by analysis)	$Et_2N \cdot NO$ decomposed, g. (calc. from Eqn. 4)	$Et_2N \cdot NO$ oxidised, g. (calc. from Eqn. 5)
$Et_2N \cdot NO$	N_2O_4				
0.560	1.537	5.60	0.012	0.057	0.010
0.579	1.242	10.1	0.004	0.103	0.019
0.576	2.034	2.61	0.008	0.028	0.005
1.176	2.163	19.9	0.035	0.202	0.037

The quantities of diethylnitrosamine decomposed during electrolysis (col. 4, Table 2) are little more than the experimental error in analysis (see p. 1398), but are clearly of a different order of magnitude from the quantities (col. 5) required by equation (4). Nevertheless, analysis leaves no doubt that a very small quantity of nitrosamine is decomposed during

FIG. 3.

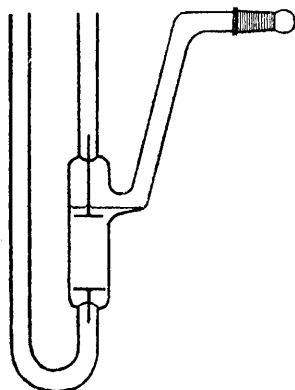
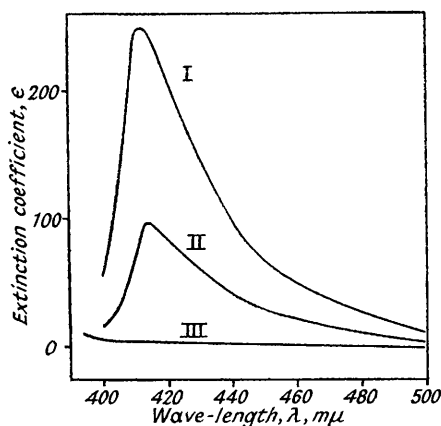


FIG. 4.

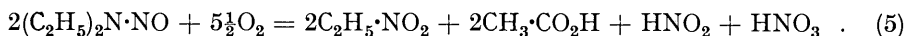


electrolysis. Ionisation schemes (3) and (4), being eliminated there are three agents which may be responsible for the oxidation of diethylnitrosamine: (a) nascent oxygen, produced by anode process (1); (b) the nitronium ion, produced in process (2); (c) in anode process (2), the NO_2^+ ions are produced in a medium containing NO_3^- ions. This combination of ions is equivalent to a solution of dinitrogen pentoxide in the liquid. Separate experiments have therefore been carried out to determine whether nitronium salts, and dinitrogen pentoxide, are able to oxidise diethylnitrosamine under normal conditions.

Reaction between Nitronium Pyrosulphate and Diethylnitrosamine.—About 0.5 ml. of diethylnitrosamine was added to about 0.2 g. (colourless crystals) of nitronium pyrosulphate. A violent reaction occurred immediately, with the evolution of oxides of nitrogen, acetaldehyde, and acetic acid. Under controlled conditions it is unlikely that the reaction would be arrested at the acetaldehyde stage; the reaction is clearly oxidative.

Reaction between Dinitrogen Pentoxide and Diethylnitrosamine.—The addition of pure diethylnitrosamine to solid dinitrogen pentoxide caused an almost explosive reaction, similar in character to the foregoing reaction. Much acetaldehyde was evolved. On addition of the nitrosamine to a 20% solution of dinitrogen pentoxide in the tetroxide, a less violent reaction occurred, so the reaction could be controlled by dilution of the reactants with dinitrogen tetroxide.

The experiments described below may be correlated on the assumption that diethylnitrosamine undergoes oxidation according to the equation



followed by



Ethylnitric acid gives a coloured anion in alkaline solution; the solution is yellow when very dilute.

(a) When freshly prepared mixtures of diethylnitrosamine and liquid dinitrogen tetroxide were hydrolysed in aqueous potassium hydroxide solution, colourless solutions were obtained. When electrolysed mixtures were hydrolysed similarly, the resulting aqueous solutions were invariably pale golden-yellow.

(b) Nitroethane, equivalent in quantity to the diethylnitrosamine decomposed during electrolysis (Table 2), was added to a volume of potassium hydroxide solution (containing an excess of potassium nitrite) equal to that employed for hydrolysis of the electrolysed mixtures. On addition of acid (insufficient to neutralise the solution) a yellow colour developed, and the resulting solution could not be distinguished from the solution obtained by hydrolysis of the electrolysis products. Some ethylnitric acid may be produced in the nitrosamine-tetroxide mixture during electrolysis, but the major portion is considered to be formed during hydrolysis of the tetroxide.

(c) The oxidation products increase the electrical conductivity of the mixture, as shown below.

Electrolysis of 35.2% Et₂N·NO solution in N₂O₄ (P.D. = 220 v)

Time (min.)	0	25	53	81	100	130	170	200
Current (milliamp.)	9.9	11.1	11.9	13.6	15.0	18.0	26.0	36.0

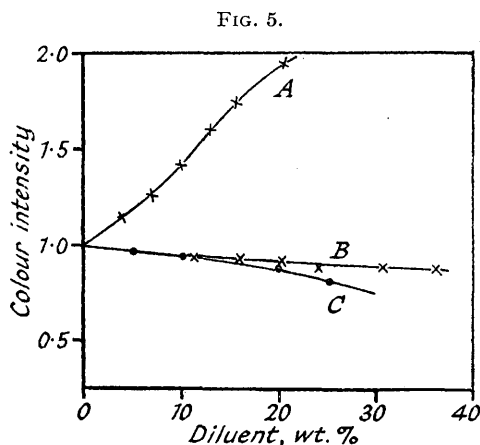
(d) 0.125 G. of dinitrogen pentoxide was allowed to react with 0.747 g. of diethylnitrosamine, each reactant being dissolved in 3 ml. of dinitrogen tetroxide. Under these conditions there were no visible signs of reaction. When the mixture was added to an aqueous solution of potassium hydroxide, a yellow colour (characteristic of the solutions obtained on hydrolysing electrolysed mixtures) developed. Analysis of this solution indicated that the dinitrogen pentoxide had reacted with 0.023 g. of diethylnitrosamine. Since dinitrogen tetroxide does not oxidise diethylnitrosamine except on long standing, the pentoxide may be regarded, in this reaction, as being reduced to the tetroxide. Equation (5) requires the oxidation of 0.0215 g. of diethylnitrosamine.

(e) Equation (5) being assumed, the quantities of diethylnitrosamine oxidised during the course of the four electrolytic experiments described in Table 2 have been calculated. The results (shown in col. 6, Table 2) are similar in order to the analytical values.

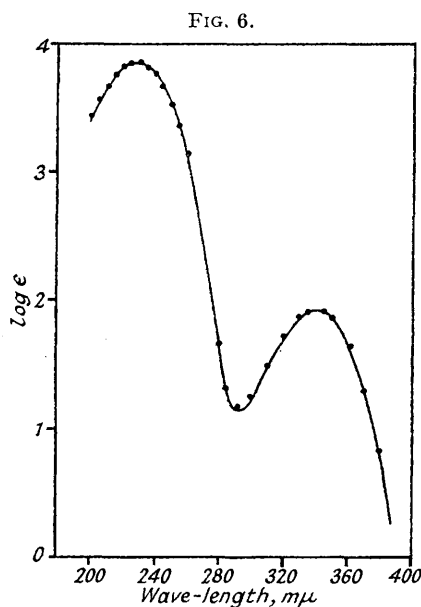
The Rôle of Diethylnitrosamine.—Light-absorption measurements (and experiments described in the following paper) provide evidence that diethylnitrosamine molecules are co-ordinated with the nitrosonium ions. Curve I (Fig. 4) is the extinction coefficient curve for a solution of nitrosonium hydrogen sulphate in diethylnitrosamine. The curve shows one sharp maximum at 412.5 m μ ; there is appreciable absorption throughout the blue region of the visible spectrum. Such absorption is not a property of the nitrosonium or hydrogen sulphate ions alone, and since the curve was derived by employing dilute solutions of the nitrosonium compound, with diethylnitrosamine in the solvent compensating cell, the absorbing species must arise by association of the solvent with one or other of the solute ions. No colour develops when the hydrogen sulphate ion (in the form of the sodium salt or sulphuric acid) is added to diethylnitrosamine; we therefore conclude that the

observed absorption arises from association of the nitrosamine molecules with the nitrosonium ion. Curve II (Fig. 4) was obtained with dilute solutions of dinitrogen tetroxide in diethylnitrosamine, and is very similar in form to curve I. The peak occurs at $414\text{ m}\mu$; the slight shift from $412.5\text{ m}\mu$ (curve I) may be attributed to the change in anion. Although the ionic nature of nitrosonium hydrogen sulphate probably leads to its complete ionisation in diethylnitrosamine solution, this will not be the case with dinitrogen tetroxide. Consequently, the concentration of absorbing species will be less than the stoichiometric concentration of dinitrogen tetroxide from which the ϵ values (curve II) were calculated, and the ϵ values are therefore smaller than for curve I. Nevertheless, it is clear that the same absorbing species is present in each solution. Curve III was obtained for a solution of dinitrogen tetroxide in carbon tetrachloride; there is no longer a peak in the curve over this wave-length range, and the slight absorption may be attributed to the nitrogen dioxide present in equilibrium with the tetroxide (Lambrey and Corbière, *Compt. rend.*, 1935, 201, 1334).

In order to determine the extinction coefficients for nitrosamine-tetroxide mixtures, it was necessary to use mixtures containing only about 1% of dinitrogen tetroxide. To



Liquid dinitrogen tetroxide diluted with:
 A = $\text{Et}_2\text{N}\cdot\text{NO}$, B = CCl_4 , C = $\text{C}_6\text{H}_5\cdot\text{NO}_2$.

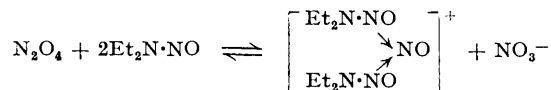


confirm the formation of a coloured compound in mixtures rich in tetroxide, the pure liquid tetroxide was diluted with diethylnitrosamine, and the variation in colour intensity compared (in a Duboscq colorimeter) with the corresponding variation when the tetroxide was diluted with carbon tetrachloride and with nitrobenzene. In each case the same artificial colour standard, an aqueous solution of methyl-orange and picric acid, was used. The results obtained at 18° are shown in Fig. 5. The vertical (colour intensity) units represent the depth of artificial standard solution required to match the experimental solution, pure dinitrogen tetroxide being regarded as unity. Although the diethylnitrosamine and nitrobenzene were pale yellow, the contribution of this colour is negligible compared with the intense colour due to the nitrogen dioxide present at 18° . On dilution with the inert solvents carbon tetrachloride and nitrobenzene, a gradual decrease in colour intensity was observed which is consistent with the decreasing concentration of nitrogen dioxide in the solutions. In spite of this, the colour intensity produced on dilution with diethylnitrosamine increases sharply.

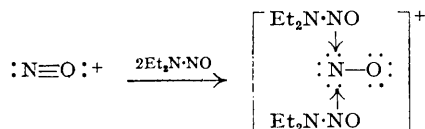
The conductivity of the tetroxide-nitrosamine mixtures, although large in comparison with the conductivity of the pure components (Part VI, *loc. cit.*), is too small to enable suitable transport measurements to be carried out. When the electrodes are placed at a

sufficient distance to avoid mixing of the contents of the electrode compartments, it is necessary to continue the electrolysis for a considerable time in order to obtain any detectable change in the distribution of nitrosamine in the cell. Before this stage can be reached, the irreversible reaction between the components takes place, and this vitiates the analyses.

Structure of Cation.—Since diethylnitrosamine and dinitrogen tetroxide react in the 2 : 1 ratio only, the equilibria in the system may be represented as :

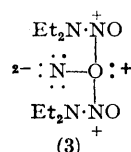
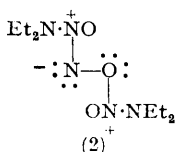
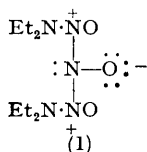


The NO^+ ion has a total of 10 valency electrons; the addition of two electron pairs involves the completion of the electron octet for both the nitrogen and the oxygen atom, with the two atoms then united by a single electron-pair bond. The electron rearrangements involved in the process



together with the possibility of extensive resonance in the complex ion, are no doubt responsible for the colour of the ion.

The two diethylnitrosamine molecules are represented as co-ordinating at the nitrogen atom of the nitrosonium ion. Consider the three possibilities :



In view of the relative electron affinities of the nitrogen and oxygen atoms, the most probable structure is one in which the oxygen atom of the nitrosonium group carries the formal negative charge. This is the case in structure (1), whereas structures (2) and (3) appear to be much less probable.

Since solutions of diethylnitrosamine in dinitrogen tetroxide are considered as "basic" in the dinitrogen tetroxide solvent system, it is of interest that the ion $[(\text{Et}_2\text{N}\cdot\text{NO})_2\text{NO}]^+$, shown to exist in these solutions, is formally analogous to the ammonium, or substituted ammonium, ions in aqueous solutions of ammonia or amines, in that it represents the association of the free base with the cation characteristic of the solvent.

EXPERIMENTAL

Measurement of Viscosities.—In correcting conductivity results for the effects of viscosity, the dynamic viscosity η has been employed by Usanovich (*Compt. rend. Acad. Sci.*, U.S.S.R., 1939, 25, 608) and others. However, there appears to be considerable justification for employing the expression $\kappa\eta/d$, where d is the density, as the "corrected conductivity" σ , since the result then refers to the conductivity of a unit mass (1 g.) of material placed between electrodes 1 cm. apart (Allmand and Nickels, *Nature*, 1923, 112, 862). The term η/d (the kinematic viscosity ν) is available directly from the viscometer measurements without separate measurement of the density of the liquid. This procedure has been used in the present work.

The instrument used was an Ostwald-type U-tube viscometer, constructed in Pyrex glass; the open ends of the vertical limbs were fitted with B14 ground-glass sockets carrying drying tubes of potassium hydroxide pellets, which protected the contents from atmospheric moisture but allowed an unrestricted passage of air to and from the apparatus. The volume of the upper bulb was 6.5 ml.; the capillary tube was 10 cm. long (bore diameter 0.7 mm.).

Constant volumes of the liquid mixtures were made up by weighing into a 10-ml. graduated flask fitted with a side-arm, through which the contents could then be poured in a closed system

into the viscometer *via* the ground joint on the reservoir limb. The liquid was brought into the upper bulb before each timed run by applying pressure to the reservoir limb rather than by using suction on the capillary limb, to avoid the formation of vapour locks in the capillary. Times of flow varied from 80 to 380 seconds.

The kinematic viscosity was determined by using the expression $\nu = At - Bt^{-1}$; B was calculated from the dimensions of the apparatus and had a value of 2.90 centistokes sec.; A was determined by measuring the time of flow of distilled water and of pure nitrobenzene and had a value of 1.454 centistokes sec.⁻¹

Measurements were made on dinitrogen tetroxide-diethylnitrosamine mixtures over the temperature range -33.0° to $+11.5^\circ$. The viscometer was placed in a bath of alcohol cooled by solid carbon dioxide. By means of an efficient mechanical stirrer, and judicious addition of solid carbon dioxide, the temperature could be controlled to $\pm 0.15^\circ$ at the lower end of the range, and to $\pm 0.05^\circ$ at the higher temperatures. Because of this, and since the temperature coefficient of viscosity increases with diminishing temperature, the results obtained were of a somewhat lower order of accuracy at the lower than at the higher temperatures. The design of the instrument was such that the change in the hydrostatic head of the liquid arising from changes in volume was rather less than 1% over the temperature range employed. These various effects lead to an overall experimental error between 1% and 2%, depending on temperature.

Temperature Coefficient of Electrical Conductivity.—The cell used (liquid capacity about 3 ml.) is shown in Fig. 3. It was constructed in Pyrex glass and was fitted with lightly platinised platinum electrodes placed about 2.5 cm. apart. The cell constant had a value of 0.460. The mixtures were made up by distilling a known weight of diethylnitrosamine under reduced pressure into a 10×1.5 cm. tube fitted with a side-arm carrying a B10 ground-glass cone. Pure dinitrogen tetroxide was then distilled in to the required composition, and the mixture filled into the cell by attaching the latter to the B10 joint and suitably tilting the apparatus: the cell was then closed by a tight-fitting stopper. The resistance measurements were made by using a Mullard Measuring Bridge Type G.M. 4140/1.

The temperature range covered was -33.0° to $+10^\circ$ and the control was similar to that used in the viscosity measurements.

Conductivity Isotherms.—In determining the variation of conductivity with the composition of the mixtures, the apparatus and the technique employed were essentially the same as those used in determining the 0° isotherm in Part VI (*loc. cit.*). The curves relating conductivity (or viscosity) with temperature were of such a form as to permit accurate extrapolation to 16° .

Current-Voltage Curves.—The current-voltage curves for mixtures of diethylnitrosamine and liquid dinitrogen tetroxide were measured in a cell similar to that used for the conductivity of the pure liquid tetroxide (Part III, *J.*, 1951, 1289, Fig. 3).

Diethylnitrosamine was purified as described in Procedure C, Part VI (*loc. cit.*), and the mixtures were made up by weighing the cell after the addition of each of the components. The measuring circuit consisted of a simple voltmeter-microammeter arrangement; the microammeter was a Pye "Scalamp" multi-range instrument and was calibrated before use. The following results show the direct proportionality between current and voltage, v being given in volts and c in microamp.

Electrolysis Experiments.—In the electrolytic measurements from which the results in Table 2 were obtained, the cell (Fig. 3) was immersed in a bath of alcohol and solid carbon dioxide at -10° to prevent the boiling of the dinitrogen tetroxide-diethylnitrosamine mixtures which

23.4 Mol. % Et ₂ N·NO (R at 1000 c/s = 2.0×10^3 ohms)										
v	0.044	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.050
c	22.4	100.5	149	196	244	290	339	386	434	506
$v/10^3c$...	1.97	1.99	2.01	2.04	2.05	2.06	2.06	2.07	2.07	2.07
28.8 Mol. % Et ₂ N·NO (R at 1000 c/s = 0.945×10^3 ohms)										
v	0.100	0.202	0.300	0.400	0.500	0.600	0.700			
c	107	211	318	422	528	630	750			
$v/10^3c$...	0.934	0.948	0.944	0.948	0.949	0.952	0.934			
69.0 Mol. % Et ₂ N·NO (R at 1000 c/s = 4.85×10^3 ohms)										
v	0.100	0.400	0.500	0.600	0.700	0.800	0.900	1.000	1.100	
c	20.0	84.0	106	126	145	164	182	201	224	
$v/10^3c$...	5.00	4.77	4.72	4.76	4.82	4.88	4.93	4.96	4.90	
79.3 Mol. % Et ₂ N·NO (R at 1000 c/s = 6.30×10^3 ohms)										
v	0.100	0.200	0.300	0.600	0.700	0.800	0.900	1.000	1.100	
c	16.0	31.2	46.9	98.0	112	126	140	156	170	
$v/10^3c$...	6.24	6.40	6.49	6.13	6.25	6.34	6.42	6.40	6.48	

otherwise occurred as a result of the heating effects of the current; 220 volts d.c. was applied, the current being measured on a milliammeter in series with the cell. Since the current passing increased with time, it was noted at 10-minute intervals during the electrolysis, and the quantity of electricity was found from the area under the curve obtained by plotting current against time. A check experiment using an iodine coulometer showed that this procedure gave results of sufficient accuracy.

After electrolysis, the contents of the cell were hydrolysed in an aqueous solution of potassium hydroxide, and the diethylnitrosamine determined as described below.

Determination of Diethylnitrosamine.—This was carried out by measurements of the ultra-violet absorption spectrum of the hydrolysed solutions, a "Unicam" S.P. 500 spectrophotometer being used with 1-cm. quartz cells and a hydrogen-discharge lamp as the source of radiation. The absorption spectrum obtained for solutions of pure diethylnitrosamine in distilled water is shown as the full curve in Fig. 6. (This curve is distinct from the experimental points shown in Fig. 6, which are discussed below.) The curve shows two maxima, at 227.5 $m\mu$ ($\epsilon = 7400$) and 340.0 $m\mu$ ($\epsilon = 85$). The maximum at 340 $m\mu$ is well suited for quantitative analyses, since the optical density D for solutions about 0.005M in nitrosamine is in the range 0.25—1.0 when measured in 1-cm. cells, and at this order of concentration Beer's law is accurately obeyed at 340 $m\mu$. This is shown by the following results:

$\text{Et}_2\text{N}\cdot\text{NO}$ concn. (M)	0.00242	0.00472	0.00514	0.00943
D at 340 $m\mu$	0.262	0.402	0.440	0.800
ϵ	85.5	85.2	85.7	84.8

The solutions to be analysed also contained nitrite and nitrate formed by hydrolysis of dinitrogen tetroxide, and both these ions absorb significantly at 340 $m\mu$. This difficulty was overcome by taking advantage of the high volatility in steam of diethylnitrosamine. A typical experiment is described below.

10 ml. of an aqueous solution of diethylnitrosamine (0.0199 g.-mol./l.) were treated with 5 g. of potassium hydroxide and 0.1 g. each of potassium nitrite and nitrate, and diluted with water to 50 ml. in a 100-ml. flask. A small water condenser was attached to the flask, and the solution was distilled gently for 15—20 minutes. All the nitrosamine distilled in the first 25 ml. of aqueous distillate. The optical density of the distillate was measured at 340 $m\mu$. Triplicate analyses gave concentrations of 0.0200, 0.0201, and 0.0199 g.-mol. of nitrosamine per litre in the original solution.

The above procedure was applied to the determination of diethylnitrosamine in admixture with liquid dinitrogen tetroxide. Known weights (about 0.5 g.) of the two liquids were mixed in a small, stoppered, sample tube. The mixture was hydrolysed by adding it to 250 ml. of N -potassium hydroxide solution in a stoppered vessel. The solution was diluted to 500 ml., and 25-ml. aliquots were treated as described above. The quantity of nitrosamine taken was 0.580 g.; analysis gave 0.571 g.

If electrolysis of tetroxide-nitrosamine mixtures produced any compound which was volatile in steam when distilled from alkaline solution, and which absorbed at 340 $m\mu$, the above method of analysis would be vitiated. An electrolysed mixture was therefore hydrolysed, and the values of D between 200 and 400 $m\mu$ were determined on the aqueous distillate. The absorption at 340 $m\mu$ being assumed to be due only to diethylnitrosamine, ϵ values over the 200—400 $m\mu$ range were calculated. These values are shown as experimental points in Fig. 6, and are seen to correspond exactly with the absorption curve for pure diethylnitrosamine.

Controlled Reaction between Dinitrogen Pentoxide and Diethylnitrosamine.—Dinitrogen pentoxide was prepared by Daniels and Bright's method (*J. Amer. Chem. Soc.*, 1920, **42**, 1131). A known weight of it (about 0.12 g.) was condensed in a 5×1 cm. tube having a B14 ground-glass cone at its open end. The pentoxide was not freed from an accompanying trace of dinitrogen tetroxide but was dissolved directly in 3 ml. of the pure tetroxide. About 0.7 g. of pure diethylnitrosamine was dissolved in 3 ml. of dinitrogen tetroxide in a similar tube fitted with a B14 socket. With both tubes closed by guard-tubes of phosphoric oxide, the contents of each were frozen completely solid; the guard-tubes were removed and the dinitrogen pentoxide tube was inverted and fitted to the top of the nitrosamine tube. The latter being kept frozen, the solution of the pentoxide was allowed to melt slowly and run down into the solid nitrosamine solution, where it resolidified. When the transfer was complete, the mixture was melted and kept at room temperature for 15 minutes. It was then added to aqueous alkali, and the nitrosamine determined.

Preparation of Nitronium Pyrosulphate.—Nitronium pyrosulphate, $(\text{NO}_2)_2\text{S}_2\text{O}_7$, was prepared

as described by Goddard, Hughes, and Ingold (*J.*, 1950, 2559), from pure dinitrogen pentoxide and sulphur trioxide (1 : 2) in nitromethane solution. After it had dried in a vacuum over phosphoric oxide, its purity was tested by determining the acid equivalent weight (Found : 45.0. Calc. : 44.7). This agreement was taken as evidence that little if any free acid was present in the product.

Extinction Curve for the Ion $(Et_2N \cdot NO)_2NO^+$.—The ϵ values recorded in Fig. 4 were obtained by using the "Unicam" spectrophotometer. In order to avoid the preparation of solutions containing less than about 1% of the nitrosonium compound, it was found convenient to use 2-mm. (rather than 1-cm.) optical cells. Nitrosonium hydrogen sulphate was prepared by the method of Angus and Leckie (*Proc. Roy. Soc.*, 1935, **149**, *A*, 327).

Colorimetric Measurements.—The artificial standard solution was contained in the normal Duboscq plunger-type cup. The cell containing the dinitrogen tetroxide mixtures was prepared by sealing a 2-mm. cell at right angles to the bottom of a 4×1 cm. tube, to form the lower limb of an L-shaped unit. The liquid was viewed through the optical faces of the cell, which were held horizontal. The colorimeter was modified to permit the immersion of the cell in a bath kept at 18°, and having an optically plane base.

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