288. *The Liquid Dinitrogen Tetroxide Solvent System. Part V. Reactions involving Some Alkylammonium Salts, with Particular Reference to Solvolysis and the Formation of Diethylnitrosamine.*

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Preliminary experiments with a number of alkyl-substituted ammonium chlorides have shown that these salts dissolve in, and react with, liquid dinitrogen tetroxide, to produce the corresponding nitrate and nitrosyl chloride. These reactions are considered from the point of view of solvolysis, and the reaction of diethylammonium chloride has been studied quantitatively. Variations with time in the physical properties of solutions of the nitrates of secondary amines in dinitrogen tetroxide indicate that a further reaction occurs between these components. The reaction between diethylammonium nitrate and dinitrogen tetroxide has been studied quantitatively; nitric acid and diethylnitrosamine are produced, and the possible significance of this nitrosamine as a true base in the dinitrogen tetroxide solvent system is discussed.

Solvolytic reactions in which a salt undergoes reaction with the medium in which it is dissolved to produce an acid and a base characteristic of that medium are well known in the aqueous system. Examples occur also in the bromine trifluoride system (Gutmann and Emeléus, *J.*, 1950, 1046), but solvolysis is much less clearly defined in liquid ammonia. On the basis of the dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ postulated in Part I (*J.*, 1949, S 211), the reactions of the alkylammonium chlorides with liquid dinitrogen tetroxide may be interpreted as solvolytic with respect to this medium. Neither ammonium chloride nor ammonium nitrate reacts with liquid dinitrogen tetroxide; pure diethylamine reacts explosively on contact with liquid dinitrogen tetroxide, but diethylammonium chloride reacts smoothly according to the equation

$$[Et_2NH_2]^+Cl^- + N_2O_4 \longrightarrow [Et_2NH_2]^+NO_3^- + NOCl \quad . \quad . \quad . \quad . \quad (1)$$

Under appropriate conditions the reaction proceeds smoothly in the direction shown; the nitrosyl chloride can be removed quantitatively under vacuum, and the diethylammonium nitrate crystallises in pure form on addition of ether.

This solvolytic reaction appears to be typical of the alkylammonium chlorides. A quantitative study of the reaction of the diethyl salt has been made; the following qualitative observations indicate the main features of the reactions between liquid dinitrogen tetroxide and some other alkylammonium salts.

Methylammonium Salts.—On the addition of crystals of the chloride to liquid dinitrogen tetroxide, a red coloration due to nitrosyl chloride developed immediately, and the liquid separated into two immiscible liquid phases. The upper phase contained a little nitrosyl chloride, but consisted mainly of methylammonium nitrate dissolved in dinitrogen tetroxide. The lower layer was a deep red solution of nitrosyl chloride in dinitrogen tetroxide, and contained only a trace of methylammonium nitrate. On warming the liquid or on applying vacuum, the nitrosyl chloride was readily removed, but the resulting liquid remained as two immiscible layers. It appears that the nitrosyl chloride has in itself little influence on the immiscibility, which arises from the presence of the amine salt. The formation of two immiscible layers is a general property of amine nitrates dissolved in liquid dinitrogen tetroxide; the range of concentration over which immiscibility extends depends upon the character and number of the substituent alkyl groups.

Dimethylammonium Salts.—The chloride dissolved readily in dinitrogen tetroxide; solvolysis occurred immediately on contact, but in this case no separation into two layers occurred. On long standing, or on rise of temperature, separation into two layers did occur; this is considered to arise from a slow reaction which follows the solvolytic reaction and introduces further components into the system. This aspect is considered in detail in connection with the diethyl compounds (p. 1300). Of the mono- and di-methylammonium salts, only the nitrates crystallised when the solution was concentrated by evaporation of the dinitrogen tetroxide.

Trimethylammonium Salts.—Solvolysis was again rapid with the chloride, and two liquid phases were produced. The nitrate appeared to be considerably less soluble than the corresponding mono- and di-methyl compounds, since it crystallised spontaneously from the medium without preliminary concentration of the solution. The crystalline product consisted of pure trimethylammonium nitrate, m. p. 155°. When 0·5 g. of the pure nitrate was added to 9 ml. of dinitrogen tetroxide, dissolution of the salt was slow, requiring 1·5 hours' constant shaking. A similar quantity of dimethylammonium nitrate dissolved almost immediately.

Tetramethylammonium Salts.—The chloride dissolved rapidly; solvolysis produced a readily soluble nitrate and the liquid separated into two immiscible phases. It appears probable that in this case other reactions in addition to solvolysis occur. The red coloration due to nitrosyl chloride was much less pronounced, and while the solid was dissolving a transient green colour was produced, although precautions were taken to ensure that the added chloride was quite dry. On removal of the volatile constituents under vacuum, the crystalline nitrate obtained was entirely free from chloride. The two liquid phases formed on the addition of a small amount of the nitrate to a large excess of dinitrogen tetroxide persisted throughout the evaporation of the tetroxide, so that the two-liquid system appears to be typical of solutions of this nitrate over the full concentration range.

Ethylammonium Salts.—The reaction of the chloride followed closely that of the monomethyl salt. The nitrate was readily soluble, and could be separated from the upper layer by evaporation of the nitrosyl chloride and dinitrogen tetroxide.

Diethylammonium Salts.—The solvolytic reaction of the chloride has been given in equation (1), and is considered in detail below.

Triethylammonium Salts.—The solvolytic reaction followed the normal course, but in contrast to the trimethyl salt no separation into two liquid phases occurred. The triethylammonium nitrate is much more soluble in liquid dinitrogen tetroxide than is the trimethyl salt.

The reactions which the alkylammonium chlorides undergo in solution in liquid dinitrogen tetroxide are therefore analogous to their well-known hydrolysis in aqueous solution, and it is of interest that the solutions of the nitrates in liquid dinitrogen tetroxide possess miscibility gaps which resemble the well-known two-phase systems given by the alkyl-substituted ammonium hydroxides in water. In each medium the solvolytic reaction reaches a state of equilibrium, but in liquid dinitrogen tetroxide this equilibrium is displaced further towards complete solvolysis than in the corresponding aqueous solutions. Consistent with this is the fact that the hydrolysis of tetramethylammonium chloride is negligible in aqueous solution, though solvolysis proceeds to a marked degree in solution in liquid dinitrogen tetroxide.

The above observations are restricted to the chlorides. Similar initial reactions probably take place with the bromides and iodides also, but such reactions are complicated by the release of nitric oxide and free halogen. For example, nitrosyl iodide is not known to exist, and the addition of an alkylammonium iodide to liquid dinitrogen tetroxide results in separation of free iodine.

Although solvolysis appears to be a typical reaction of the alkylammonium chlorides, it is noteworthy that the general chemistry of liquid dinitrogen tetroxide includes very few other examples. The chlorides of silver, sodium, potassium, and many other metals are not attacked by liquid dinitrogen tetroxide, though it has been observed (by Mr. J. Lewis in this laboratory) that anhydrous zinc chloride reacts to give the nitrate and nitrosyl chloride. Partington and Whynes (*J.*, 1949, 3135) have observed that titanic chloride reacts to give some nitrosyl chloride, and although the nature of the metal salt produced is not certain, the reaction is no doubt solvolytic in character.

True solvolysis necessarily involves reactions which are of ionic nature. However, there are certain reactions involving non-ionic compounds which would appear, on a formal analogy, to be solvolytic in character; *e.g.*, methyl iodide is said to react according to the equation $2CH_3I + 2N_2O_4 = 2CH_3{\cdot}NO_3 + 2NO + I_2$ (Henry, *Bull. Acad. Belg.*, 1874, **38**, 7). Reactions carried out with methyl and ethyl iodides show that the iodine is produced slowly (over periods of minutes or hours depending on conditions); there seems to be no doubt that the mechanism of such reactions differs from the almost instantaneous ionic reactions involving the alkylammonium halides and reactions of this type are not considered to be solvolytic.

Stability of Solutions of Diethylammonium Nitrate.—In considering liquid dinitrogen tetroxide as a solvent system, we have assumed that the dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ is possible. It is known (Goulden and Millen, *J.*, 1950, 2620) that this heterolytic dissociation does in fact occur in solutions of dinitrogen tetroxide in nitric acid, and there appears to be no reason to doubt that it is possible in the pure liquid tetroxide. On this basis, the alkyl-substituted ammonium nitrates may be regarded as " bases " in this system (Cady and Elsey, *J. Chem. Educ.*, 1928, **5**, 1425). Solutions of these nitrates in liquid dinitrogen tetroxide have been found to possess some of the properties typical of hydroxides in the aqueous system, *e.g.*, the rapid reaction with zinc metal to give soluble zinc complexes referred to in Part I (*loc. cit.*). During the course of the preliminary experiments on solvolytic behaviour described above, it was observed in some cases that slow reactions between the dissolved nitrate and liquid dinitrogen tetroxide followed the more rapid solvolytic reactions. This was pronounced in the case of the disubstituted salts, and since diethylammonium nitrate is amongst the most soluble, a qualitative and quantitative examination has been made of the nature of the reaction between this salt and liquid dinitrogen tetroxide in order to determine the stability of such " basic " solutions, and the significance of the reaction products in this solvent system.

Attempts were made to measure the freezing points, miscibility ranges, and electrical conductivity of solutions of diethylammonium nitrate in liquid dinitrogen tetroxide. In each case reaction between the two components gave rise to drifting values. Fig. 1 shows the variation in freezing point of a 62% w/w solution of the nitrate, and similar variations were found to occur at other concentrations. There is an approximately linear relationship between the freezing point and the logarithm of the age of the solution. At concentrations of the nitrate greater than 20% the solutions remained homogeneous even on long standing. In the 0—20% concentration range, the solutions were homogeneous immediately after preparation, but separated into two immiscible layers on standing for periods of time which depended on the concentration.

FIG. 1.

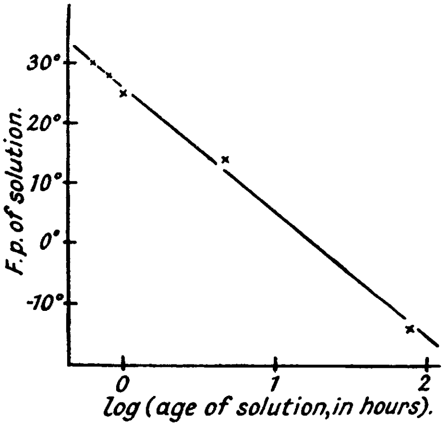
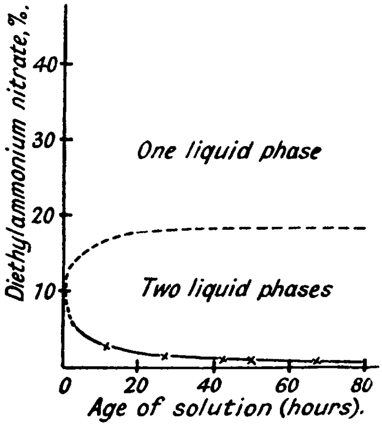


FIG. 2.



Within the 8—12% concentration range the two layers appeared within seconds of preparation of the solution. Below this concentration range the times required for formation of the two layers extend into hours, and are shown by the full line in Fig. 2, determined at 15°. The upper (broken) part of the curve has not been determined with the same degree of accuracy, but lies approximately in the position shown. It appears that if the system could be restricted to two components, *i.e.*, diethylammonium nitrate and liquid dinitrogen tetroxide, there would be no miscibility gap, but the immiscibility arises from the formation of further components in the solution owing to chemical reaction. Consistently with this, the position of the miscibility curve (Fig. 2) on the time axis is influenced considerably by variations in temperature.

Although freshly prepared solutions of diethylammonium nitrate have a negligible electrical conductivity, the solution becomes highly conducting on standing. The specific conductivity of an 11·5% solution (originally $<5 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$) kept at 0°, increased to $1{\cdot}7 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ after 45 minutes, and to $2{\cdot}5 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ after 24 hours. A study of the reaction products in the light of the dinitrogen tetroxide solvent system therefore becomes of further importance since in spite of the low dielectric constant of dinitrogen tetroxide (Part IV, preceding paper) the products of reaction are highly conductive even in dilute solution.

Products of reaction. Diethylammonium salts and nitrosyl chloride react in the accepted manner (Sidgwick, " The Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, p. 24) to give diethylnitrosamine. This reaction occurs if the products of the solvolysis reaction (equation 1) are heated further, without preliminary removal of the nitrosyl chloride :

$$NOCl + Et_2NH_2NO_3 \longrightarrow Et_2N{\cdot}NO + HCl + HNO_3 \quad . \quad . \quad . \quad . \quad (2)$$

The usual laboratory method for the preparation of diethylnitrosamine from nitrous acid in aqueous solution follows a similar course

$$NO{\cdot}OH + Et_2NH_2Cl \longrightarrow Et_2N{\cdot}NO + H_2O + HCl \quad . \quad . \quad . \quad . \quad (3)$$

If dinitrogen tetroxide can be regarded as reacting as a nitrosyl compound ($NO{\cdot}NO_3$), the reaction with diethylammonium nitrate would be expected to follow a similar course :

$$NO{\cdot}NO_3 + Et_2NH_2NO_3 \longrightarrow Et_2N{\cdot}NO + 2HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Experiment has shown that this is indeed the case, and analysis indicates that the reaction proceeds quantitatively.

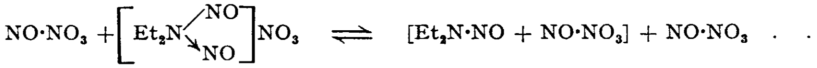
It is well known that reaction (3) may proceed in the reverse direction by boiling diethylnitrosamine with aqueous hydrochloric acid under reflux ; the reaction $(Et_2NH_2)Cl + NOCl \longrightarrow Et_2N{\cdot}NO + 2HCl$, which resembles reaction (2) above, is also reversible, and may be used for the quantitative determination of diethylnitrosamine provided that the nitrosyl chloride is removed from the system. In the investigation of equation (4), liquid dinitrogen tetroxide was added to an excess of the nitrate, and the mixture kept in a sealed tube at room temperature. After it had stood for periods up to one week, 20—30% of the tetroxide could be recovered from the mixture, and reaction (4) appeared to proceed to an equilibrium. It is therefore probable that under appropriate conditions this reaction is also fully reversible.

Previous experiments (Part I, *loc. cit.*) have indicated that in its reaction with ionic compounds, heterolytic dissociation of the N_2O_4 molecule into NO^+ and NO_3^- ions is the significant feature, as opposed to the alternative (NO_2^+–NO_2^-) dissociation in reactions with covalent molecules ; reaction (4) is consistent with this generalisation. However, it is not implied that the products of reaction are necessarily ionic. In reaction (1) the nitrosyl chloride produced has no more than 50% ionic character (Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629) ; in reaction (4) the nitric acid produced in solution in dinitrogen tetroxide will give rise to ions (Goulden and Millen, *loc. cit.*), but the diethylnitrosamine is unlikely to have, *per se*, any appreciable degree of ionic character, although solutions of this compound in dinitrogen tetroxide show considerable electrical conductivity * (Part VI, following paper).

The significance of the nitrosamines in the dinitrogen tetroxide solvent system may be illustrated by consideration of the three equations

$$HOH + Et_2NH_2OH \rightleftharpoons [Et_2NH + HOH] + HOH \quad . \quad . \quad . \quad . \quad (5)$$

$$NO{\cdot}NO_3 + Et_2NH_2NO_3 \rightleftharpoons [Et_2N{\cdot}NO + HNO_3] + HNO_3 \quad . \quad . \quad . \quad (6)$$



$$NO{\cdot}NO_3 + \left[Et_2N\begin{smallmatrix}\nearrow NO\\ \searrow NO\end{smallmatrix}\right]NO_3 \rightleftharpoons [Et_2N{\cdot}NO + NO{\cdot}NO_3] + NO{\cdot}NO_3 \quad . \quad . \quad (7)$$

In a complete formal analogy between reactions involving amine salts in water and in liquid dinitrogen tetroxide, the replaceable H atoms should be replaced by the NO group, and the OH group by the NO_3 group. Aqueous solutions of ammonia or amines are known to contain free ammonia or amine molecules in equilibrium with the hydroxides ; this equilibrium can be represented as in equation (5), and the complete analogy on the dinitrogen tetroxide solvent system is represented by equation (7).

Freezing-point curves for aqueous solutions of diethylamine show that several hydrates may exist (Pickering, *J.*, 1893, **63**, 141) ; the most pronounced peak occurs at an amine : water ratio of 2 : 1. Physical studies of solutions of diethylnitrosamine in liquid dinitrogen tetroxide described in Part VI (following paper) have shown that definite compound formation occurs, but clear evidence has been obtained for one ratio only (nitrosamine : $N_2O_4 = 2 : 1$). Other ratios may exist, but for the purpose of the formal analogy, the 1 : 1 ratio is employed in equations (5) and (7). Diethylnitrosamine may be regarded as the true analogue, in the dinitrogen tetroxide system, of the free base diethylamine in the aqueous system. Equation (6), which is treated experimentally in this paper, is then seen to represent a half-way stage between the two true solvent reactions (5) and (7), since the OH group in diethylammonium hydroxide is replaced by the NO_3 group, but the two replaceable hydrogen atoms remain. In consequence, nitric acid instead of dinitrogen tetroxide is produced, but the reaction may be regarded as involving the conversion of the free base (on the aqueous system) into the true free base on the dinitrogen tetroxide system.

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* The maximum electrical conductivity reached by a solution of diethylammonium nitrate on long standing is greater than that of a solution containing an equivalent quantity of diethylnitrosamine.

EXPERIMENTAL.

The alkylammonium chlorides used were B.D.H. materials recrystallised from alcohol–ether and dried *in vacuo* over phosphoric oxide. The tetramethylammonium chloride was prepared by shaking a solution of the pure iodide in aqueous alcohol with excess of freshly precipitated silver chloride. The filtered solution was evaporated on a water-bath, and the crystals of chloride dried for 3 days over phosphoric oxide. The reactions between the chlorides and liquid dinitrogen tetroxide were carried out in 10 × 1·5 cm. test-tubes having B 14 ground-glass joints. The tube containing a sample of the chloride was attached by ground joints to the condenser containing freshly prepared dinitrogen tetroxide (Part II, *J.*, 1949, S 218), and the liquid poured from the condenser into the tube within a closed system and in the absence of moist air. When solutions of the corresponding nitrates were required for the preliminary study of solubility and miscibility, they were obtained from the chlorides as described below.

Reaction between Diethylammonium Chloride and Liquid Dinitrogen Tetroxide.—The reaction was carried out as above, and the products were identified as follows: (a) *Diethylammonium nitrate.* Removal of the nitrosyl chloride and dinitrogen tetroxide under reduced pressure gave a very pale yellow solid, which was washed with dry ether to remove traces of nitrosamine, nitric acid, and occluded dinitrogen tetroxide, then recrystallised from absolute alcohol. Qualitative tests indicated diethylammonium nitrate and the product had m. p. and mixed m. p. 102°. (b) *Nitrosyl chloride.* Although the odour, and colour in solution, were characteristic of nitrosyl chloride, it was possible that other volatile chlorine compounds (*e.g.*, nitryl chloride) were present. The volatile products removed from the reaction mixture were therefore condensed in a trap cooled to −15°, and the chloride content and m. p. of the condensate determined by the methods described in Part II (*loc. cit.*). The chlorine content was 7·13%. This is equivalent to a nitrosyl chloride content of 13·2% if all the chlorine was present in this form. On warming the condensate, the last crystals disappeared at −17·2°. When this m. p. was plotted on the $NOCl–N_2O_4$ phase diagram (Fig. 3, Part II, *loc. cit.*) it was found to lie on the liquidus curve for that system, and the condensate therefore contained only nitrosyl chloride and dinitrogen tetroxide.

The reaction was established quantitatively as follows: (a) *Diethylammonium nitrate.* 0·95 G. of the chloride was treated with about 4·5 g. of liquid dinitrogen tetroxide at −10°. The reaction mixture was then evaporated to dryness at 25—30°, and brown fumes were removed from the reaction tube by vacuum. After being washed with dry ether, the resulting solid was dried to a constant weight of 1·18 g., which is the theoretical yield for complete conversion of diethylammonium chloride into the nitrate. Since the reaction was completed within a few minutes, the quantity of nitrosamine produced was negligible. (b) *Nitrosyl chloride.* In a second experiment, 1·095 g. of the chloride were treated with about 5 g. of liquid dinitrogen tetroxide at −10°. The mixture was warmed slowly to 30°, and the gases evolved were bubbled into a bead-packed absorption tube containing 2N-potassium hydroxide. When all the nitrosyl chloride had been removed from the reaction mixture, the alkaline solution was acidified with nitric acid and boiled with a little hydrazine sulphate to destroy nitrite. Gravimetric analysis of this solution gave 0·352 g. of chlorine, equivalent to 0·650 g. of nitrosyl chloride. The theoretical yield of nitrosyl chloride [equation (1)] is 0·655 g.

Preparation of Diethylammonium Nitrate.—Appreciable quantities of this compound, in a pure dry state, were required for the experiments described in this and later papers. The following technique was found suitable. 20 G. of diethylammonium chloride were added to about 30 ml. of liquid dinitrogen tetroxide in a two-necked flask. One neck was fitted with an inlet tube passing below the liquid surface, and the other (outlet) neck was protected by a calcium chloride drying tube. Nitrosyl chloride was then eliminated by passing a stream of dry nitrogen through the liquid until the red colour gave way to the characteristic amber of the tetroxide. When the reaction was complete (*i.e.*, when a few ml. of the evolved gases when hydrolysed gave no test for chloride), excess of dry ether was added to the paste-like mass remaining, and the nitrate was precipitated as glistening plates. The product was filtered off, and washed again with ether to remove any traces of diethylnitrosamine. The nitrosyl chloride and dinitrogen tetroxide were removed as rapidly as possible from the reaction mixture in order to reduce the extent to which the subsequent reaction (forming diethylnitrosamine) could occur.

Reaction between Diethylammonium Nitrate and Liquid Dinitrogen Tetroxide.—(a) *Change in physical properties of solutions.* Changes in the freezing point of these solutions over long periods of time (Fig. 1) were determined by sealing known quantities of the two components in glass tubes, and observing the freezing point by the thaw–melt method. Similar tubes, kept in a thermostat at 15°, were employed to observe the appearance of a second liquid phase (Fig. 2).

(b) *Products of reaction.* About 6 g. of liquid dinitrogen tetroxide were poured, in a closed system and in the absence of moist air, into a 10 × 1·5 cm. Pyrex glass tube (drawn out to a constriction immediately below the ground joint) containing excess (about 10 g.) of dry diethylammonium nitrate. The tube was then separated from the tetroxide container, and a phosphoric oxide guard tube fitted to the ground joint. The lower portion of the tube was surrounded by pieces of solid carbon dioxide, and the tube sealed at the constriction as soon as the contents had solidified. The reaction was then allowed to proceed at room temperature. During the first day, the contents of the tube changed from a " moist " solid to a yellow liquid containing a small quantity of undissolved solid. About two days were required for the disappearance of all crystals. As the reaction progressed, the colour of the liquid changed from deep yellow to olive-green; the green colour arises from a slight side reaction (discussed in the following paper) which does not occur to a sufficient extent to be relevant here. The tube was set aside for one week before being opened. It was then placed in a stout glass-stoppered bottle containing 250 ml. of dry ether, and the bottle was shaken, so that the tube broke, the excess diethylammonium nitrate was precipitated, leaving an orange-coloured supernatant liquid. The analysis was carried out as follows:

(1) 25 Ml. of the liquid were withdrawn by use of a guarded pipette, and run under the surface of an excess of approximately 2N-potassium hydroxide solution held in a separating funnel. After shaking,

the aqueous layer was run off and the nitrite content determined by means of standard hydrazine sulphate solution (Mellan, "Organic Reagents in Inorganic Analysis," Blakiston Co., Philadelphia, 1941, p. 488). The usual method for nitrite estimation employing potassium permanganate solution is invalidated by the presence of diethylnitrosamine. From the nitrite content, the quantity of unchanged dinitrogen tetroxide in the reaction mixture was calculated.

(2) A further 50-ml. portion of the ethereal solution was transferred to a stoppered flask and evaporated at room temperature under reduced pressure to about half the volume; this removed unchanged dinitrogen tetroxide, as shown by fading of the orange colour to very pale yellow. A stream of dry air-borne ammonia gas was then aspirated through the ethereal solution, and a flocculent white precipitate was formed. When precipitation was complete, the solid was filtered off, washed with dry ether, and weighed. Analysis showed it to be pure ammonium nitrate, and from its weight, the quantity of nitric acid produced in the reaction was calculated.

(3) The filtrate and ether washings from the ammonium nitrate precipitation were evaporated under reduced pressure at about 0° until all the ether was removed. The pale yellow liquid remaining was weighed, and characterised as pure diethylnitrosamine (b. p. 174—176°). The weight of nitrosamine was corrected for that lost during the evaporation of the ether, by carrying out blank experiments with ether–nitrosamine mixtures of known concentration.

(4) The unreacted diethylammonium nitrate which was precipitated from the original ether solution on breaking the reaction tube, was filtered off, washed with dry ether, and weighed.

Three separate experiments were carried out, and the results, given in the following table, confirm that the reaction between diethylammonium nitrate and liquid dinitrogen tetroxide proceeds almost entirely in accordance with equation (4).

	G.-mols. reacting with, or produced from, 1 g.-mol. of $Et_2NH_2NO_3$.		
Expt. no.	N_2O_4 reacted.	$Et_2N{\cdot}NO$ produced.	HNO_3 produced.
1	1·31	1·13	2·19
2	0·95	0·82	1·91
3	0·95	0·95	1·94

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