628. *The Liquid Dinitrogen Tetroxide Solvent System. Part VII.* Products of Reaction of Zinc with Liquid Dinitrogen Tetroxide.*

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The reaction between zinc and liquid dinitrogen tetroxide involves the evolution of nitric oxide, and the formation of a compound insoluble in the tetroxide having the empirical formula $Zn(NO_3)_2,2N_2O_4$. The action of heat on this compound, and its reactions with organic solvents (particularly ethyl ether) are considered in the light of possible structures for the compound. Heating at 100° results in the removal of the two molecules of dinitrogen tetroxide, leaving zinc nitrate in the pure anhydrous form. This method of preparation is simpler than methods previously described. Zinc nitrate is stable at 100°, but decomposes slowly in the temperature range 100—240°, and rapidly above 240°.

In Part I (*J.*, 1949, S 211), reactions between metals and liquid dinitrogen tetroxide (and solutions of " acids " and " bases " in this medium) have been shown to be analogous, in some respects, to the corresponding reactions involving water or liquid ammonia. A range of metals is under consideration from this point of view, and the reactions with zinc are now described. Reaction between certain metals and liquid dinitrogen tetroxide provides a suitable method for the preparation of anhydrous nitrates which may be difficult to prepare in aqueous medium, and the preparation of anhydrous zinc nitrate is a suitable example of this method.

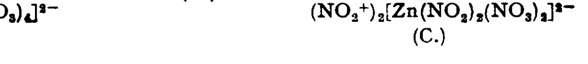
It was stated in Part I (*loc. cit.*) that in contact with liquid dinitrogen tetroxide, " zinc develops a coating of nitrate after about 20 hours " ; the surface was then given no preliminary treatment before reaction, and the temperature of the reaction was controlled at 0°. It has been found that if the zinc is cast to a block, so that a fresh surface can be produced by filing, and if the reaction is carried out at a higher temperature, reaction is much more rapid. (Reaction rates are discussed in more detail in the following paper.)

When a block of zinc having a freshly filed surface was added to liquid dinitrogen tetroxide at about 20°, a slight evolution of nitric oxide occurred immediately. After about 10 minutes the metal was covered by a thin layer of white, finely crystalline solid, and the liquid immediately in contact with the metal was coloured green by dinitrogen trioxide. As the crystalline coating became thicker, the crystals were more clearly defined, and about 1 g. of product was formed after 24 hours, and was readily separated from the zinc block. As with other heterogeneous reactions, the yield may be increased by increasing the surface area; by using zinc dust the same yield may be obtained within a few minutes. However, this method of preparation was not used, since it was difficult to confirm that the product was not contaminated with unreacted zinc.

When the dinitrogen tetroxide was allowed to evaporate at a temperature slightly below its boiling point (21·3°), the product was obtained as a free-flowing finely crystalline powder, which was stable for long periods (in a stoppered tube) provided that the atmosphere of dinitrogen tetroxide was maintained. (If this atmosphere was removed, either by evacuating the vessel, or by blowing out the dinitrogen tetroxide with a stream of dry nitrogen, the crystals rapidly decomposed to a pale yellow, viscous liquid.) When the original product was heated, dinitrogen tetroxide was evolved, leaving anhydrous zinc nitrate. Two molecules of tetroxide were originally present for each molecule of zinc nitrate, so the reaction may be represented as follows :

$$Zn + 4N_2O_4 = 2NO + Zn(NO_3)_2,2N_2O_4 \qquad . \; . \; . \; . \; . \; . \; . \quad (1)$$

This product can be formulated in three ways, (A), (B), and (C). In a compound having structure (A) the N_2O_4 molecules may be regarded as " N_2O_4 of crystallisation "; as in the analogous case of salts containing water of crystallisation, some or all of the N_2O_4 molecules may be associated with the metal ion in the crystal lattice. Bonding is likely to be weak, so the



(A.)

$(NO^+)_2[Zn(NO_3)_4]^{2-}$
(B.)

$(NO_2^+)_2[Zn(NO_2)_2(NO_3)_2]^{2-}$
(C.)

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* Part VI, *J.*, 1951, 1303.

compound should show the properties of both zinc nitrate and dinitrogen tetroxide. In a compound having structure (B), the ion $[Zn(NO_3)_4]^{2-}$ is analogous to the ion $[Zn(OH)_4]^{2-}$ and $[Zn(NH_2)_4]^{2-}$ in the aqueous and the liquid ammonia system, respectively. As dinitrogen tetroxide is no longer present as such, the compound may be expected to exhibit chemical properties differing from either the tetroxide or zinc nitrate alone, although thermal decomposition of the compound should still result in evolution of dinitrogen tetroxide. Relatively few co-ordination complexes containing four or more nitrate groups are known, although a group of compounds of formula $M^1_2[M^2(NO_3)_6]$, where M^1 = Cs, Rb, Tl, or K, and M^2 = Pu, Th, or Ce, have recently been discussed (see Lister, *Quart. Reviews*, 1950, **4**, 37) and these compounds are considered to contain the complex anion $[M^2(NO_3)_6]^{2-}$. Structure (C), although less probable than (B), is analogous to (B), in that it involves the alternative mode of ionisation of the N_2O_4 molecules.

The compound is quite insoluble in liquid dinitrogen tetroxide, and is only rendered soluble by the addition of other compounds (such as alkylammonium salts or diethylnitrosamine) whose presence will result in further chemical reaction, so it is not possible to employ conductimetric or electrolytic methods to differentiate between these structures.* An attempt has been made to electrolyse the viscous liquid which results when part of the dinitrogen tetroxide is removed from the compound. Preliminary experiments indicate that the liquid has a low electrical conductivity, and no electrode effects were observed when electrolysis between Nichrome wires (placed 3 mm. apart) was continued for 30 hours at 250 v. potential difference. It is hoped, later, to obtain evidence of structure by crystallographic methods. However, the following properties of the compound may now be considered in the light of these possible structures.

(1) *Action of Heat.*—The tube containing the white solid was fitted with a phosphoric oxide guard tube (to maintain atmospheric pressure in the tube), and its temperature increased slowly. Decomposition proceeded in the following stages :

(*a*) When dinitrogen tetroxide vapour was allowed to leak from the guard tube, the solid (at a temperature about 15°) changed from free-flowing crystals to a pasty mass in about 2 hours and to a pale yellow viscous liquid after 2 days.

(*b*) The change from solid to liquid was accelerated by slight increase in temperature, being complete within a few minutes at about 25°. The removal of not more than 10% of the available dinitrogen tetroxide resulted in the complete conversion of solid into liquid. This phase change may arise from the depression of the freezing point of the original compound by the zinc nitrate produced, but the considerable degree of supercooling shown by the liquid has prevented the preparation of the relevant phase diagram.

(*c*) On further heating, the liquid continued to lose dinitrogen tetroxide vapour. The mode of decomposition indicates that the reaction

$$Zn(NO_3)_2,2N_2O_4 \rightleftharpoons Zn(NO_3)_2 + 2N_2O_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is reversible, for on keeping the temperature of the liquid at (say) 40°, evolution of dinitrogen tetroxide appeared to cease after some hours, although the liquid still contained 60—70% of the compound $Zn(NO_3)_2,2N_2O_4$. On reduction of the temperature by 10—15°, dinitrogen tetroxide vapour was reabsorbed by the liquid.

(*d*) Complete removal of dinitrogen tetroxide required about 6 hours at 100°; the slow conversion arises mainly from the slow rate of release of the tetroxide from the viscous liquid. The rate of removal of the last traces of tetroxide could be increased somewhat by heating the liquid under reduced pressure or at a higher temperature, but temperatures appreciably above 100° are undesirable because of the danger of decomposition of the zinc nitrate to zinc oxide.

The behaviour of the compound $Zn(NO_3)_2,2N_2O_4$ on heating clearly does not direct emphasis towards any particular structure. It is significant, however, that during the heating the equilibrium between zinc nitrate and its compound with dinitrogen tetroxide was maintained at all temperatures; the position of this equilibrium appeared to be adjusted smoothly with change in temperature, and at no particular temperature was a pronounced change in the rate of evolution of the tetroxide observed. In the aqueous system, this type of behaviour is characteristic of hydrates formed by complex molecules (*e.g.*, the heteropoly-acids) in which the number of water molecules is large and variable, rather than of salt hydrates containing a small and integral number of water molecules. On the basis of such an analogy, structure (A) above would appear less probable than (B) or (C). In order to confirm that the reaction given in equation (2) proceeds completely in the reverse as well as the forward direction, pure zinc

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* The compound dissolves in nitromethane to give a conducting solution; experiments being carried out to determine the nature of the dissociation (or decomposition) will be described in a later paper.

nitrate (prepared as described above) was treated with excess of liquid dinitrogen tetroxide. The white powder was converted almost immediately into a pasty mass, and conversion into clear crystals of $Zn(NO_3)_2,2N_2O_4$ was complete within 20 hours. When a similar reaction was attempted with anhydrous sodium or calcium nitrate, these salts were recovered unchanged when the excess of tetroxide was removed. In structures (B) and (C) the zinc atom occurs in an anionic co-ordination complex, and it is noteworthy that when the zinc nitrate is replaced by the nitrate of a metal which is unable to form such complexes, no combination with dinitrogen tetroxide occurs.

(2) *Action of Organic Solvents.*—A significant reaction occurs between the compound $Zn(NO_3)_2,2N_2O_4$ and dry ethyl ether. At about $-5°$, no reaction takes place; when warmed, a reaction commences which becomes vigorous at about 20°, and the temperature rises rapidly to the boiling point of the ether. The issuing ether vapour was shown to contain an appreciable quantity of acetaldehyde (but no formaldehyde), as well as dinitrogen tetroxide. On cooling, the liquid phase was found to contain acetic acid, acetaldehyde, and ether, with a little dissolved zinc nitrate. No nitrite was present in the liquid. The solid phase consisted almost entirely of zinc oxide, with only a trace of zinc nitrate. For comparison, both pure zinc nitrate and liquid dinitrogen tetroxide were treated separately with ethyl ether. No reaction whatever occurred with the nitrate, but the tetroxide caused slight oxidation of the ether; this reaction, however, occurred at a scarcely detectable rate.

The reaction of the compound with ethyl ether is therefore quite different in character from that of its two components. This is not consistent with the " hydrate " type of structure (A); on the other hand, a compound having structure (B) would be expected to display chemical properties differing widely from the sum of the properties of zinc nitrate and dinitrogen tetroxide considered separately. Again, anhydrous calcium nitrate, dinitrogen tetroxide, and ether show no appreciable reaction when mixed together, so reaction with ether is not a general property of metal nitrate–dinitrogen tetroxide mixtures. The fact that the solid product of reaction consists almost entirely of zinc oxide supports the belief that the type of bonding between the zinc atom and the nitrate groups is different from that occurring in the normal salt. Any breakdown of the $[Zn(NO_3)_4]^{2-}$ complex (structure B) under these conditions may well be expected to lead to removal of all the nitrate groups.

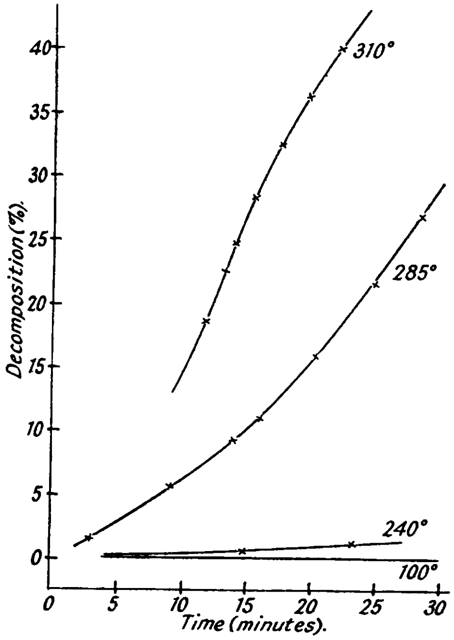
No reaction takes place between the compound and chloroform, carbon tetrachloride, or benzene. On addition of (say) benzene to the crystals, the benzene layer becomes coloured by dinitrogen tetroxide, and the crystals change to a pasty mass. After a few hours a state of equilibrium is reached; the addition of benzene is therefore equivalent to the application of reduced pressure to the crystals, and repeated treatment with fresh benzene can ultimately convert the crystals into pure zinc nitrate. This process is reversible: when dinitrogen tetroxide is added to benzene containing crystals of zinc nitrate, the latter change to the pasty mass typical of the $Zn(NO_3)_2$–$Zn(NO_3)_2,2N_2O_4$ mixture. The behaviour of the compound with chloroform and carbon tetrachloride is similar to that with benzene. These reactions, considered alone, are of the type to be expected of a compound containing " N_2O_4 of crystallisation " (structure A), and are not readily correlated with the reaction of the compound with ether.

Zinc Nitrate.—The anhydrous salt cannot be prepared from the hydrate, since removal of water of crystallisation leads to decomposition of the nitrate, and the formation of basic salts (Marketos, *Compt. rend.*, 1912, **155**, 210; Dubsky and Nevralova, *Chem. Listy*, 1931, **25**, 373). Marketos (*loc. cit.*) prepared the anhydrous nitrate by heating the tri- and tetra-hydrate at 130—135° in a current of carbon dioxide and dinitrogen pentoxide; a pasty substance was obtained which crystallised on cooling, and commenced to decompose at temperatures slightly above 135°. Ewing, Bradner, and Guyer (*J. Amer. Chem. Soc.*, 1939, **61**, 260) found that " the preparation of anhydrous zinc nitrate offered extreme difficulties." They prepared the material by reaction of gaseous dinitrogen pentoxide with zinc oxide, using ozone to inhibit the slow decomposition of the dinitrogen pentoxide. It is relevant that the compound $Zn(NO_3)_2,2N_2O_4$, and thus anhydrous zinc nitrate, may also be prepared rapidly from zinc oxide and liquid dinitrogen tetroxide: $ZnO + 4N_2O_4 = Zn\,(NO_3)_2,2N_2O_4 + N_2O_3$. Jander and Wendt (*Z. anorg. Chem.*, 1949, **258**, 1) were able to prepare anhydrous zinc nitrate from zinc picrate and absolute nitric acid. The method of preparation described in this paper is considered to be much more convenient than the methods referred to above, and to give a product which is quite pure.

In order to obtain information on the rate of decomposition of zinc nitrate, samples were heated at various temperatures within the range 100—310°, and the rates of decomposition are shown in the figure. Zinc nitrate was found to be stable at 100°, and this temperature was employed for its preparation. Very slight decomposition occurred at 150°, but even at 240°, measurements over a longer time range than is shown in the figure indicated that decomposition did not exceed 2% per hour. Above 240°, the rate of decomposition increased rapidly, as indicated in the figure. The quantity of nitrogen dioxide evolved, and the corresponding loss in weight of zinc nitrate, were in accord with the equation $2Zn(NO_3)_2 = 2ZnO + 4NO_2 + O_2$.

Measurements of decomposition rates, over temperature ranges narrower than in the experiments described above, are in hand to determine whether intermediate compounds between zinc nitrate and zinc oxide are formed during decomposition.

Rate of decomposition of zinc nitrate.



EXPERIMENTAL.

Analysis of Product.—A rectangular block of zinc, weighing about 5 g., was suspended in about 10 ml. of liquid dinitrogen tetroxide by means of a glass hook, which passed through a small hole bored in the zinc block. The whole was contained in a glass tube about 3 cm. long, fitted with a B19 ground joint and a phosphoric oxide guard tube. When a quantity (about 1—3 g.) of product had formed, the zinc block was quickly removed by means of the glass rod and hook, and the excess of liquid tetroxide allowed to evaporate at room temperature (about 20°). The tube and contents were then weighed. By preparing the crystals in a short tube with an internal volume of only 12 ml. (approx.) weighing errors due to the atmosphere of tetroxide were reduced to negligible proportions. Great care was necessary to ensure that the product as weighed was in a pure state. Two methods of analysis were used.

(a) *Ignition.* The product was heated at 100—120° until evolution of tetroxide ceased. The nitrate was then ignited to zinc oxide, and from the weight of oxide the zinc content of the original substance, and the zinc nitrate, was calculated :

Expt. no. :	1	2	3	4
Zn, %, in original *product* *	17·5	17·5	17·6	17·5
Zn, %, in intermediate product †	34·7	34·5	35·1	34·6

* $Zn(NO_3)_2,2N_2O_4$ requires Zn, 17·5%. † Calc. for $Zn(NO_3)_2$: Zn, 34·5%.

Since nitric oxide is produced in the zinc–dinitrogen tetroxide reaction, the possibility existed that the original product may contain molecules of N_2O_3 rather than N_2O_4. However, the zinc contents of $Zn(NO_3)_2,N_2O_3,N_2O_4$ and $Zn(NO_3)_2,2N_2O_3$ are 18·29 and 19·15%, respectively, and the experimental results in the above table exclude this possibility.

(b) *Determination of dinitrogen tetroxide evolved.* 1·257 g. of crystals were heated to the zinc nitrate stage in a tube fitted with a trap containing potassium hydroxide pellets, and calcium oxide to absorb moisture produced in the reaction between the potassium hydroxide and the tetroxide. The weight of tetroxide evolved (determined from increase in the weight of the trap) was 0·620 g. or 49·3% [$Zn(NO_3)_2,2N_2O_4$ requires N_2O_4, 49·3%].

Products of Reaction with Ethyl Ether.—The evolved gases were passed through a guard tube containing calcium chloride, and absorbed in an ice-cold, very dilute solution of sodium hydroxide. The acetaldehyde was redistilled from the alkaline solution into an aqueous-alcoholic solution of dimedone, and characterised as the dimedone derivative. The presence of acetaldehyde was confirmed by passing the gases evolved from the reaction mixture directly into an acid solution of 2 : 4-dinitrophenylhydrazine. The anhydrous calcium nitrate used in comparison experiments was obtained by heating the tetrahydrate (prepared from A.R. calcium carbonate) at 160°. Its purity was confirmed by determining the extinction coefficient of a standard solution, at 3020 A., by means of an ultra-violet spectrophotometer.

Decomposition of Zinc Nitrate.—The tube containing the zinc nitrate was immersed in a fused sodium nitrate–potassium nitrate bath controlled at the desired temperature. A stream of dry oxygen was passed over the zinc nitrate, and the gas stream (containing oxides of nitrogen produced by decomposition) was passed through an absorption trap containing standard sodium hydroxide solution. The absorption trap was replaced at frequent intervals, and the remaining alkali titrated against standard acid.

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