

The Liquid Dinitrogen Tetroxide Solvent System. Part XVI. Reactions with Ethylammonium Nitrate Solutions: Ethylammonium Tetranitratozincate.*

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The reaction of solutions of ethylammonium nitrate in liquid dinitrogen tetroxide with metallic zinc gives a crystalline product, $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{EtNH}_3\text{NO}_3$. Properties of this compound, and of its solutions in nitromethane, liquid dinitrogen tetroxide, and hydroxylic and other solvents are described. Conductivity and electrolytic measurements indicate that the compound may be formulated as $(\text{EtNH}_3^+)_2[\text{Zn}(\text{NO}_3)_4]^{2-}$. Ethylammonium salts undergo some decomposition in liquid dinitrogen tetroxide, and this side reaction has also been studied.

COMPOUNDS which give rise to "basic" solutions in liquid dinitrogen tetroxide fall into two types. The first type (typified by diethylnitrosamine) enhances the ionisation $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$ by formation of addition compounds with the NO^+ ion (*J.*, 1952, 1390, 1399). Compounds of the second type (typified by the alkylammonium nitrates) introduce the nitrate ion directly into the system. Solutions of compounds of each type attack metals more rapidly than does dinitrogen tetroxide alone, and from solutions of the second type it is possible to separate crystalline reaction products. The product of reaction of monoethylammonium nitrate with zinc, obtained over a wide range of experimental conditions, may be represented as $(\text{EtNH}_3)_2[\text{Zn}(\text{NO}_3)_4]$, and contains no combined dinitrogen tetroxide. The present paper describes the preparation and the properties of this compound, together with some properties of other closely related compounds, such as $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$ and anhydrous zinc nitrate, which have not already been described but have direct significance in the study of ethylammonium tetranitratozincate. The reaction products obtained by using di-, tri-, and tetra-ethylammonium nitrate solutions contain an amount of combined dinitrogen tetroxide which varies with conditions (*J.*, 1954, 1143).

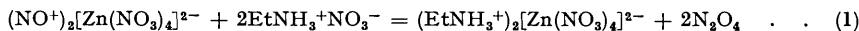
Mixtures of ethylammonium nitrate and dinitrogen tetroxide containing up to 58% of the former separate into two liquid phases immediately on being mixed. The upper phase contains all the nitrate and some dinitrogen tetroxide, the lower layer being pure tetroxide. Concentrated solutions containing more than 58% of the nitrate consist of one liquid phase only. A side reaction occurs between the components of the mixture, but not to a sufficient extent to complicate the metal-solution reactions reported here.

Reaction with Metallic Zinc.—When a block of zinc was suspended in the upper layer of an ethylammonium nitrate-dinitrogen tetroxide mixture, reaction was immediate, but the rate varied widely with temperature. At 0° the green colour of dinitrogen trioxide was perceptible only after 2 hr., although above 20° reaction was vigorous, with effervescence of nitric oxide. Although the reaction rate is much greater than with dinitrogen tetroxide alone, its variation with temperature follows the same course as with the pure tetroxide (Part VIII, *J.*, 1951, 2833), where the rate of the electron-transfer reaction $\text{Zn} + 2[\text{NO}^+][\text{NO}_3^-] = \text{Zn}(\text{NO}_3)_2 + 2\text{NO}$ is limited by the very low concentration of ion-pairs. The polar nature of added ethylammonium nitrate will increase the dielectric constant of the medium, the concentration of NO^+ ions, and the rate of reaction. In reaction with tetroxide alone, the insoluble product $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$ is formed, whereas in the presence of ethylammonium nitrate this initial product reacts to form a soluble complex.

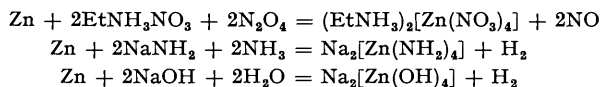
On continued reaction, the product accumulated exclusively in the upper layer until the density of this layer exceeded that of dinitrogen tetroxide, whereupon inversion occurred. With an 11.5% solution inversion took place after 2 hr. at room temperature. Small needle crystals which separated from the lower layer after a further hour were shown

* Part XV, *J.*, 1953, 2631.

by analysis to contain no nitrite or combined dinitrogen tetroxide, and to contain zinc, ethylamine, and the nitrate ion in the ratio 1 : 2 : 4. On the basis of properties described below, the compound is formulated as $(\text{EtNH}_3)_2[\text{Zn}(\text{NO}_3)_4]$, and is produced by the acid-base reaction

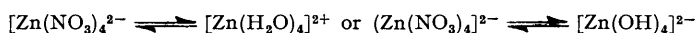


This reaction illustrates the amphoteric behaviour of zinc salts in dinitrogen tetroxide medium, and the equations



relate similar properties of zinc in the three solvent systems.

4-Co-ordinate complexes containing nitrate groups only are little known; Jander and Wendt (*Z. anorg. Chem.*, 1949, **258**, 1) found that the solubility of cadmium nitrate in pure nitric acid is increased on addition of potassium nitrate, and a similar nitrato-complex may be formed. The formation of such complexes in aqueous medium is improbable, since the equilibria



will be displaced far in the forward direction. The nitrato-uranyl complexes are similarly unstable in hydroxylic solvents (Addison and Hodge, *Nature*, 1953, **171**, 569). With ligands containing nitrogen and oxygen atoms, the ligand is, in general, preferentially

co-ordinated through the nitrogen rather than the oxygen atom (hence $\leftarrow \text{N} \begin{array}{l} \text{O}^- \\ \text{O} \end{array}$ is a more stable co-ordinating group than $\leftarrow \text{O} \cdot \text{N} = \text{O}^-$); but with the nitrate ion co-ordination is necessarily with an oxygen atom since the nitrogen atom has no available electron pair, and the formation of nitrato-complexes is therefore only likely in media (such as nitric acid or dinitrogen tetroxide) which provide no competing ligands.

Properties of Ethylammonium Tetranitratozincate.—The compound is extremely deliquescent, necessitating transfer and manipulation in a closed system. The properties of its solutions vary with the solvent used.

(a) *Nitromethane.* This is an excellent solvent for the compound. Anhydrous zinc nitrate dissolves slowly in it (solubility 0.025M), but more rapidly, and to a greater extent, in the presence of ethylammonium nitrate, its solubility being 0.055M in a 0.064M-solution, *i.e.*, the increase in quantity of dissolved zinc nitrate is nearly that required to convert ethylammonium nitrate into the tetranitratozincate.

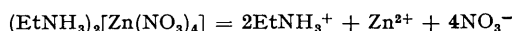
(b) *Liquid dinitrogen tetroxide.* The compound is insoluble in this medium; on prolonged immersion the crystals became partially liquefied, forming a separate yellow, viscous phase. (When the tetroxide was removed in a current of dry air the original compound was recovered.) Analysis showed the viscous liquid to contain an excess of ethylammonium nitrate whereas the crystals contained an excess of zinc nitrate. These observations may be interpreted by reference to equation (1). The equilibrium lies largely to the right, but the reverse reaction accounts for the degeneration of the crystals. Equilibrium is rapidly produced in the forward direction; when the equivalent quantity of liquid ethyl ammonium nitrate was added to the compound $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$, free liquid dinitrogen tetroxide was immediately produced, which could be decanted to leave the equilibrium mixture.

(c) In benzene, ether, dioxan, carbon tetrachloride, and chloroform the crystals were insoluble, and showed no physical or chemical change on prolonged immersion.

(d) *Ketonic solvents.* With acetone and *cyclohexanone*, a colourless solution was obtained, which became brown on storage. The absorption spectrum of a fresh solution in *cyclohexanone* (given below) shows no characteristic feature over the available range.

λ , m μ	340	350	360	370	390	410	430	450	470	490
ϵ	9.09	6.27	3.56	2.13	1.07	0.64	0.47	0.38	0.31	0.28

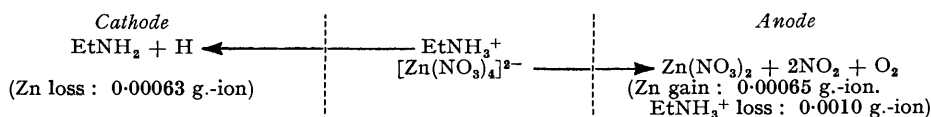
(e) *Hydroxylic solvents.* The compound dissolves readily in water and absolute alcohol, but dissociates as follows:



The ultra-violet absorption spectrum of the aqueous solutions shows a peak characteristic of the nitrate ion at 304 m μ ; $\epsilon_{\text{max.}} = 7.06$ being assumed, then the concentration of free nitrate ions in the solution, calculated from the absorption curve, is in exact agreement with the above equation. The spectrum of the solution in absolute alcohol shows a peak at 300 m μ and $\epsilon_{\text{max.}} = 5.79$. The value of $\epsilon_{\text{max.}}$ for the nitrate ion in absolute alcohol (determined with a solution of ammonium nitrate) is 6.3, so that the compound is largely, if not completely, dissociated in absolute alcohol also.

Action of Heat.—The compound melted sharply at 83–84° without decomposition, giving a colourless liquid. Between 190° and 210° the melt changed to deep yellow brown, with slight decomposition. At 220° the compound decomposed rapidly but quietly, with 45% loss in weight. At 270° a vigorous decomposition occurred, leaving a white solid which was mainly zinc oxide. The decomposition occurring at 190–220° is probably due to ethylammonium nitrate, which decomposes over the same temperature range. The decomposition at 270° involves thermal disruption of the nitrate group, and oxidation of the remaining organic material. When a sample was heated rapidly to 270°, without delay at 190–220°, decomposition was explosive and the gaseous products ignited.

Electrolysis of Solutions.—Electrolysis was carried out at 20° in a three-compartment cell. The electrode compartments had a capacity of 36 ml., the total capacity being 95 ml. Bright platinum electrodes were used. From a 4% solution of ethylammonium tetranitratozincate in nitromethane, oxygen gas was liberated from the anode. When the platinum anode was replaced by zinc, no gas evolution occurred. The zinc became coated with zinc oxide, and zinc nitrate was eventually precipitated from the solution. Analysis of the cathode compartment showed a decrease in zinc content, indicating the presence of zinc in the anion. The electrolysis was studied quantitatively by use of an iodine coulometer. A 4.23% solution was electrolysed for 9 hr. at 220 v p.d., and 0.00216 F was passed, and the changes in concentration in the cathode and the anode compartment compared with those expected on the assumption that ethylammonium tetranitratozincate ionises in nitromethane solutions of this concentration into EtNH_3^+ and



$[\text{Zn}(\text{NO}_3)_4]^{2-}$ ions only. The transport number of the EtNH_3^+ ion (t_+) is $0.0010/0.00216 = 0.46$. Similarly, the transport number of the $[\text{Zn}(\text{NO}_3)_4]^{2-}$ ion (t_-) is $0.00126/0.00216 = 0.58$. The fact that $t_+ + t_- = 1.04$ suggests that no other ions make a significant contribution to the transport of current.

The above effects have been compared with those observed on electrolysis of a 0.7% solution of the compound $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$ in nitromethane. The presence of the NO^+ ion in solution was shown by a green colour round the cathode, with evolution of nitric oxide. The solution, and the atmosphere above it, contained appreciable quantities of dinitrogen tetroxide, so the equilibrium $(\text{NO}^+)_2[\text{Zn}(\text{NO}_3)_4]^{2-} \rightleftharpoons \text{Zn}(\text{NO}_3)_2 + 2\text{N}_2\text{O}_4$ exists in the solution. Oxygen was evolved from the anode by the discharge of NO_3^- or $[\text{Zn}(\text{NO}_3)_4]^{2-}$ ions, and reversal of the current discharged the green colour round the cathode. No zinc was deposited on the cathode; it was probably dissolved, as soon as deposited, by the dinitrogen trioxide and tetroxide in the solution (Part IX, *J.*, 1951, 2838).

Conductometric Experiments.—The molar conductivity of solutions of zinc nitrate and ethylammonium nitrate in nitromethane at 20° has been determined over a concentration range, and the results are shown graphically in Fig. 1, together with values for solutions of the compounds $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ and $(\text{EtNH}_3)_2[\text{Zn}(\text{NO}_3)_4]$. None of the $\Lambda - \sqrt{M}$ curves approaches linearity, and all the solutes are weak electrolytes in nitromethane (cf. Walden and Birr, *Z. phys. Chem.*, 1932, 163, 263; Wynne-Jones, *J.*, 1931, 795). The conductivity

values shown in curves *D* and *E* cannot be read with accuracy from Fig. 1 and are given below :

Molar concn. $\times 10^4$	1.36	3.27	9.9	13.6	30.7	68.0	102	153
Molar conductivity, $\text{ohm}^{-1} \text{cm.}^2$								
$\text{Zn}(\text{NO}_3)_2$	—	—	22.6	13.8	10.6	9.5	8.8	7.9
$\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$	36.0	17.9	11.2	9.9	8.4	7.4	6.8	6.3

The magnitude of these values, and the shape of the curves, indicate that ionic dissociation is small. The similarity in the values is not significant, since differing degrees of dissociation may be balanced by the difference in the mobilities of the ions concerned. Curve *B* is obtained by summation from curves *C* and *D*, and represents the conductivity of a solution containing ethylammonium nitrate and zinc nitrate in the molar ratio 2 : 1, assuming that no complex ion formation occurs. Curves *B* and *A* coincide at high dilution; this is consistent with a shift in the equilibrium $[\text{Zn}(\text{NO}_3)_4]^{2-} \rightleftharpoons \text{Zn}^{2+} + 4\text{NO}_3^-$ towards the right-hand side with decreasing concentration. The fact that curve *A* shows the highest conductivity values may be attributed to a smaller degree of association between the ions EtNH_3^+ and $[\text{Zn}(\text{NO}_3)_4]^{2-}$. With ethylammonium salts of simple anions association of the hydrogen of the cation with the anion is known to be pronounced, and in

FIG. 1.

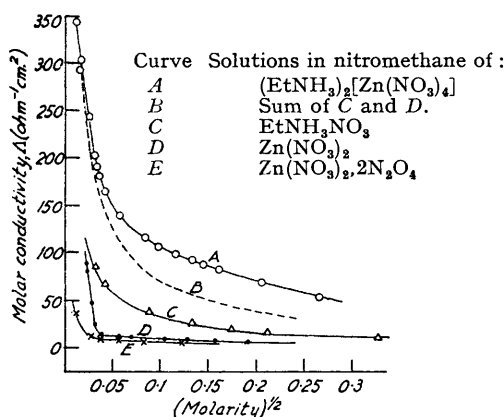
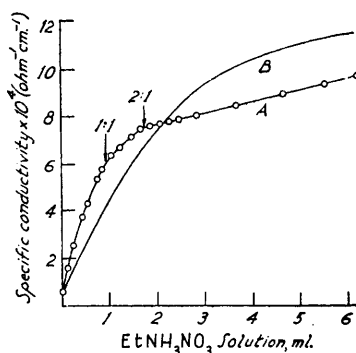


FIG. 2.



the compound $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$ strong association between the NO^+ groups and the nitrate groups in the cation will result in low conductivity values.

Curve *A*, Fig. 2, shows the titration curve obtained when a 1.56% solution of ethylammonium nitrate in nitromethane was added progressively to a solution of 0.0386 g. of zinc nitrate in 10 ml. of nitromethane at -15° . At a molecular ratio of 1 : 1 the curve shows a change in direction, and at 2 : 1 a sharp break occurs. Up to the 2 : 1 ratio, the weakly conducting salt $\text{Zn}(\text{NO}_3)_2$ is replaced by the more strongly conducting $(\text{EtNH}_3)_2[\text{Zn}(\text{NO}_3)_4]$. The departure from linearity is attributed to decrease in the degree of dissociation of the ion $[\text{Zn}(\text{NO}_3)_4]^{2-}$, whose concentration varies widely over this range. Beyond the 2 : 1 ratio, no change in conducting species is involved, and the slow increase in conductivity is due only to changing concentration of ethylammonium nitrate. Curve *B*, Fig. 2, was obtained when titrating a corresponding solution of the compound $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$. The $\text{N}_2\text{O}_4\text{-EtNH}_3\text{NO}_3$ reaction gives highly conducting products, which mask the break in the curve which would otherwise occur.

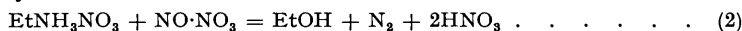
EXPERIMENTAL

Reaction of Ethylammonium Salts with Dinitrogen Tetroxide.—A weighed quantity of the nitrate (Table 1) was treated with dinitrogen tetroxide. After reaction, the tetroxide and readily volatile products were removed under reduced pressure, and the product weighed. The percentage increase in weight (col. 7) is a suitable measure of the extent of reaction.

TABLE 1.

Expt. No.	Wt. of EtNH ₃ NO ₃ (g.)	Conditions of soln. in N ₂ O ₄	Duration of reaction (hr.)	Temp.	Wt. of product (g.)	Increase in wt., %	HNO ₃ produced (g.)
1	1.1720	8 g. N ₂ O ₄ (two layers)	4	0°	1.1729	0.08	—
2	0.9727	8 g. N ₂ O ₄ (two layers)	30	20	0.9974	2.54	—
3	0.7810	80% concn. in N ₂ O ₄ (one phase)	30	20	0.9096	16.46	0.219

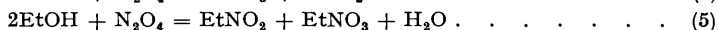
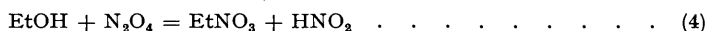
In its reaction with diethylammonium nitrate (Part V, *J.*, 1951, 1298) the behaviour of the N₂O₄ molecule is analogous to that of nitrous acid (NO·OH). With the monoethyl compound, it would be represented by



Under conditions which give more rapid reaction (Expt. 3) bubbles of an insoluble gas were produced, and a deep green-blue colour developed in the liquid, owing to subsequent reaction of ethyl alcohol. Yoffe and Gray (*J.*, 1951, 1412) find the reaction to occur largely as



but under the different conditions used in this work, the alternative reactions



must be considered as occurring also. Comparison of Expts. 1 and 2 (Table 1) shows the increase of reaction rate with temperature, and expts. 2 and 3 illustrate the considerable increase in rate when the two components form one homogeneous phase. Reactions of these solutions with metallic zinc were carried out at ethylammonium nitrate concentrations below 58%, and were normally completed within 4—6 hr. at 20°, so that decomposition of the nitrate was not significant, although it does no doubt account for the high electrical conductivity ($\kappa = 10^{-3}$ — 10^{-4} ohm⁻¹ cm.⁻¹) of the upper liquid layer in these mixtures.

Reaction with nitrosyl chloride is analogous to that with dinitrogen tetroxide. When ethylammonium chloride is added to the tetroxide, solvolysis occurs immediately; the subsequent reaction



is analogous to equation (2). Table 2 gives the results of experiments in which the liquid phase contained nitrosyl chloride also.

TABLE 2.

Expt. No.	Wt. of EtNH ₃ Cl (g.)	Duration of reaction (hr.)	Temp.	Wt. of product (g.)	Increase in wt., %	Analysis of product :	
						HNO ₃ (g.)	EtNH ₃ NO ₃ (g.)
4	2.83	10	-5° to +20°	4.00	6.10	—	—
5	6.11	8	-10° to +20°	8.42	3.95	—	—
6	8.89	6	-15° to 0°	11.84	0.40	—	—
7	2.263	4.75	20°	3.110	3.67	0.162	—
8	1.612	6	20°	2.271	6.28	0.220	1.980
9	0.935	3.25	20°	1.280	3.50	0.094	1.171

In Expts. 4—6, gentle suction was applied to remove nitrosyl chloride immediately after dissolution of the ethylammonium chloride, so the nitrosyl chloride was present in diminishing quantity. The low temperature was maintained by evaporation of solvent, but rose gradually during the experiment. The % weight increase (col. 6) is calculated on the basis of the weight of ethylammonium nitrate equivalent to the quantity of chloride used. Expts. 4—6 show clearly the pronounced decrease in decomposition rate which results from decrease in temperature. In Expts. 7—9 the nitrosyl chloride was not removed from the solution, and these experiments may be compared directly with Expts. 1—3 to show the greater rate at which nitrosyl chloride causes decomposition of ethylammonium nitrate.

Analysis of the product gave the number of moles of nitric acid produced from the decomposition of each mole of ethylammonium nitrate. Equations (2) and (3) require a HNO₃/EtNH₃NO₃ ratio of 3; equations (6) and (3) require a ratio of 2. The results of Expts. 8 and 9 are in close agreement, with ratios of 2.36 and 2.33, respectively.

Preparation of Pure Ethylammonium Nitrate.—Slightly more than the theoretical quantity of dinitrogen tetroxide was added at -20° to about 10 g. of dry ethylammonium chloride.

Suction was applied immediately on mixing to remove nitrosyl chloride and excess of dinitrogen tetroxide; the resulting liquid was dissolved in absolute alcohol, and dry ether added at -30° . The precipitate was filtered off rapidly at this temperature and washed with cold ether, and the ether removed under reduced pressure below 0° . The product had m. p. 12° (cf. 8° , Sugden and Wilkins, *J.*, 1929, 1297; $13-14^{\circ}$, Walden, *Chem. Zentr.*, 1914, I, 1800) (Found: EtNH_2 , 41.5. Calc. for EtNH_3NO_3 : EtNH_2 , 41.68%).

Product of Reaction with Zinc.—The impure crystals were filtered on a Grade 2 sintered-glass filter tube. After purification of the product (outlined below), the crystals were dissolved in water; the zinc content was determined by means of 8-hydroxyquinoline, and the amine content by addition of alkali and distillation into standard acid. Nitrate was determined in the solution remaining after distillation by use of Devarda's alloy. Analytical results are given in Table 3: all results are referred to 1 g.-atom of zinc.

TABLE 3.

Prepn. No.	Zn (g.-atoms)	EtNH_3^+ (g.-ions)	NO_3^- (g.-ions)	N_2O_4 (mole)
1	1.0	1.82	3.79	0.125
2	1.0	2.20	4.20	—
3	1.0	1.99	4.00	—

Prepn. 1 was carried out by reaction of a 5-g. block of zinc with a solution of 3.8 g. of ethylammonium nitrate in 25 ml. of dinitrogen tetroxide for 10 hr. On filtration and suction, the product gave dry crystals, but the analytical results show that these conditions gave a product contaminated with the compound $(\text{NO})_2[\text{Zn}(\text{NO}_3)_4]$. In prepn. 2 the concentration was increased (6.6 g. of ethylammonium nitrate in 20 ml. of tetroxide) and the reaction time reduced to 4 hr. Passage of dry air for 30 min. through the mat of crystals removed all the tetroxide, leaving a dry powder (analysis 2). Under these conditions the product is therefore contaminated with ethylammonium nitrate. Prepn. 3 was carried out as described for prepn. 2, but the product was washed with nitromethane (in which ethylammonium nitrate dissolves more rapidly) before analysis. The results (analysis 3) confirm the preparation of the pure compound $(\text{EtNH}_3)_2[\text{Zn}(\text{NO}_3)_4]$.

Conductivity Measurements.—These were carried out in an apparatus similar to that described in Part XV (*loc. cit.*).

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