629. *The Liquid Dinitrogen Tetroxide Solvent System. Part VIII.* Rates, and Possible Mechanisms, of Reaction of Zinc with Liquid Dinitrogen Tetroxide.*

By C. C. Addison and J. Lewis.

Experimental conditions are described under which the measured rate of reaction between dinitrogen tetroxide and zinc metal is considered to be uninfluenced by diffusion, passivity, or products of reaction, and thus to represent the true rate of chemical reaction. Under these conditions, reaction rates have been determined over the available liquid temperature range (−11·2° to 21·3°). These rates are considered in the light of the possible active species. Two mechanisms of reaction appear to operate. Below 14° the predominant reaction is attibuted to the $[NO^+][NO_3^-]$ ion-pairs ($E_A = 4500$ cals.); above 14° the reaction ($E_A = 26,000$ cals.) is considered to involve the fission of the N–N bond at the zinc surface, followed by reaction between zinc and nitrogen dioxide to give zinc oxide. This rate-determining step is followed by further reaction of the zinc oxide to give the compound $Zn(NO_3)_2,2N_2O_4$.

Liquid dinitrogen tetroxide is known to contain a small quantity of nitrogen dioxide, the concentration depending on the temperature. In order to account for the difference between molar polarisation and molar refraction in the liquid, the presence of $[NO^+][NO_3^-]$ ion-pairs has been postulated in Part IV (*J.*, 1951, 1294). Alternatively, this difference could be attributed to $[NO_2^+][NO_2^-]$ ion-pairs. In addition to the undissociated molecules, the liquid therefore contains, or can give rise to, a number of species, some or all of which may take part in the reactions between liquid dinitrogen tetroxide and metals. In consequence, a large number of mechanisms is theoretically possible.

The study of reaction mechanism gains further significance from the fact that the structure of the dinitrogen tetroxide molecule has now been shown by Broadley and Robertson (*Nature*, 1949, **164**, 915) to be (I) in the solid state. It is to be presumed that this structure is predominant in the liquid state also, yet it is this particular structure which is least readily reconciled with the ionic reactions of liquid dinitrogen tetroxide. Direct reaction between zinc metal and the

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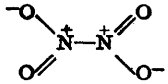

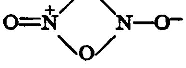

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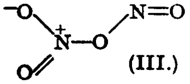

(III.)

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* Part VII, preceding paper.

tetroxide molecule (I) to give zinc nitrate and nitric oxide involves an unlikely atom transfer across the weak N–N bond, whereas either of the structures (II) (Longuet-Higgins, *Nature*, 1944, **153**, 408) or (III) (Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 271) would require electron transfer only in these reactions.

The present paper is concerned with the deductions regarding mechanism which can be made from a study of the influence of temperature on reaction rates; consistently with the above, the experiments suggest that the undissociated molecule does not, in fact, take part directly in reaction with metals in such a way as to involve atom transfer.

Experimental.—Zinc blocks. Zinc metal (A.R.; arsenic free) was cast into rectangular blocks measuring approximately 0·6 × 0·6 × 2 cm., weight 5 g., surface area 5 cm.^{2}. The surfaces of the block were smooth, and the surface area could therefore be determined with accuracy by micrometer measurement of the block dimensions.

Reaction tube. A hole, approx. 2 mm. in diameter, was bored through the zinc block, and the block, held on a glass hook formed on the end of a glass rod, was suspended in 15 ml. of liquid dinitrogen tetroxide [prepared as described in Part II (*J.*, 1949, S 218)] contained in a 12 × 2·5 cm. Pyrex-glass tube. The tube was fitted with side arm (for venting) guarded by phosphoric oxide; the glass rod carrying the zinc block was attached tightly into a Quickfit Type ST 4/2 stirrer gland, which fitted the B.24 ground joint on the reaction tube. The small area of stirrer-gland metal which was exposed to the tetroxide vapour inside the reaction tube was prevented from contaminating the tetroxide by a thin coating of silicone grease. The stirrer gland was connected to an electric motor, which was so geared that the zinc block could be rotated at speeds up to about 300 r.p.m. The reaction tube was immersed, to within 2 cm. of its top, in a thermostat.

RESULTS AND DISCUSSION.

Preliminary Study of Conditions influencing Reaction Rates.—(a) *Condition of surface.* The method used to prepare the metal surface for reaction with the tetroxide has a considerable influence on reaction rates; typical observations are collected in Table I, and throughout the experiments discussed below the zinc surface was prepared for reaction by method (4), Table I.

TABLE I.

Treatment of surface.	Rate of loss of zinc (unstirred) (g. × 10^{-4}/cm.^{2}).		
(1) Exposed to atmosphere for long period or heated for short period (*e.g.*, at 150° for 20 mins.)	Scarcely detectable		
(2) Acid-washed; zinc immersed in 2N-HCl for 10 mins., washed with water, alcohol, ether, and dried in vacuum desiccator	5·3 (10 mins. at 18°)	3·2 (1 hour at −11°)	7·8 (1 hour at 15°)
(3) Alkali-washed; as for (2) but 2N-HCl replaced by 5N-NaOH	7·1 (10 mins. at 18°)	4·2 (1 hour at −11°)	13·8 (1 hour at 15°)
(4) Surface freshly filed, washed with water, alcohol, ether, dried in vacuum desiccator	Results similar to (3) above		

(b) *Rate of stirring.* The measured rates of a heterogeneous reaction involving solid–liquid interfaces may (i) represent the true reaction rate, or (ii) reflect (in systems inadequately stirred) the rate of diffusion of reaction products from the surface. The rates of reaction of zinc have therefore been determined over a range of stirring rates, and the results are shown in curve *A* (Fig. 1). Each experimental point represents the quantity of zinc lost from 1 cm.^{2} of surface on immersion in dinitrogen tetroxide at 17° for 15 minutes. Above a stirring rate of about 40 r.p.m., the rate of loss of zinc remained constant at rates up to 300 r.p.m. This is considered to indicate that at stirring rates greater than 40 r.p.m. the measured rate is a true rate of chemical reaction and is not influenced by any diffusion process. All reaction rates discussed below were measured with stirring rates of 250 r.p.m.

(c) *Influence of reaction products.* In most heterogeneous reactions cited in the literature, the products of reaction have no further chemical action in the system; their only effect is to hinder physically the initial reaction, and therefore to reduce the reaction rate. In consequence, stirring results in an increase in rate of reaction. In the present system, the reverse is the case; as the stirring rate is increased over the range 0—40 r.p.m., the rate of reaction shows an appreciable decrease. The reaction taking place is $Zn + 4N_2O_4 = Zn(NO_3)_2,2N_2O_4 + 2NO$. Although much of the nitric oxide produced is evolved as such, a proportion is retained in the liquid as dinitrogen trioxide. A separate investigation (Part IX, following paper) has shown that dinitrogen trioxide, in solution in the tetroxide, reacts with zinc at a greater rate than does the liquid tetroxide alone. The higher rate of reaction in the unstirrred system (Fig. 1, curve *A*) is therefore attributed to the accumulation of the more active trioxide in the immediate neighbourhood of the surface. Stirring leads to the dispersion of this accumulated trioxide throughout the bulk of the tetroxide, and consequently results in a decrease in the rate of reaction. The rate of reaction represented by the level portion of curve *A* may be regarded as typical of dinitrogen tetroxide alone, since the concentration of the trioxide, when dispersed throughout the volume of tetroxide used, has been shown to be insignificant over the time ranges employed. For example, the highest reaction rates (Fig. 2, curve *B*) are equivalent to the production of 0·01 g.-mol./l. of trioxide, all the nitric oxide produced being assumed to be converted into trioxide. This concentration is without detectable influence on reaction rates (Part IX, following paper). In this connection it is of interest that if solutions are used in which the concentration of dinitrogen trioxide produced is sufficiently high to influence the reaction rate, this rate may be appreciably decreased by bubbling a gentle stream of oxygen over the surface of the metal.

In many solid–liquid reactions in which diffusion is considered to influence the reaction rate (*e.g.*, King and Braverman, *J. Amer. Chem. Soc.*, 1932, **54**, 1744; Bircumshaw and Riddiford, *J.*, 1951, 598), the products of reaction are soluble in the liquid phase, and the rate of reaction is influenced by the rate at which molecules of the active species can diffuse through that region, in immediate contact with the surface, containing a high concentration of dissolved reaction product. Again, the active species (*e.g.*, acid or iodine) is chemically independent of (and is not formed by dissociation of) the aqueous medium. In the zinc–dinitrogen tetroxide reaction different conditions are involved. There is no concentration gradient in the neighbourhood of the surface, since the reaction product $Zn(NO_3)_2,2N_2O_4$ is insoluble in the tetroxide, and the dinitrogen trioxide is readily dispersed by stirring; the active species may be either the tetroxide molecules themselves or the dissociation products with which they are in equilibrium. Therefore provided that the liquid medium has unhindered access to the surface, there is no diffusion mechanism which can operate. With certain metals (*e.g.*, sodium) the rate of reaction falls rapidly with time of contact, ultimately reaching negligible proportions. This may be attributed directly to the cohesive nature of the film of sodium nitrate produced in the reaction. In the case of zinc, however, the reaction product is readily detached from the surface; the rate of reaction is constant, under standard conditions, during the first 15 minutes, and the reaction will continue indefinitely. Experimental observations therefore indicate that the liquid has unhindered access to the surface, and in consequence the diffusion processes which must be considered in many heterogeneous reactions have no application in the present system.

FIG. 1.

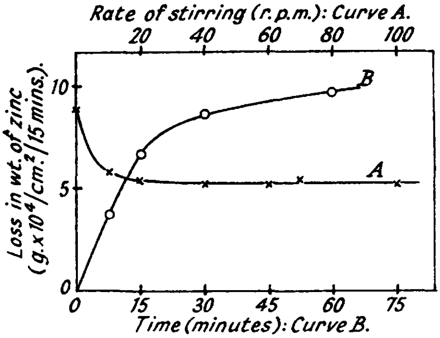
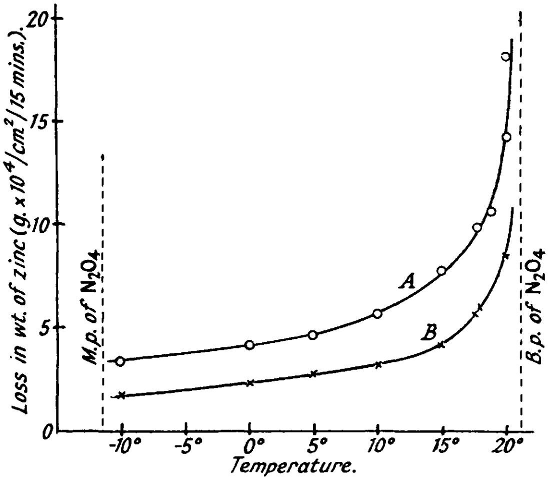


FIG. 2.



(d) *Period of immersion.* Curve *B* (Fig. 1) shows the change in the rate of reaction of zinc for various periods of immersion. The experimental points shown were obtained at 18·5°, and a stirring rate of 250 r.p.m. During the first 15 minutes there is a linear relation between the amount of zinc reacting and the time of immersion. Thereafter the rate of attack diminishes; this is attributed to the development of passivity by the zinc. Periods of 15 minutes' immersion have been employed throughout in the determination of temperature coefficients; the loss in weight of the zinc (and the accuracy of measurement) is thus the maximum available experimentally if interference from passivity effects is to be avoided.

Influence of Temperature on Rate of Reaction.—The experiments described above show that the optimum conditions for the determination of true rates of reaction in this system involve (1) a high stirring rate (250 r.p.m.), (2) a short period of immersion (15 minutes), (3) a volume of tetroxide sufficiently large that the concentration of trioxide produced is negligible (15 ml.), and (4) a freshly filed surface. Under these experimental conditions, the variation of reaction rate with temperature has been studied, and the results are shown in curve *B* (Fig. 2). Over the major portion of the temperature range the temperature coefficient is small, but increases rapidly near the b. p. of the liquid. It is of interest that, although variations in experimental conditions influence the magnitude (and the accuracy of determination) of the reaction rate, the general form of the curve is maintained. For example, the experimental points shown on curve *A* were obtained without stirring, zinc being used which had been given a preliminary acid wash, and the loss in weight of the zinc block was determined during one hour's immersion. Although these conditions vary widely from the ideal conditions, the general shape of curve *A* closely resembles that of *B*.

FIG. 3.

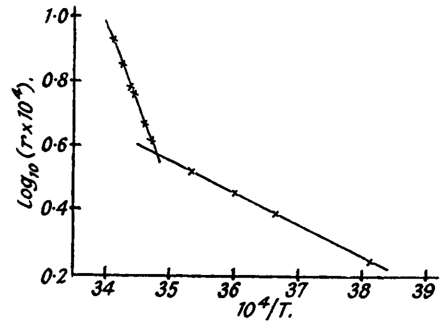


FIG. 4.

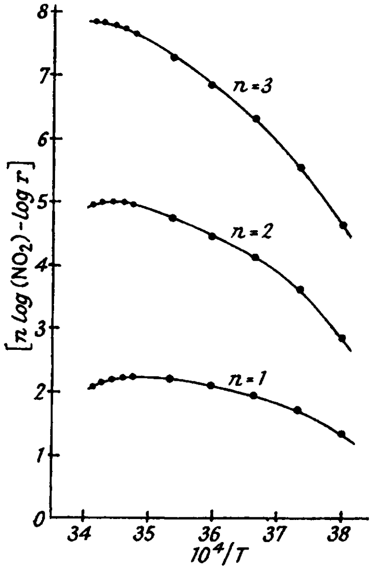


Fig. 3 shows the relation between $\log_{10} r$ [where r is the rate of reaction of zinc (g./15 mins.) per cm.^{2}] and the inverse of the absolute temperature. If it is assumed, as a first step, that r is proportional to the velocity constant k, then since $k = Be^{-E/RT}$, it appears from Fig. 3 that two distinct mechanisms of reaction are operating within the liquid temperature range. The true relationship between the rate of reaction and k is given by an equation of the form :

$$\text{Rate of reaction} = k\,[\text{Zn}][\text{X}]^n$$

where X represents the active species. If the zinc loss is expressed per unit area, then the term [Zn] may be eliminated and therefore

$$\log r = -E/\boldsymbol{R}T + n \log [\text{X}] + A \quad \ldots\ldots \quad (1)$$

where A is a constant.

The points recorded in Fig. 3 appear to lie on two straight lines; this would imply that the concentration of the active species remains virtually constant over the temperature range, *i.e.*, for both mechanisms. However, it is not possible to dismiss, without further consideration, the possibility that the points should be regarded as falling on a continuous curve. It is clear from Fig. 3 and equation (1) that such a continuous curve could only arise if the concentration of the active species varies considerably with temperature. Of the available species, the concentration of the N_2O_4 molecules may be regarded as constant, since the degree of dissociation into NO_2 molecules is very small in the liquid phase (Sone, *Tohoku Imp. Univ. Sci. Rep.*, 1922, **11**, 139) and the concentration of ion-pairs (Part IV, *loc. cit.*) is negligible with respect to the tetroxide present. The concentration of ion-pairs is a function of the absolute temperature only (Part IV), and is thus not sufficiently variable to produce the observed effects over the full range of temperature. Molecules of NO_2 form the only species present whose concentration does vary considerably with temperature, and the experimental results have therefore been considered from the point of view that NO_2 may be the active species. Fig. 4 shows the relation between $[n \log [NO_2] - \log r]$ and $1/T$ for possible values of n (*i.e.*, 1, 2, and 3). The concentration values for nitrogen dioxide were interpolated, where necessary, from the values given by Sone (*loc. cit.*), which are as follows :

Temperature	−16°	0°	7·2°	11·2°	20°
Nitrogen dioxide, %	0·0	0·15	0·29	0·37	0·72

If an NO_2 mechanism operates, then the points shown in Fig. 4 for one of the values of n should lie on a straight line, with a positive slope. This condition is not fulfilled, and it is deduced that the free NO_2 molecules take no part in the reaction between zinc and liquid dinitrogen tetroxide. This conclusion is without prejudice to the mechanism postulated below, which involves only those NO_2 molecules produced by fission of N_2O_4 molecules of higher activation energy at the zinc surface.

In consequence of the above, the results shown in Fig. 3 are regarded as falling on two straight lines; two distinct mechanisms therefore operate, with a demarcation temperature of 14°.

Low-temperature Mechanism.—From the slope of the straight line concerned, it may be calculated that the activation energy for this reaction is about 4500 cals. The two alternative mechanisms to be considered for this temperature range are (*a*) direct reaction of zinc with the tetroxide molecule, and (*b*) the reaction between zinc and the ion-pairs, since the concentration of ion-pairs over this concentration range varies so little as to involve the results in Fig. 3 in an inappreciable deviation from linearity. Mechanism (*a*) is considered to be the less attractive; it is difficult to envisage a reaction which must involve the breaking of N–O or N–N bonds, but at the same time involves an activation energy of this low order, particularly since it has been shown that the N–N bond, the weakest bond in the N_2O_4 molecule, has an energy of 12,800 cals. (Giauque and Kemp, *J. Chem. Physics*, 1938, **6**, 40). On the other hand, the observed activation energy of 4500 cals. is of the same order as the apparent energy of activation (4230 cals.) for the reaction between zinc and aqueous solutions of hydrochloric acid (Moelwyn-Hughes, "Kinetics of Reaction in Solution," O.U.P., 1947, p. 372), which may be assumed to involve zinc–proton electron transfer. Although diffusion is a controlling factor in this zinc–acid reaction, the diffusion barrier will reduce the rate of reaction, so that the true energy of activation for the reaction will be even less than the apparent value of 4230 cals. James (*J. Amer. Chem. Soc.*, 1943, **65**, 39) obtained the value $E_A = 5000$ cals. for the magnesium–hydrochloric acid reaction, where the rate-controlling step is electron transfer at the metal surface rather than diffusion.

It is therefore considered that the most probable mechanism operative over the low-temperature range involves an electron-transfer reaction between the zinc metal and the ion-pairs. These ion-pairs may be of the form $[NO^+][NO_3^-]$ or $[NO_2^+][NO_2^-]$. On the latter alternative, reaction with metals should produce a metal nitrite as a final, or at least an intermediate, product of reaction. It is significant that no metal–dinitrogen tetroxide reactions yet studied have given even a trace of nitrite in the product. Nitrite is also an improbable intermediate, since sodium nitrite has been found to be entirely unchanged after several weeks in contact with liquid dinitrogen tetroxide. Although a direct analogy between sodium and zinc nitrite may not be fully justified (and anhydrous zinc nitrite is unknown in the solid state), the available chemical evidence does not support a structure $[NO_2^+][NO_2^-]$ for the ion-pairs, and the low-temperature mechanism is therefore considered to be $Zn + 2[NO^+][NO_3^-] = Zn[NO_3]_2 + 2NO$.

High-temperature Mechanism.—From the slope of the straight line concerned, the energy of activation is approximately 26 kcals. This is higher than the activation energy normally associated with simple electron-transfer processes. Since the active species is again independent of temperature, the reaction at higher temperatures appears to arise primarily from the dinitrogen tetroxide molecules themselves. The reaction results in the formation of nitrate, and must therefore involve the breaking of more than one of the bonds concerned. A value of $E_A = 26$ kcals. is consistent with such a process; Giauque and Kemp (*loc. cit.*) have shown that for the reaction

$$N_2O_4 = 2NO_2, \qquad \Delta H = 12{,}873 \text{ cals.}$$

and for

$$NO_2 = NO + \tfrac{1}{2}O_2, \qquad \Delta H = 13{,}562 \text{ cals.}$$

It is considered improbable that the reaction occurs in a single stage, since the nature of the products involves the fission of more than one bond in the N_2O_4 molecule. Structure (I) being assumed for the tetroxide molecule, the first bond to be broken (presumably the weaker N–N bond) would again lead to the unlikely formation of nitrite as product if a single stage $Zn + N_2O_4 \longrightarrow Zn(NO_2)_2$ operated.

Present experimental evidence is in agreement with the following postulated mechanism : (1) The impact of the N_2O_4 molecules at the metal surface results in the fission of the N–N bond to give two NO_2 units. (2) For those N_2O_4 molecules possessing the requisite initial energy, the NO_2 units produced are sufficiently activated to react with the metal as follows : $Zn + NO_2 = ZnO + NO$. (3) The zinc oxide reacts with dinitrogen tetroxide as follows : $ZnO + 4N_2O_4 = Zn(NO_3)_2,2N_2O_4 + N_2O_3$.

Reaction (3) is known to proceed readily, and stages (1) and (2) above are considered to be the rate-determining steps.

The available temperature range over which dinitrogen tetroxide is in the liquid state necessarily restricts any kinetic studies to a narrower temperature range than would otherwise be desirable. However, the mechanisms postulated above are in accord with all experimental evidence now available, and form the theoretical basis on which reactions with other metals will be studied.

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[*Received, March* 19*th*, 1951.]