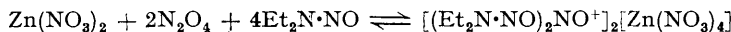


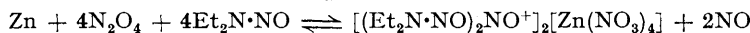
255. *The Liquid Dinitrogen Tetroxide Solvent System. Part XII.**
Amphoteric Reactions involving Zinc Compounds.

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

Metallic zinc reacts readily with solutions of diethylnitrosamine in liquid dinitrogen tetroxide with evolution of nitric oxide and the formation of a red liquid immiscible with dinitrogen tetroxide. This liquid product is indistinguishable from that formed by dissolving the compound $Zn(NO_3)_2 \cdot 2N_2O_4$ in diethylnitrosamine, or by adding dinitrogen tetroxide to a solution of anhydrous zinc nitrate in diethylnitrosamine. Colorimetric and spectroscopic measurements show that the state of the liquid product may be represented by the equilibrium



The reaction of metallic zinc is represented as :



These reactions are analogous to the corresponding reactions of zinc hydroxide, and of metallic zinc, with aqueous solutions of alkali hydroxides.

METALLIC zinc has been found to react rapidly with solutions of "bases" in liquid dinitrogen tetroxide. Since diethylnitrosamine is able to enhance the ionisation of the tetroxide, its presence in the system increases the concentration of NO_3^- ions (Part XI, preceding paper), and in consequence metallic zinc reacts rapidly with these solutions. The present paper describes the reaction between metallic zinc or zinc nitrate and solutions of diethylnitrosamine in liquid dinitrogen tetroxide.

It was observed (by R. Thompson in this laboratory) that when a block of pure metallic zinc (about 5 g.) was added to about 15 ml. of a 30% solution of the nitrosamine at 15°, reaction commenced immediately, with rapid evolution of nitric oxide gas. The latter was recognised by closing the reaction vessel with a guard-tube containing activated alumina; this reagent absorbs nitrogen dioxide but not nitric oxide, which could be observed on oxidation in the atmosphere. Some nitric oxide dissolved in the liquid mixture, the colour of which changed within a few minutes to dark green, and at the end of one hour the liquid was opaque to strong light. The zinc compound(s) formed during reaction were readily soluble in the liquid mixture, so the surface of the zinc block remained bright throughout the reaction. On cooling, the liquid became highly viscous, and it was not possible to separate the reaction product in solid form by crystallisation.

* Part XI, preceding paper.

The addition of liquid dinitrogen tetroxide to the reaction mixture produced two liquid layers, and the reaction product appeared to be immiscible with the pure tetroxide. The above experiment was therefore repeated with a solution containing only 8% of diethylnitrosamine. As before, nitric oxide was rapidly evolved, but within one minute, globules of an immiscible liquid product were formed on the zinc surface. After one hour, this product collected as a lower liquid phase forming about 30% of the total liquid volume. This layer was found to have a high zinc and nitrosamine content; when dissolved nitric oxide was removed by warming, a red oil remained. The upper layer consisted of dinitrogen tetroxide, containing traces only of zinc compounds and diethylnitrosamine.

Rate of Reaction.—The increase in rate of reaction of zinc on addition of diethylnitrosamine to the liquid tetroxide is illustrated in the following table. The reaction rates in pure dinitrogen tetroxide are calculated from Part VIII (*J.*, 1951, 2833); the difference in the temperature at which the two experiments were carried out is approximately compensated by the different stirring conditions, so that the rates recorded in the table reflect the relative velocities of the two reactions.

Period of immersion (min.)	Wt. of Zn reacting ($\text{g.} \times 10^{-3}/\text{cm.}^2$)	
	(a) In liquid N_2O_4 alone (18.5° , stirring rate 250 r.p.m.)	(b) In 6.5% $\text{Et}_2\text{N}\cdot\text{NO}$ solution (15° , stirred by shaking)
5	0.24	4.7
10	0.47	9.3
15	0.69	14.0
30	0.84	27.0
45	0.90	39.3
60	0.96	51.6
90	—	75.0
120	—	95.4

Whereas the rate of reaction with pure tetroxide decreases after an immersion period of 15 minutes, this rate is almost independent of period of immersion in diethylnitrosamine solutions. The addition of 6.5% of diethylnitrosamine therefore increases the initial rate of reaction by a factor of 20, and this factor is increased considerably by longer periods of immersion.

The reaction with nitrosamine solutions, like the reaction with tetroxide alone, is strongly temperature dependent. This is illustrated below for 5.6% of diethylnitrosamine in liquid dinitrogen tetroxide:

Temp.	-12.2°	-7.0°	-0.5°	5.0°	10.0°
Wt. of Zn reacting (10^{-3} g./cm. ² /15 min.)	1.57	2.23	5.01	7.23	9.11

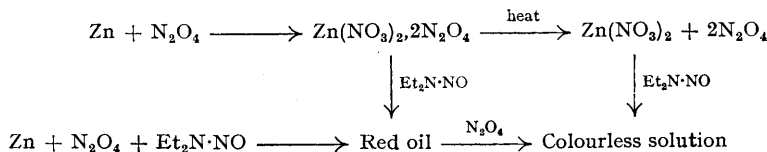
Product of Reaction.—The product of reaction is obtained in the form of a red oil which is immiscible with liquid dinitrogen tetroxide. The following preliminary experiments were carried out to determine the nature of this oil.

(a) *Action of organic solvents.* The red oil was immiscible with chloroform, carbon tetrachloride, and chlorobenzene, but shaking with these solvents reduced the intensity of the red colour. The oil was immiscible with diethyl ether, but reacted rapidly at the liquid interface; acetaldehyde was recognised as a decomposition product. This reaction is significant in the light of the observation (Part VII, *J.*, 1951, 2829) that the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ also oxidises ether to acetaldehyde.

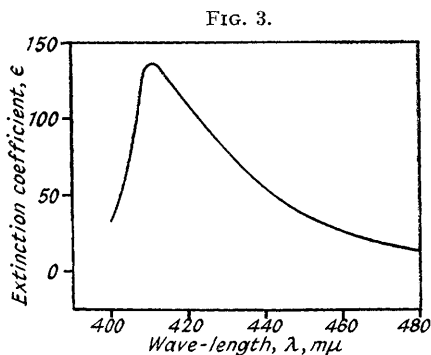
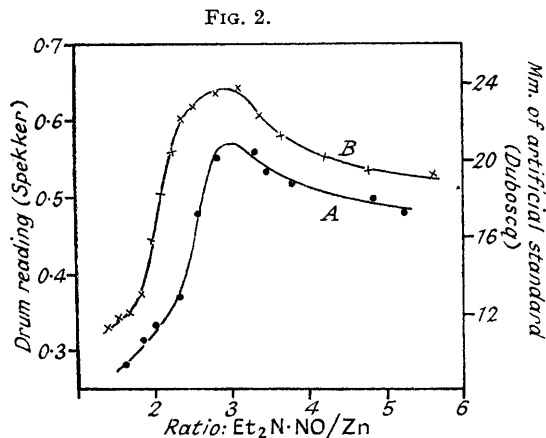
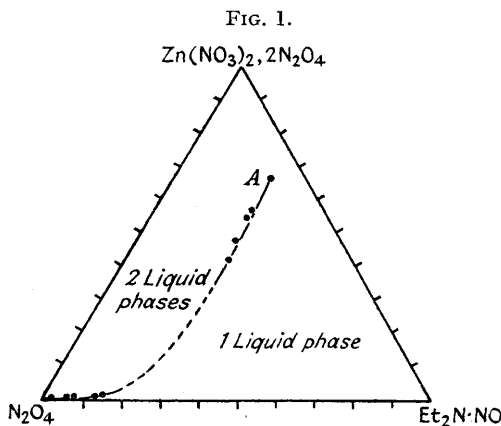
(b) *Thermal decomposition.* On warming to 40 – 50° , the colour of the oil deepened somewhat; at higher temperatures (up to about 80°) dinitrogen tetroxide evaporated rapidly, accompanied by a fading of the colour to pale yellow. No further change occurred thereafter until the temperature reached 170 – 180° , whereat diethylnitrosamine began to evaporate. At this stage the rate of thermal decomposition increased sharply, and unless the heating was carefully controlled, decomposition occurred explosively. The white solid which remained was identified as a mixture of zinc nitrate and zinc oxide.

These results suggest that the product of reaction consists of zinc nitrate combined with diethylnitrosamine and dinitrogen tetroxide. This has been confirmed by the preparation, directly from these three materials, of a red oil having the same properties as that prepared from metallic zinc. Anhydrous zinc nitrate is readily soluble in diethylnitrosamine to give

a colourless solution. The addition of dinitrogen tetroxide to this solution produced a deep red colour. The compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ was also treated directly with diethylnitrosamine. The solid dissolved to give a deep red solution, and the red oils prepared by either of these two methods could not be distinguished from that prepared from metallic zinc. The reactions may be summarised as follows.



Phase Equilibria.—The results in Fig. 1 were obtained at 18°. In mixtures containing up to about 10% of diethylnitrosamine, the dinitrogen tetroxide phase contains very little of the zinc compound. Thereafter, the miscibility curve rises sharply in the direction of increasing zinc content. In the concentration range 5–10% of diethylnitrosamine, sufficient



zinc is dissolved in about 1 minute to carry the system into the two-phase region. With 30% diethylnitrosamine solution the system is still homogeneous after 1 hour's reaction. The miscibility curve terminates at the invariant point *A*, which represents the composition of the system at which both liquid phases are saturated with the component $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$.

Constitution of Red Oil.—Attempts were made to determine the ratio of the constituents by measurement of the rate of solution of the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ in diethylnitros-

amine under various experimental conditions, it being expected that a break in the rate curve would occur when a quantity of the zinc compound had dissolved, equivalent to the nitrosamine present. No such break was observed. Attempts to obtain the constituent ratios by solvent extraction were also unsuccessful. Each of these experiments failed owing to the operation of an equilibrium between the compound and its constituents (see below).

(a) *Colorimetric analysis.* A known weight (about 1.5 g.) of $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ was treated with successive small amounts of diethylnitrosamine in an optical cell. After each addition, the colour of the liquid was compared with that of an artificial standard in a Duboscq visual colorimeter. The results are shown as curve *A*, Fig. 2. The experiment was repeated in a "Spekker" photoelectric absorptiometer, and the results are shown as curve *B*. The shapes of the curves are closely similar; the addition of diethylnitrosamine produces at first a rapid increase in colour intensity, and the curves pass through a somewhat rounded maximum at a $\text{Et}_2\text{N} \cdot \text{NO} : \text{Zn}$ ratio of about 3 : 1. Thereafter a gradual fall in colour intensity occurs.

The shape of these curves supports the existence of an equilibrium $\text{Et}_2\text{N} \cdot \text{NO} + \text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4 \rightleftharpoons$ coloured product, rather than an irreversible reaction proceeding from left to right. In the latter case, the system could be considered as consisting initially of a pure liquid compound containing a dissolved excess of the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$. Additional nitrosamine would then react with this excess to produce a greater quantity, but not a greater concentration, of coloured product. The colour intensity should therefore remain constant until no zinc compound remains in excess, and then decrease gradually on dilution with further nitrosamine. However, the shapes of the curves (Fig. 2) are consistent with the operation of two effects on addition of diethylnitrosamine, (a) dilution of the mixture, causing a decrease in colour intensity, and (b) a displacement of the above equilibrium to the right-hand side. At first, the latter effect predominates, leading to a net increase in colour intensity. At the maximum on the curves, the equilibrium shift becomes almost complete, so the dilution effect is then the larger of the two, and the colour intensity falls.

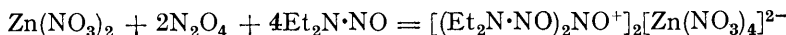
(b) *Absorption spectrum.* In Part VII (*J.*, 1951, 2829) the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ was considered as a nitrosonium compound $(\text{NO}^+)_2[\text{Zn}(\text{NO}_3)_4]$. In Part XI (preceding paper) it was shown that mixtures of dinitrogen tetroxide and diethylnitrosamine contained the red ion $(\text{Et}_2\text{N} \cdot \text{NO})_2\text{NO}^+$. On correlation of these facts, the red colour of the oil produced in the reaction of zinc with N_2O_4 - $\text{Et}_2\text{N} \cdot \text{NO}$ mixtures is attributed to the compound $[(\text{Et}_2\text{N} \cdot \text{NO})_2\text{NO}^+]_2[\text{Zn}(\text{NO}_3)_4]^{2-}$. The absorption spectrum for a solution of the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ in diethylnitrosamine is shown in Fig. 3. In the range 400—500 $\text{m}\mu$ the curve shows a single clearly defined peak at 410.5 $\text{m}\mu$, and $\epsilon_{\text{max.}} = 136$. The $\lambda_{\text{max.}}$ value is very close to that for solutions of nitrosonium hydrogen sulphate and for dinitrogen tetroxide dissolved in diethylnitrosamine. The $\epsilon_{\text{max.}}$ value lies above that for the pure tetroxide alone ($\epsilon_{\text{max.}} = 95$) but below that for the highly ionised nitrosonium hydrogen sulphate ($\epsilon_{\text{max.}} = 250$). The addition of zinc nitrate, by virtue of its ability to co-ordinate the NO_3^- ions, is therefore able to enhance the ionisation of dinitrogen tetroxide in diethylnitrosamine, and two equilibria may be considered to operate in this system :



and



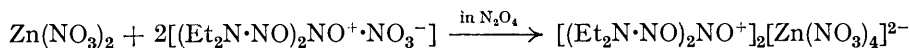
If the full equation for this reaction, *i.e.*,



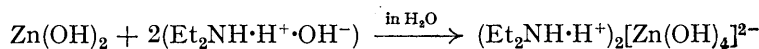
proceeded irreversibly in the forward direction, this would require a break in the colour intensity curves (Fig. 2) at a $\text{Et}_2\text{N} \cdot \text{NO} : \text{Zn}$ ratio of 4 : 1. Equilibrium (1) above is responsible for the lower ratio observed experimentally. For example, in any system $\text{A} + 2\text{B} \rightleftharpoons \text{C}$, it may be shown that the equilibrium concentration of C is a maximum when the initial amounts of A and B taken are in the ratio 1 : 2. Both the above equilibria (1) and (2) are of this form. In (1), if the solution in diethylnitrosamine is prepared by using

the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$, then the available concentration of nitrosonium ions is automatically at its maximum value. In (2), the ion $(\text{Et}_2\text{N} \cdot \text{NO})_2\text{NO}^+$ being assumed to be responsible for colour, then the maximum colour intensity will occur when the initial concentrations of NO^+ and $\text{Et}_2\text{N} \cdot \text{NO}$ are in the ratio 1 : 2. If reaction (1) proceeded to completion, then the $\text{Et}_2\text{N} \cdot \text{NO} : \text{Zn}$ ratio would be 4 : 1 at the colour maximum. However, the ϵ_{max} value determined from the absorption spectrum (Fig. 3) shows that reaction (1) is not complete, and in consequence the $\text{Et}_2\text{N} \cdot \text{NO} : \text{Zn}$ ratio must fall below 4 : 1 to an amount dependent upon the equilibrium constant of equation (1). The observed ratio of 3 : 1 is therefore consistent with equilibria (1) and (2).

Amphoteric Nature of Reactions.—The reaction

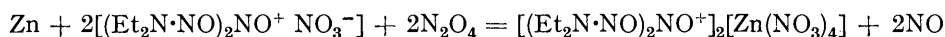


illustrates clearly the amphoteric properties of zinc nitrate in the liquid dinitrogen tetroxide solvent system. The analogous reaction in the aqueous system

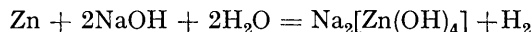


does not take place because the available hydroxyl-ion concentration is not sufficiently great to stabilise the $[\text{Zn}(\text{OH})_4]^{2-}$ ion, but the corresponding reaction involving alkali hydroxides $\text{Zn}(\text{OH})_2 + 2\text{NaOH} = \text{Na}_2[\text{Zn}(\text{OH})_4]$ is well known.

The close analogy between the reactions of metallic zinc described above and the reactions of zinc in the aqueous system is well illustrated by the following equations :



and



EXPERIMENTAL

Three-component diagram. The data in Fig. 1 were obtained by adding dinitrogen tetroxide and diethylnitrosamine in approximately the desired quantities to 1—2 g. of solid $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$, contained in a 7×1.5 cm. stoppered tube. The mixture was kept with frequent shaking, in a water-bath at 18° for about one hour. From each layer, two weighed samples of liquid (about 0.5—1 g. depending upon the zinc and the diethylnitrosamine content) were withdrawn. One sample was ignited to zinc oxide, the weight of which was used to calculate the percentage of $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$. Diethylnitrosamine was determined in the second sample as follows. The sample was hydrolysed in water; a suitable aliquot was made 7N with respect to hydrochloric acid and the mixture was boiled for 2 hours under an efficient reflux. This was sufficient to complete the reaction $\text{Et}_2\text{N} \cdot \text{NO} + \text{H}_2\text{O} + \text{HCl} = \text{Et}_2\text{NH}_2\text{Cl} + \text{HNO}_2$. The reaction mixture was cooled and made strongly alkaline by careful addition of solid potassium hydroxide. The liberated diethylamine was then distilled into an excess of standard acid.

Colorimetric analysis. Methyl-red, sodium nitroprusside, and mixtures of these reagents were found to provide suitable colour standards. For the "Spekker" absorptiometer measurements a 10×2 mm. microcell (light path 2 mm.) was sealed longitudinally by means of Silicone cement to a 5×1 cm. glass tube. The tube was closed by a Silicone rubber plug carrying a microburette. The compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ was placed in the cell, dissolved in the minimum quantity of diethylnitrosamine, and the titration carried out by adding successive additional quantities of diethylnitrosamine from the burette. After each addition, the colour intensity of the mixture was compared with that of the artificial colour standard contained in a 1-cm. optical cell, the "direct reading" method being used.