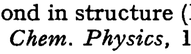
630. *The Liquid Dinitrogen Tetroxide Solvent System. Part IX.* Products, Rates, and Possible Mechanisms of the Reaction of Zinc with Liquid Dinitrogen Trioxide–Tetroxide Mixtures.*

By C. C. Addison, J. Lewis, and R. Thompson.

The rate of reaction between zinc metal and liquid dinitrogen tetroxide is increased by addition of dinitrogen trioxide. Rates of reaction between zinc and dinitrogen trioxide–tetroxide mixtures over the 0—40% trioxide concentration range, and the electrical conductivity of the mixtures over the 0—70% range, have been measured. Notwithstanding the higher reaction rate, the product of reaction with the trioxide–tetroxide mixtures is identical with the compound $Zn(NO_3)_2,2N_2O_4$ produced by reaction of zinc with pure dinitrogen tetroxide. Possible mechanisms of reaction of the trioxide with zinc are considered; the experimental results are satisfactorily explained on the assumption that no species peculiar to dinitrogen trioxide take part in the reaction, but that the trioxide augments mechanisms already in operation between zinc and dinitrogen tetroxide (Part VIII, preceding paper).

The experiments now described were carried out in consequence of the observation that the rate of reaction between zinc metal and dinitrogen trioxide–tetroxide mixtures was much greater than that with the tetroxide alone. It was already known that reaction between zinc and nitrosyl chloride (in solution in the tetroxide) is rapid (Part I, *J.*, 1949, S 211), and the high rate of reaction with dinitrogen trioxide appeared to be capable of interpretation on the basis that this molecule could be regarded as a nitrosyl compound. If such was the case, then dinitrogen trioxide would become a formal " acid " in this solvent system, and would react as nitrosyl nitrite. This behaviour would be consistent with either of the structures postulated for the trioxide molecule, *i.e.*, (I) and (II), except that the formation of nitrosyl nitrite involves

(I.) 

$$O{=}N{-}O{-}N{=}O$$

(II.)

the fission of an N–N bond in structure (I), but an N–O bond in structure (II). Structure (II) is proposed by Liefer (*J. Chem. Physics*, 1940, **8**, 301) on the basis of the ready exchange of the ^{15}N isotope between NO and NO_2 molecules, and is favoured by Sidgwick (" Chemical Elements

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* Part VIII, preceding paper.

and their Compounds," O.U.P., 1950, Vol. 1, p. 688). Although this stucture may represent that of the intermediate compound formed during isotope exchange between NO and NO_2 molecules in the gaseous state, it is considered that the structure of the dinitrogen trioxide molecule in the liquid state is better represented by (I), both by analogy with the tetroxide, and on the basis of Ingold's evidence for this structure (*Nature*, 1947, **159**, 743). Structure (I) is therefore assumed in the considerations below.

There are at least two objections to the formulation of dinitrogen trioxide as nitrosyl nitrite. First, the formal acid–metal equation $Zn + 2[NO^+][NO_2^-] = Zn(NO_2)_2 + 2NO$ would require the formation of nitrite. Analysis of the product has shown that this is not the case. Secondly, Le Fèvre (*Nature*, 1932, **130**, 400) states that the tautomeric electron-attraction of the nitroso-group is greater than that of the nitro-group; fission of the N–N bond would therefore lead to $[NO_2^+][NO^-]$ rather than $[NO^+][NO_2^-]$.

The experiments described below have therefore been carried out in order to assess the rôle which dinitrogen trioxide may be regarded as playing in the dinitrogen tetroxide solvent system, and to determine how far the nature of the reaction can be reconciled with the mechanism postulated in Part VIII for reaction between zinc and the pure tetroxide.

RESULTS AND DISCUSSION.

The identity of the product of reaction between zinc and liquid dinitrogen trioxide–tetroxide mixtures was established by two methods.

(a) *Ignition.* By ignition of a known weight of the powder to zinc oxide, the zinc content was shown to be 17·5%. On initial heating, the compound evolved dinitrogen tetroxide only; evolution of tetroxide ceased at about 120° and the remaining white powder (zinc content, 34·6%) was shown to be pure zinc nitrate. The ignition experiment therefore indicated that the product of reaction was the compound $Zn(NO_3)_2,2N_2O_4$.

(b) *Hydrolysis.* Since the present experiments were particularly concerned with the detection of nitrite, or combined dinitrogen trioxide, in the reaction product, the ignition method of analysis is less desirable because of the small variation in zinc content over the range of possible products. On the other hand, the quantity of nitrite produced on hydrolysis of the compound enables a definite conclusion to be reached. This is illustrated in the table below. On hydrolysis of the product in 0·1N-sodium hydroxide solution, two equivalents of nitrite were produced. This confirms that the product of reaction is $Zn(NO_3)_2,2N_2O_4$, uncontaminated by any other of the possible products.

Possible products	Equivs. of nitrite produced on hydrolysis	Zinc content, %
$Zn(NO_3)_2,2N_2O_4$	2	17·51
$Zn(NO_3)_2,N_2O_3,N_2O_4$	3	18·29
$Zn(NO_3)_2,2N_2O_3$	4	19·15
$Zn(NO_2)_2,2N_2O_4$		
$Zn(NO_2)_2,N_2O_3,N_2O_4$	5	20·09
$Zn(NO_2)_2,2N_2O_3$	6	21·13

The product of reaction between zinc and mixtures containing up to 70% of dinitrogen trioxide is therefore identical with that produced from zinc and pure dinitrogen tetroxide. Similarly, it has been shown that the reaction between metallic sodium and dinitrogen trioxide–tetroxide mixtures produces sodium nitrate free from any trace of nitrite. These results indicate that the mechanism of reaction between these metals and dinitrogen trioxide must be closely interlinked with that involving the tetroxide.

Rates of Reaction.—The influence of dinitrogen trioxide concentration on the rate of reaction with zinc is shown in Fig. 1 (curve *A*). The measurements recorded were obtained for 15-minute immersion periods at 0°, a stirring rate of 250 r.p.m. being used. Preliminary experiments on which the choice of these experimental conditions was based (including a study of the stability of tetroxide–trioxide mixtures) are described on p. 2842. The results shown in Fig. 1 cover a concentration range of about 0—40% of trioxide; the increase in reaction rate in the presence of trioxide is pronounced, the rate in a mixture containing 40% of trioxide being eight times that in the pure tetroxide. It is of interest that the rate of reaction appears to be a linear function of the square root of the dinitrogen trioxide concentration (Fig. 1, line B). For experimental reasons a kinetic study of the present system, similar to that described in Part VIII (*loc. cit.*) for the zinc–dinitrogen tetroxide reaction, presents considerable difficulties. Although it is observed that for solutions of any given concentration the rate of reaction increases with increase in temperature, the stability of the trioxide–tetroxide mixtures (especially at temperatures above 0°) is such that it was not found possible to maintain the concentration of the mixture at a sufficiently constant value over the full range of temperature to permit the accurate determination of activation energies for this reaction.

Electrical Conductivity of Mixtures.—The addition of dinitrogen trioxide to the tetroxide increases the electrical conductivity. Conductivity measurements over a wide range of concentration are given below. As with dinitrogen tetroxide alone (Part III, *J.*, 1951, 1289)

N_2O_3 concn., % (wt./wt.)	0	8·8	28·0	31·5	34·8	40·5	43·0	55·5	61·5	73·0
κ, ohm^{-1} cm.$^{-1}$ at $-10°$	6 $\times 10^{-13}$	1·7 $\times 10^{-10}$	6·7 $\times 10^{-8}$	7·5 $\times 10^{-8}$	8·9 $\times 10^{-8}$	1·2 $\times 10^{-7}$	1·3 $\times 10^{-7}$	2·5 $\times 10^{-7}$	4·9 $\times 10^{-7}$	1·3 $\times 10^{-6}$

the trioxide–tetroxide mixtures show a positive temperature coefficient of conductivity. From the results recorded in the third table, the temperature coefficient has a mean value of $0·03 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$ per degree.

N_2O_3 concn., %	Temp.	$10^7\kappa$, ohm^{-1} cm.$^{-1}$	N_2O_3 concn., %	Temp.	$10^7\kappa$, ohm^{-1} cm.$^{-1}$
58·0	−13°	3·6	61·5	−10°	4·9
	−24	3·4		−14	4·5
	−36	3·1		−40	3·8
	−40	3·0			

Possible Mechanisms of Reaction.—The fact that the product of reaction with trioxide–tetroxide mixtures, at any concentration, is identical with that formed with the tetroxide alone is regarded as strong evidence that the mechanism of the more rapid reactions with the mixture does not involve any species peculiar to the trioxide molecule. Thus, reaction of the trioxide as nitrosyl nitrite would involve the formation of nitrite as the final, or at least an intermediate, product. No nitrite occurs in the final product. Sodium metal reacts with trioxide–tetroxide mixtures to give sodium nitrate, and since sodium nitrite is quite stable in trioxide–tetroxide mixtures it may be presumed that the formation of nitrite as an intermediate in the zinc reaction is also improbable.

FIG. 1.

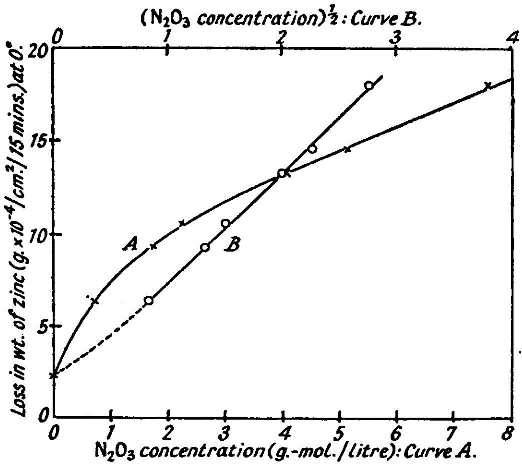
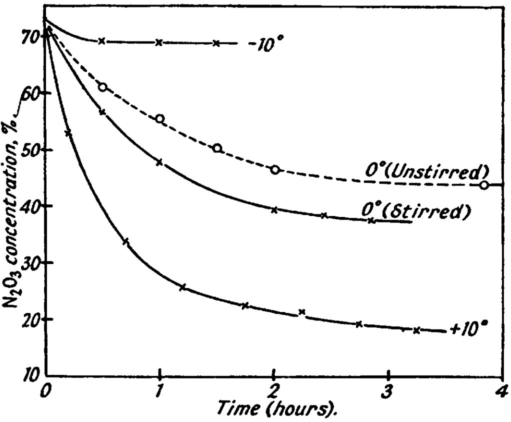


FIG. 2.



However, the experimental observations given above are readily interpreted on the basis that dinitrogen trioxide can augment reaction mechanisms which are already in operation between zinc and dinitrogen tetroxide (Part VIII, preceding paper).

Dinitrogen trioxide is considered to be capable of increasing the velocity of the reactions occurring by either mechanism. Since both mechanisms may well operate under appropriate conditions, it is not necessary, or desirable, to place emphasis on either mechanism. The reaction in pure liquid dinitrogen tetroxide at low temperatures necessarily involves ion-pairs only, and not free ions, since the low dielectric constant of the pure tetroxide (2·42; Part IV, *J.*, 1951, 1294) prevents separation into discrete ions. Again, the low dielectric constant is a direct consequence of the symmetry, and hence the lack of dipolar character, in the N_2O_4 molecule. However, the N_2O_3 molecule [assumed to have structure (I)] does not possess this symmetry. It is therefore to be expected that the molecule will show dipolar properties, and its addition to liquid dinitrogen tetroxide should result in an increase in the dielectric constant of the medium. In consequence, some dissociation of the ion pairs may be considered to occur; this is in accord with the increase in the electrical conductivity of the liquid, and the well-known stability of the NO^+ and NO_3^- ions is consistent with the observed positive temperature coefficient of conductivity. We may assume that reaction between metal atoms and free ions is a process which occurs somewhat more readily than that between the metal and the ion pairs, and it follows from the relation $k = Pe^{-E/RT}$ that a small decrease in the energy of activation E can give rise to a relatively large increase in the velocity constant k. However, the small concentration of ion-pairs which is considered to exist in the pure tetroxide limits the significance to be attached to this particular aspect. A more significant factor is the increase in the ionic concentration which may result from the relative instability of the dinitrogen trioxide molecule. The complete equilibrium between the species present in the tetroxide may be represented as follows :

$$N_2O_4 \underset{(1)}{\rightleftharpoons} 2NO_2 \underset{(2)}{\rightleftharpoons} [NO^+][NO_3^-] \underset{(3)}{\rightleftharpoons} NO^+ + NO_3^-$$

Increase in the dielectric constant of the medium will result in displacement of equilibrium (3). There is considerable chemical and physical evidence to suggest that the N–N bond in the trioxide molecule is much weaker than in the tetroxide; the molecule does not exist in the gaseous state, and in the liquid state the equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$ is no doubt displaced further towards the right-hand side than in the case of the tetroxide equilibrium (1) above. As a result, the addition of dinitrogen trioxide to the tetroxide will give rise to a higher proportion of NO_2 molecules in the medium, and in consequence a greater concentration of NO^+ and NO_3^- ions. This may be compared with the reverse reaction which can be observed in solutions of dinitrogen tetroxide in pure nitric acid. Goulden (Ph.D. Thesis, London, 1949) found that addition of potassium nitrate to such solutions resulted in an increase of yellow colour in the solution. This coloration was attributed to the presence of nitrogen dioxide, and the increase in colour to a shift in the equilibrium $NO^+ + NO_3^- \rightleftharpoons 2NO_2$ towards the right-hand side on addition of potassium nitrate.

Further evidence for this mode of action of the trioxide is provided by the linear relation between the rate of reaction and the square root of the trioxide concentration. Direct participation by the trioxide in the reaction might have been expected to involve a relation between reaction rate and some power (1, 2, or 3) of the trioxide concentration (as occurs in the nitrosyl chloride reaction described in the following paper). A square-root relationship is unusual, and is more readily explained on the assumption that it is this power of the concentration which is related to (say) the concentration of ions in the medium.

At the higher temperatures we may regard the reaction between a dinitrogen trioxide molecule and a zinc atom as involving the fission of the N–N bond, followed by reaction between zinc and the nitrogen dioxide so produced. This second stage is identical with that considered to occur with the tetroxide, but since the N–N bond in the trioxide is weak, then the sum of the energies required to break first the N–N bond in the trioxide molecule, and secondly the N–O bond in the NO_2 molecule produced, will be less than the corresponding total energy for the tetroxide molecule. In consequence, the energy of activation for the $Zn–N_2O_3$ reaction will be less than that for the $Zn–N_2O_4$ reaction, which leads directly to an increase in the rate of reaction. Such a mechanism results in the formation of the same final product as in the case of the tetroxide.

In view of the above, it is clearly unnecessary to seek a mechanism which is peculiar to the trioxide (in addition to those believed to occur in the pure tetroxide) in order to explain the identity of the reaction products or the higher rates of reaction.

EXPERIMENTAL.

Preparation of Dinitrogen Trioxide–tetroxide Mixtures.—When nitric oxide was bubbled through liquid dinitrogen tetroxide at −5° the rate of absorption was slow; when using about 10 ml. of the liquid tetroxide at this temperature, it was necessary to bubble the nitric oxide for several hours to prepare a mixture containing 5—10% of dinitrogen trioxide. Although it is probable that the absorption of nitric oxide is greater at lower temperatures, the lower limit of temperature is set by the freezing point of the tetroxide (−11·2°). A sufficient concentration range was not therefore readily available by this method. Methods of preparation involving nitric acid (or dilute sulphuric acid) were undesirable in the present work because of the moisture carried with the evolved gases, and the consequent difficulty in eliminating moisture from the liquid product. The mixtures used in the reactions with metals and in conductivity measurements were therefore prepared from concentrated sulphuric acid and solid sodium nitrite as follows. About 250 g. of sodium nitrite were contained in a 500-ml. flask fitted with a dropping funnel containing concentrated sulphuric acid. The acid was added to the nitrite at the rate of approx. 1 ml. per minute, and the evolved mixture of nitric oxide and dinitrogen tetroxide gases was passed through a series of drying tubes (equivalent to a tube 1·5 m. long and 2 cm. in diameter) packed with asbestos wool and phosphoric oxide. The dry gas mixture was passed into a condenser similar to that shown in Fig. 1(a) of Part II (*J.*, 1949, S 218), kept at −40° in a solid carbon dioxide–alcohol bath, an ink-blue condensate being obtained. Under these conditions the liquid product contained about 75% of dinitrogen trioxide, and was prepared at the rate of about 15 ml. per hour. More dilute solutions of the trioxide were obtained when required by dilution of the above mixture with pure tetroxide.

Analysis of Mixtures.—Because of the unstable nature of dinitrogen trioxide–tetroxide mixtures, it was essential to use a method of analysis sufficiently rapid to be completed within a few minutes of the time when the mixture was being used. In the reactions with metals and in conductivity measurements it was also desirable to analyse the mixture before, and immediately after, the experiment in order to confirm that no appreciable decomposition had taken place. Withdrawal of samples of the mixtures for chemical analysis involved considerable practical difficulties, and the volatility of the liquid gives rise to appreciable experimental errors in such a technique. For present purposes the composition of the mixture was available with sufficient accuracy from its m. p., which was determined from warming curves as described in Part II (*loc. cit.*). The liquidus curve given by Baum and Roberts (*Compt. rend.*, 1919, **169**, 968) was used. These authors quote a value of −11·5° for the f. p. of pure liquid dinitrogen tetroxide. Wittorf (*Z. anorg. Chem.*, 1904, **41**, 85) records this freezing point as −10·0°. However, when corrections are made for these deviations from the true value (−11·2°), the two liquidus curves for trioxide–tetroxide mixtures are in close agreement.

The thermometers used were calibrated by using a series of standard liquids, *viz.*, water, liquid dinitrogen tetroxide, carbon tetrachloride, mercury, chlorobenzene, and chloroform. The error in f. p. determinations did not exceed 0·2°, which is equivalent to a maximum error in the trioxide concentration of 0·1—0·4%, depending on the slope of the liquidus curve over the concentration range.

Stability of Mixtures.—In order to determine appropriate experimental conditions under which the dinitrogen trioxide–tetroxide mixtures would be stable during the 15-minute immersion periods employed for the measurement of reaction rates, the stability of these mixtures has been determined over a range of temperature and concentration. The full curves in Fig. 2 show the rate of decrease in trioxide concentration at three temperatures. In each case the same original mixture containing 73% of trioxide (prepared as above) was used. 20 Ml. of the mixture were contained in a reaction tube similar to that described in Part VIII (*loc. cit.*) and was stirred at a rate of 250 r.p.m., the stirrer being a glass stirrup similar in dimensions to the zinc block used in the measurement of reaction rates. At −10°, solutions containing up to about 70% of trioxide were stable for long periods, the trioxide concentration varying by not more than 0·05% in 15 minutes. At 0°, solutions containing more than 40% of trioxide changed rapidly in concentration. In the 0—40% concentration range, the trioxide concentration changed at rates up to 0·5% in 15 minutes; 0° was a convenient temperature at which to determine the rates of reaction with zinc, and therefore the results recorded in Fig. 1 were obtained at this temperature and were restricted to the 0—40% concentration range. At +10°, solutions containing more than 20% of trioxide were unstable.

The broken curve shows the rate of decrease in trioxide concentration at 0° in the absence of stirring. Comparison with the corresponding rates for stirred solutions shows that stirring has not a considerable effect on the rate of decomposition, and reduces the trioxide concentration at which mixtures may be regarded as stable at this temperature by only about 5%.

Period of Immersion.—The influence of time of immersion is shown below. There is a linear relation between the loss in weight of zinc and the period of immersion, so that for periods up to 15 minutes the rates recorded in this table (and in Fig. 1) are regarded as true rates of reaction. The rates of reaction were measured precisely as described in Part VIII (*loc. cit.*); stirring rates of 250 r.p.m. were employed throughout, since under these conditions the rate of reaction was independent of stirring rate.

(N_2O_3 concentration, 39·0%.)

Period of immersion at 0° (mins.)	7	10	15
Loss in weight of zinc (g. × 10^{-4}/cm.^{2})	8·5	12·1	18·1

Density of Mixtures.—In calculating the concentration of dinitrogen trioxide in the mixture in g.-mol./l. units, the values for the density of the trioxide given by Geuther (*Annalen*, 1888, **245**, 96) were used.

Electrical Conductivity.—Specific conductivity values of the order of 10^{-8} ohm^{-1} cm.$^{-1}$ and above recorded on p. 2840 were determined by using a Mullard Measuring Bridge Type G.M. 4140/1, in conjunction with a Mullard Cell Type G.M. 4221. The cell was adapted as described in Part VI (*J.*, 1951, 1303), and a thermometer was incorporated in such a way that the bulb was immersed in the liquid near the electrodes. The conductivity of the 8·8% trioxide solution was obtained by using the condenser method described in Part III (*loc. cit.*).

Product of Reaction.—The product was obtained by immersing a block (about 5 g.) of A.R. zinc in about 15 ml. of 70% (wt./wt.) dinitrogen trioxide in dinitrogen tetroxide, contained in a 10 × 1·5 cm. tube fitted with a B.14 ground-glass joint and a phosphoric oxide guard tube, so that the gas space in the tube was kept dry and at atmospheric pressure. The contents of the tube were kept at −5° for about 10 hours, during which approximately 0·5 g. of product formed. During this period the initial volume of liquid was maintained, by the addition of further quantities of the liquid, although its trioxide content decreased to about 40%. The zinc block was then removed, the liquid decanted in a closed system, and the temperature allowed to rise to about 20°. On evaporation of the adhering liquid, the product remained as a finely-crystalline white powder.

Analysis of Reaction Product.—In the hydrolytic method, approximately 0·5 g. of product was sealed into a glass phial. The phial was immersed in a stout glass bottle containing an excess of 0·1N-sodium hydroxide solution, and the minimum of air space, and was broken by shaking. The nitrite content of the resulting solution was determined by using standard potassium permanganate solution. It was observed that if there was any appreciable volume of air in the bottle above the solution, an acid spray formed in the air space; the estimated nitrite content was then low, owing to atmospheric oxidation of the nitrous acid in the spray.

Reactions with Sodium.—A piece (approx. 1 g.) of clean sodium was added to 20 ml. of a 70% solution of dinitrogen trioxide in the tetroxide. A reaction (more vigorous than with the tetroxide alone) ensued, and the metal became coated with a layer of white solid. The liquid was decanted, and the solid remaining was freed from oxides of nitrogen under slightly reduced pressure. The reaction product separated from the remaining sodium metal, was dissolved in dilute sodium hydroxide solution. This solution was found to contain sodium nitrate only; the complete absence of nitrite was confirmed by chemical methods, and from the ultra-violet absorption spectrum.

About 1 g. of pure sodium nitrite was added to 20 ml. of a solution of 40% dinitrogen trioxide in the tetroxide. After 10 hours the solid was freed from oxides of nitrogen, and analytical methods similar to those referred to above confirmed that the sodium nitrite was recovered unchanged.

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[*Received, May 3rd,* 1951.]