758. *The Rates of Reaction of Copper, Zinc, and Uranium with Organic Solvent–Dinitrogen Tetroxide Mixtures.*

By C. C. Addison, J. C. Sheldon, and (in part) N. Hodge.

The rate of reaction between metals and liquid dinitrogen tetroxide is increased considerably when the tetroxide is mixed with certain organic solvents; this is illustrated by measurements with copper, zinc, and uranium. Solvents which act as electron-donors (Don) to the tetroxide set up the equilibrium $[(\mathrm{Don})_n,\mathrm{NO}^+]\mathrm{NO}_3^- \rightleftharpoons n(\mathrm{Don}) + \mathrm{N}_2\mathrm{O}_4 \rightleftharpoons (\mathrm{Don})_n,\mathrm{N}_2\mathrm{O}_4$, in the liquid state, and the enhanced reaction reflects the increase in concentration of ionic species. Rates of reaction with the oxygen-donor solvents diethyl ether, ethyl acetate, dioxan, and acetic anhydride, the nitrogen-donor solvents phenyl cyanide, benzyl cyanide, methyl cyanide, and diethylnitrosamine, and the non-donor solvent nitromethane are reported over the full liquid concentration range. The variation of reaction rate with concentration has been classified into three types, and each type is interpreted in terms of the dielectric constant of the liquid, the concentration of simple NO^+ ions or complex $(\mathrm{Don})_n,\mathrm{NO}^+$ ions, the relative powers of the solvent and the NO_3^- ion to act as desorbing agent for the metal cation formed on initial reaction at the metal surface, and the minimum stable valency of the metal. The activation energy of the reactions has been determined. Stirring influences the speed of the reaction, but not its type or activation energy.

The chemical and physical properties of liquid dinitrogen tetroxide are profoundly modified in the presence of solvents whose molecules can act as electron-pair donors.[1-3] This is attributed to the formation of addition compounds, which may be molecular or ionic in character. The equilibrium in the liquid state between dinitrogen tetroxide and donor solvent (Don) is represented by:

$$[(\mathrm{Don})_n,\mathrm{NO}^+]\mathrm{NO}_3^- \rightleftharpoons n(\mathrm{Don}) + \mathrm{N}_2\mathrm{O}_4 \rightleftharpoons (\mathrm{Don})_n,\mathrm{N}_2\mathrm{O}_4$$

Since the ionic and the molecular form of the complex are very different structurally, and since the ionic form can be most easily produced from the molecular form by the dissociation of the latter into its components, we do not consider there to be any direct equilibrium between the ionic and the molecular form of the addition compound. Many of the physical properties of the mixtures (freezing point, viscosity, deviation of vapour pressure from ideality, modification of the absorption spectrum of dinitrogen tetroxide) result from the presence of the molecular complex. It is quite clear from a survey of the properties of the mixtures (including electrical conductivity) that the ionic form of the complex is present in very small proportion, and can often be ignored; it does, however, play the important role in the reaction of these mixtures with metals. Under appropriate conditions the reaction rates with metals reflect the ionic concentration in the medium, but not necessarily the total degree of compound formation. Since there are two electron-deficient species (NO^+ and $\mathrm{N}_2\mathrm{O}_4$), a change in the structure of the solvent may not influence the two equilibria shown above to the same extent, so that a list of solvents drawn up in order of donor strength according to the chemical reactivity of the mixture need not agree precisely with

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[1] Addison and Sheldon, *J.*, 1956, 1941.
[2] *Idem, J.*, 1956, 2705.
[3] *Idem, J.*, 1956, 2709.

one drawn up on the basis of a physical method which takes into account the molecular form of the addition compound also.

This investigation was carried out for two main reasons. First, very few studies of rates of solution of metals in non-aqueous media have been attempted. This is perhaps because diffusion of reactants to (or products from) the surface can play such a predominant rate-determining role as to prevent interpretation of the results in terms of reaction mechanism. In the systems described here, diffusion is less important and it has been possible to define some general features which may be typical of other metal–non-aqueous media reactions. Secondly, many of these reactions result in the formation of new compounds, and a knowledge of the factors controlling reaction rates aids in the selection of new preparative methods. (The products of reaction will be described in later papers.)

Solution rates have been measured for copper, zinc, and uranium. Copper was selected because it has a stable univalent state; zinc because it shows bivalency only, and its rates of reaction with pure dinitrogen tetroxide are known.[4] A limited number of measurements on uranium (carried out by Dr. N. Hodge in this laboratory) are included to show the influence of the higher valency states. Few metals react at a perceptible rate with the pure tetroxide, but mixtures with donor solvents react rapidly with many metals (including cobalt and manganese). Iron, nickel, and chromium and their alloys remain inert, and are thus useful constructional materials in the handling of these mixtures.

Typical Reaction Rate–Composition Curves.—These are shown in Fig. 1. Copper does not react with dinitrogen tetroxide or with diethyl ether, yet reaction is vigorous with the mixture, which clearly contains some reactive species. The rates (curve *D*) pass through a very sharp maximum. The position of the peak on the composition axis varies with the donor solvent and does not coincide with any particular N_2O_4 : solvent molecular ratio. The zinc curve (*F*) is similar in shape; the rate curve follows that for copper at high tetroxide concentrations (curves *E* and *F*) but the rapid increase in rate with addition of ethyl acetate is arrested sooner. The following experiments were carried out to determine the factors responsible for this unusual behaviour.

Reaction with Nitromethane Mixtures.—The N_2O_4 molecule ionises into NO^+ and NO_3^- in media of high dielectric constant.[5] Before attempting to interpret the rate curves with donor solvents, it is necessary to determine the manner in which metals react with the ionised tetroxide, since the simplest mechanism of reaction involves direct electron transfer from the metal atom to the NO^+ ion, with evolution of nitric oxide. Nitromethane (ε 37) is a suitable solvent for this purpose as it does not form an addition compound with dinitrogen tetroxide.[6] The broken line (Fig. 2) traces the variation in electrical conductivity of the mixtures with composition. The conductivity of the tetroxide increases on addition of nitromethane owing to enhanced ionisation, reaching a maximum near 90 mol.% of nitromethane.[6] Thereafter we may assume that the dielectric constant of the mixture does not change appreciably; the degree of ionisation is not further increased, and the fall in conductivity is due to dilution of the ions. The reaction rate curve for copper with this mixture is of the same form, and its peak coincides with the maximum in the conductivity values on the composition axis. The fastest reaction therefore occurs when the number of NO^+ ions is greatest, and the basic reaction is considered to be :

$$Cu + NO^+ \longrightarrow Cu^+ + NO$$

The rate of stirring of the metal in the solution does not alter the shape of the rate curve, or the position of its maximum, but only modifies the actual rate. Since it is therefore of less significance, consideration of the influence of stirring rate is deferred until later in this paper. The simple correlation observed for copper does not hold when the lowest stable valency of the metal exceeds unity. The zinc curve has a shape similar to that for copper, though the maximum is somewhat displaced. The uranium values are magnified in Fig. 2 to show that the maximum in the uranium rate curve bears no relation to the electrical conductivity measurements. In such cases the metal–NO^+ reaction is

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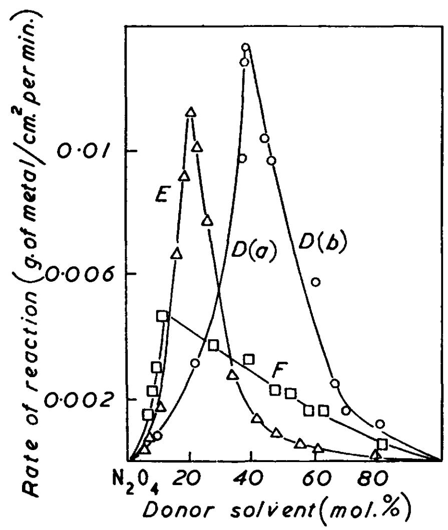
[4] Addison and Lewis, *J.*, 1951, 2833.
[5] Goulden and Millen, *J.*, 1950, 2620.
[6] Addison, Hodge, and Lewis, *J.*, 1953, 2631.

of a higher order, and the interpretations which follow are applied primarily to copper as representing the simplest case.

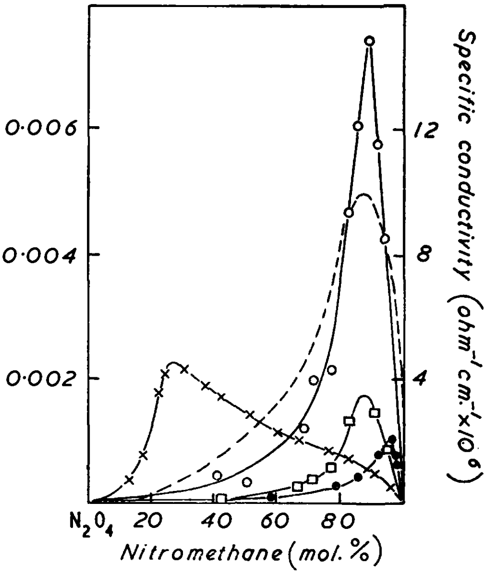
Classification of Systems.—The curves obtained are of three distinct types. Type (1) is shown by the curves for copper in Fig. 2, and is the type obtained when the solvent has no appreciable donor properties but a high dielectric constant; it reflects the concentration of NO^+ ions in the mixture, so that reaction rates in the 0—50 mol. % concentration range of solvent are often very small indeed. Most electron donor solvents give curves of type (2) (Fig. 1). Addition of such a solvent gives rise immediately to $[(Don)_n,NO^+]NO_3^-$ ion pairs; these increase the dielectric constant of the medium, which leads to separation of the ions, and the rapid increase in reaction rate on addition of small quantities of donor solvent indicates that electron transfer from the metal (M) to the complex, *i.e.* :

FIG. 1. *Rates of reaction at* 15° *and* 400 *r.p.m.*



Curve	Metal	Donor solvent
D	Copper	Diethyl ether
E	Copper	Ethyl acetate
F	Zinc	Ethyl acetate

FIG. 2. *Rates of reaction with* N_2O_4*-nitromethane mixtures at* 15°.



—○——○—	Copper : stirring rate 400 r.p.m.
—□——□—	Copper : unstirred.
—●——●—	Zinc : stirring rate 400 r.p.m.
—×——×—	Uranium : stirring rate 350 r.p.m. (the uranium rates shown are magnified by a factor of 50).
— — — — —	Electrical conductivity of mixture.

$$M + (Don)_n,NO^+ \longrightarrow M^+ + n(Don) + NO$$

is possible with many solvents. The greater the donor strength of the solvent with respect to NO^+, the steeper is the initial increase in reaction rate. It might have been expected therefore that reaction rates with donor solvents would greatly exceed those in the presence of non-donor solvents. While this is invariably true at low solvent concentrations, some restrictive effect appears in donor-solvent systems which reduces reaction rate in the 50—100 mol. % solvent-concentration range. The onset of this effect is sudden, giving rise to sharp maxima in the rate curves (Fig. 1, and Figs. 3—5). Most of the solvents studied fall into type (1) or (2). It is of particular interest that a system has been found (copper with methyl cyanide mixtures, Fig. 7) which is of a third type, in which the solvent behaves both as a donor- and an ionising-solvent system.

Oxygen- and Nitrogen-donors.—Rate curves for acetic anhydride mixtures are given in

Fig. 3. They are of the same type (1) as is observed for diethyl ether and ethyl acetate (Fig. 1). No inferences should be drawn from the relative magnitudes of the rates with acetic anhydride mixtures and with the other mixtures reported. In all other mixtures the weight of metal dissolved was proportional to the time of immersion for much longer periods than the half-minute immersion time used; acetic anhydride mixtures were found to be poor solvents for the reaction product, which rapidly separated from solution. The results recorded in Fig. 3 were again obtained from half-minute immersion times, but even within this time the presence of reaction product caused the reaction rate to fall somewhat.

A study of mixtures with 1 : 4-dioxan was of particular significance in view of the unusual stability of the addition compound. This is only possible over narrow concentration ranges, since the 1 : 1 addition compound $C_4H_8O_2,N_2O_4$ crystallises rapidly from mixtures prepared in the 15—85 mol. % dioxan range. Measured rates are given in Table 1. The reaction rates for copper in 0—15 mol. % dioxan solutions lie close to the diethyl ether curve (Fig. 1), and in spite of the high stability of the molecular addition compound the reaction rates again indicate the presence of ionic species in solution.

TABLE 1. *Rates of reaction (g. of metal per cm.² per min.) with dioxan–dinitrogen tetroxide mixtures at* 15° *and* 400 *r.p.m.*

Dioxan (mol. %)	Rate	Dioxan (mol. %)	Rate	Dioxan (mol. %)	Rate	Dioxan (mol. %)	Rate
	Copper				Zinc		
3·4	0·00038	13·5	0·00234	8·2	0·00050	89·6	0·00015
5·5	0·00047	—	—	9·5	0·00055	94·5	0·00008
9·5	0·00085	83	~0·0	12·0	0·00081	—	—
10·6	0·00132	94·5	~0·0				

Some cyanides and nitrosamines give extreme examples of type (2) curves, as shown in Figs. 4 and 5. Because of their relatively stronger donor properties, the presence of higher concentrations of ions $(Don)_n,NO^+$ gives a rapid increase in reaction rate on addition of only a few mol. % of the donor. The restrictive effect also sets in at lower solvent concentration, so that under conditions of stirring the reaction rate is falling continuously throughout the 5—100 mol. % solvent-concentration range. Figs. 4 and 5 show that with nitrogen-donor solvents also, stirring may influence the rate of reaction, and may modify slightly the position of the maximum, but does not influence the type of rate curve obtained.

Reaction Processes.—We will consider first some general aspects of these processes, and then show how they may be used to explain the shapes of the reaction rate curves. The processes by which a metal atom on a metal surface becomes an ion in solution may be divided into two stages: I, an electronic reaction at the metal surface to give a metal cation; and II, the formation of a solvation or co-ordination sphere round the ion, which is necessary before the cation can be removed from the surface into solution. Process I involves the transfer of electrons from the metal to an electron-acceptor in solution; the ions H_3O^+ and I^+ perform this function in the reaction of metals with aqueous acid or iodine solutions, and in the present systems simple (NO^+) or complex $(Don)_n,NO^+$ ions. It is convenient to regard the metal as consisting not of discrete atoms, but as possessing a fund of electrons; each electron removed leaves a metal cation which is adsorbed at the surface by electrostatic attraction. The cation may be desorbed from the surface (process II) if the liquid medium contains molecules or ions which can solvate the cation, thus decreasing this attraction. This process is therefore somewhat analogous to the dissolution of salts in polar solvents.

Cation desorption may therefore be brought about by polar molecules capable of simple solvation only, or more efficiently by molecules or ions able to donate electrons to the metal ion to give a co-ordination complex. Nitrobenzene and nitromethane are typical polar solvating molecules, and have similar dipole moments and dielectric constants. However, nitromethane is the better solvent for ionic compounds and increases the rate of metal–N_2O_4 reactions to a greater extent, indicating that dipole moment in relation to molecular volume is a more satisfactory measure of solvating power than is the dipole moment alone. Since dinitrogen tetroxide has zero dipole moment it is considered to be a weakly solvating species. The only species common to these media which is capable of co-ordination to the metal ions is the nitrate ion. Previous papers [7-9] have given evidence for the existence of nitrato-anions of zinc and uranium in the solid state and in solution in

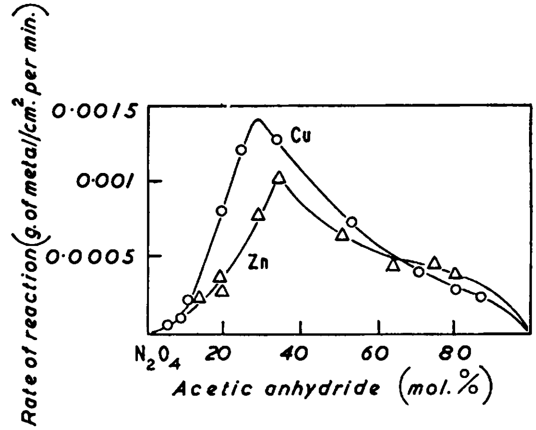
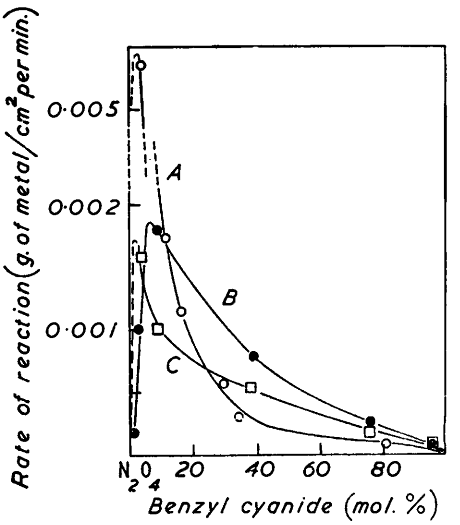


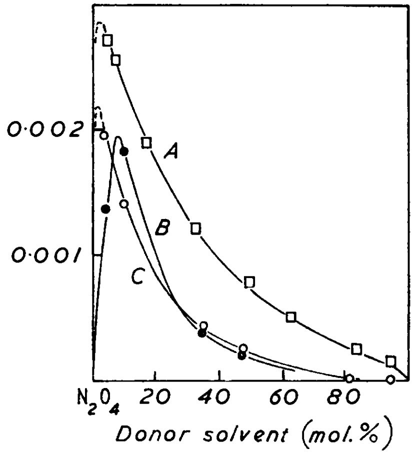
FIG. 3. *Rates of reaction with* N_2O_4*–acetic anhydride mixtures at* 15° *and* 400 *r.p.m.*

FIG. 4. *Rates of reaction in* N_2O_4*–benzyl cyanide mixtures.*



A, Copper, stirring rate 400 r.p.m.
B, Zinc, unstirred.
C, Zinc, stirring rate 400 r.p.m.

FIG. 5. *Rates of reaction of copper at* 15° *with various mixtures.*



A, Diethylnitrosamine mixtures, stirring rate 400 r.p.m.
B, Phenyl cyanide mixtures, unstirred.
C, Phenyl cyanide mixtures, stirring rate 400 r.p.m.

non-aqueous solvents. Desorption of metal ions by nitrate ions would appear to be a favourable process, since co-ordination neutralises the charge on the cation. The concentration of nitrate ions in the bulk liquid phase is unlikely to be sufficient for desorption of metal ions, but it is feasible that the N_2O_4 molecule can ionise in the neighbourhood of the unco-ordinated metal cation as a result of the electrostatic forces at the surface.

Preferential adsorption of one component from the liquid mixture on the metal

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[7] Addison and Hodge, *J.*, 1954, 1138.
[8] Addison, Hodge, and Thompson, *J.*, 1954, 1143.
[9] Addison and Hodge, *Nature*, 1953, **171**, 569.

surface is also an important factor in these processes. Polar solvent molecules will be adsorbed to a greater extent than the non-polar dinitrogen tetroxide. Of the solvents investigated, nitromethane and methyl cyanide have high dipole moments and the smallest molecular volumes. They are therefore excellent solvating agents, and the results reported here may be interpreted satisfactorily on the assumptions that (*a*) desorption involving solvation by these two solvents occurs more readily than by nitrate-ion co-ordination, and (*b*), except for these two solvents, co-ordination by nitrate ions is the fastest means of removing the metal ions from the metal surface.

Interpretation of Reaction Rate Curves.—We may now attempt an analysis of the curves in the light of the principles outlined above.

Type (1). It being assumed that nitromethane, by virtue of its high solvating powers, can remove unipositive metal ions from the metal at least as quickly as they are produced, type (1) represents the simplest system, and the shape of the copper–nitromethane curve (Fig. 2) reflects the concentration of NO^+ ions throughout the concentration range. It is also consistent that stirring of the metal specimen in the solution should influence only the rate at which NO^+ ions reach the surface, and thus the actual reaction rate, without influencing the shape of the curve. Even though zinc is more electropositive than copper, its reaction rate is slower. Zinc ions can leave the metal only in the Zn^{2+} state, and this implies a greater electrostatic attraction between the ion and the metal surface. Since a non-donor molecule such as nitromethane forms a loose solvation cage round the ion, but without direct bonding to it, removal of ions from the surface will be less efficient.

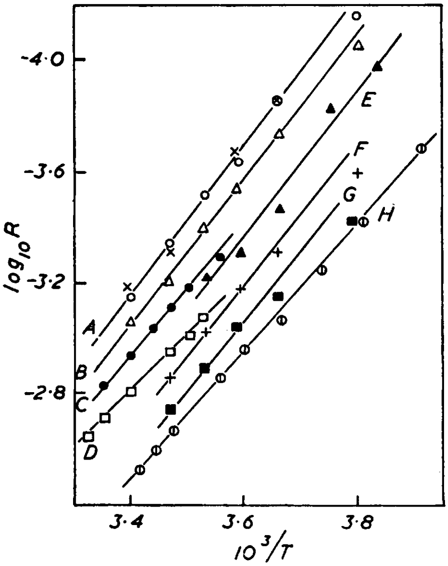
Type (2) (Fig. 1). Consider first section $D(a)$ of curve D, where reaction rate is increasing rapidly with concentration of solvent. The solvents which show type (2) curves are poor desorbing agents for the particular metal cation concerned. The concentration of $(\mathrm{Don})_n,NO^+$ ions will increase with the donor properties of the solvent with respect to NO^+ ions. Reaction rates of copper increase accordingly in the order nitromethane $<$ diethyl ether $<$ ethyl acetate $<$ phenyl cyanide, benzyl cyanide, methyl cyanide, diethyl nitrosamine.

Increase in the concentration of the complex ions will result in a corresponding increase in the reaction rate as long as the metal cations formed can be transferred to the liquid phase with corresponding rapidity. In the presence of these relatively poor solvating liquids desorption of metal ions is carried out by NO_3^- ions. Over section (*a*) of the curve, the dinitrogen tetroxide (and its ionisation products) is assumed to have direct access to the metal surface. The sharp maxima in the curves of this type occur at solvent concentrations much lower than those which represent maximum concentration of reactive ions in the bulk of the liquid. The more polar the solvent, the lower is the solvent concentration at which the maximum occurs; the order of these concentrations is thus broadly the reverse of the list given above. This leads us to suggest that these solvents are preferentially adsorbed at the metal surface, and that the maximum in the rate curve corresponds with the concentration at which the surface is covered by a film of the solvent which is sufficient to restrict severely direct access of the tetroxide. Thereafter [*e.g.*, along section $D(b)$ of curve D, Fig. 1] the concentration of N_2O_4, and therefore of NO_3^- ions for desorption of metal ions will decrease, with a corresponding decrease in reaction rates.

Uranium in nitromethane mixtures gives a type (2) curve (Fig. 2). From its general chemistry it seems likely that uranium reaches the U^{3+} stage before desorption. That nitromethane, which desorbs Cu^+ readily, is unable to desorb U^{3+} is indicated by the very low reaction rate. The maximum in reaction rate which occurs at a low nitromethane concentration is then the result of preferential adsorption of nitromethane at the metal surface which limits access of the only species (NO_3^-) capable of desorbing the more highly charged ion. If reaction took place by the route $U \longrightarrow U^+ \longrightarrow UO^+$, no difficulties in desorption by nitromethane should arise, and a rate curve of type (1) would have been expected.

That the reaction rate is determined by desorption is indicated by two factors. First, it enables the rate curve of type (3) (Fig. 7) obtained with methyl cyanide to be correlated with the curves of type (2) (see below). Secondly, it is supported by the value of the activation energy E for the process operating over section (*b*) of the curve. Rates of reaction R for several mixtures [at concentrations corresponding to section (b)] have been determined over a temperature range. The plots of log R against $1/T$ are shown in Fig. 6; the values of E obtained show little variation (mean, $E = 11$ kcal./mole). This clearly

FIG. 6. *Effect of temperature on reaction rates.*



Plot	Metal	Mixture : N_2O_4 with	Stirring rate (r.p.m.)	E (kcal./mole)
A	Copper	56 mol. % of $CH_3{\cdot}CO_2Et$	× 800 ○ 400	12 12
B	Copper	56 mol. % ,,	Δ Unstirred	12
C	Copper	46 mol. ,,	400	10
D	Zinc	64 mol. % ,,	400	9
E	Zinc	7·1 mol. % of $Et_2N{\cdot}NO$	Unstirred	12
F	Copper	10 mol. % of $Ph{\cdot}CN$	400	12
G	Copper	10 mol. % ,,	Unstirred	12
H *	Uranium	47·5 mol. % of $CH_3{\cdot}NO_2$	350	10

* The rates R recorded on line H are magnified by a factor of 100.

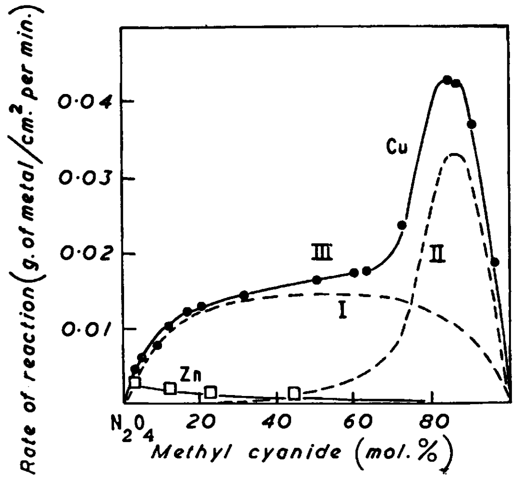
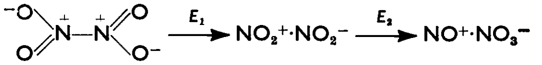
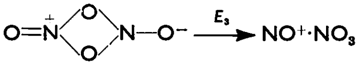


FIG. 7. *Comparison of reaction rates for copper* (III) *and zinc in* N_2O_4–*methyl cyanide with that* (II) *of copper in* N_2O_4–*nitromethane and with the concentration* (I; *arbitrary units*) *of the ionic complex* $[(Don)_n,NO^+]NO_3^-$.

represents the same stage in each reaction, and is associated with one distinct step in the transfer of the free ion on the metal surface to the stage at which it is fully co-ordinated in solution. Since we believe that the NO_3^- ions necessary for desorption are provided largely by the N_2O_4 in the region of the metal surface, the E value of 11 kcal. can be related to the energy of ionisation of N_2O_4 under these conditions. The N_2O_4 molecule in the reaction step $M^+ + N_2O_4 \longrightarrow M^+NO_3^- + NO^+$ can dissociate via the routes



or



and it is suggested that $E_1 + E_2$, or E_3, equals 11 kcal. If E_2 is very small,[10] it is significant that ΔH for the homolytic dissociation of the N–N bond in N_2O_4 is 12·9 kcal.[11] Whatever process E may represent, its value indicates that reaction rates are not determined by a diffusion-controlled electron-transfer reaction; for magnesium–aqueous acid [12] and zinc–dinitrogen tetroxide [4] reactions, E is near 5 kcal.

Type (3) : *Reaction of copper with methyl cyanide mixtures.* The reaction rate curve is shown in Fig. 7. Methyl cyanide combines all the features desirable for high reaction rate. Because of its polar nature and small molecular volume it has good ion-solvating powers comparable with those of nitromethane. Also, it can co-ordinate to a copper ion; the copper salts separated as solid reaction products contain combined methyl cyanide. The results suggest that methyl cyanide is at least as good as the nitrate ion as desorbing agent for unipositive metal ions. Finally, methyl cyanide forms addition compounds with dinitrogen tetroxide, thus enhancing the $(Don)_n,NO^+$ ion concentration. Reaction of copper with methyl cyanide mixtures proceeds vigorously, at rates which are much higher than with any other solvent studied, and are in marked contrast to the rates with benzyl and phenyl cyanide mixtures (Figs. 4 and 5). Because of the desorbing properties of methyl cyanide, there is no longer any reason for the arrest in the rate curve which occurs in type (2) systems, and throughout the concentration range the rate curve should reflect the ionic concentration in solution. This will be determined by two effects. First, the concentration of the ionic complex $[(Don)_n,NO^+]NO_3^-$ passes through a maximum when the liquids are in 1 : 1 mol. ratio; this is represented by the broken curve I in Fig. 7. Secondly, the dielectric constant, and thus the degree of ion separation in the ionic complex, is not at a maximum at the 1 : 1 ratio. In the absence of compound formation the rate curve would follow the broken curve II (as with the nitromethane–copper curve in Fig. 2). Since methyl cyanide is a donor solvent, an ionising medium, and an efficient desorbing agent, the actual variation in reaction rate should represent a summation of these factors. That such is the case is shown by the experimental curve III of Fig. 7. The dielectric constants of methyl cyanide and nitromethane are almost identical; the rate curve rises to a high maximum at the same concentration (85 mol. % solvent) in each system, but the donor properties of methyl cyanide result in a higher concentration of free ions, and a reaction rate which is six times the nitromethane value.

Fig. 7 also emphasises the marked difference between rates of reaction of zinc and copper. Methyl cyanide is apparently unable to desorb Zn^{2+} ions, so that the curve reverts to type (2), resembling that for benzyl cyanide (Fig. 4).

Influence of Stirring Rates.—The variation in reaction rate with the speed at which the metal specimen is rotated in the liquid mixture is shown in Figs. 8 and 9. In order to collect the results, an arbitrary vertical axis is employed. The actual reaction rates at any given stirring rate can be obtained by cross-reference between Figs. 8 and 9 and the other Figures where reaction rates are quoted for a constant stirring speed. The reaction rates are influenced by stirring in two ways, and the results are readily interpreted in terms of the principles outlined above.

(*a*) Under conditions in which nitromethane or methyl cyanide can act as desorbing agents, reaction rate increases constantly with stirring rate (Fig. 8). There is then no

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[10] Addison and Lewis, *J.*, 1953, 1869.

[11] Giauque and Kemp., *J. Chem. Phys.*, 1938, **6**, 40.

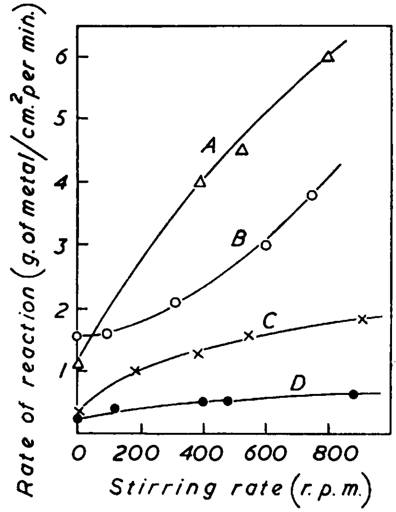
[12] James, *J. Amer. Chem. Soc.*, 1943, **65**, 39.

restriction on the availability of desorbing species, so that the reactions are diffusion-controlled throughout. For the unstirred reaction of copper with a 92·5 mol. % nitromethane solution, E is near 5 kcal. over the temperature range 0—20°.

(*b*) In solvents with solvating powers lower than that of the nitrate ion (Fig. 9), the reaction rates become constant at stirring rates above about 300 r.p.m. Diffusion from the surface is then faster than desorption, which is thus truly represented by the measurements at 400 r.p.m. in Figs. 1—7. The rate-determining process is again independent of stirring, since the same activation energy is found in stirred and unstirred reactions (Fig. 6).

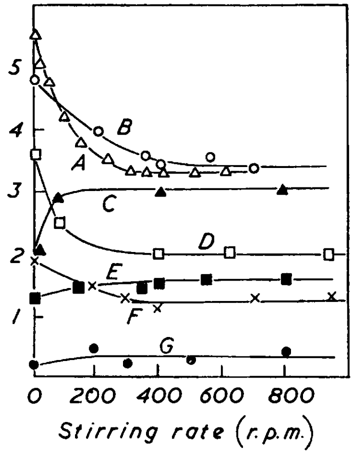
Other Solvents.—It was not possible to obtain reproducible results for the reaction of copper with acetic acid–dinitrogen tetroxide mixtures; copper reacts with pure acetic acid at negligible rate, yet reaction rates with the liquid mixtures were of similar magnitude to those for the ether and the ethyl acetate mixtures. Acetic acid differs from the other solvents used in this work in having a hydrogen atom which can be replaced by the NO group. (This reaction is already well illustrated in the conversion of alcohols into alkyl nitrites,[13] and alkyl- or aryl-substituted anilines into the corresponding nitrosamines,[14] by dinitrogen tetroxide.) Such replacement gives rise to the equilibrium :

FIG. 8. *Systems showing a continuous variation in reaction rate with stirring rate* (15°).

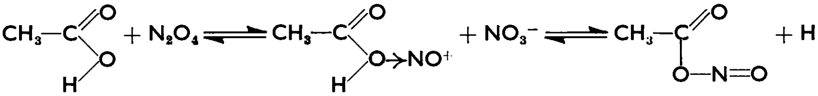


Metal	Mixture : N_2O_4 with
A, Copper	91 mol. % of $CH_3{\cdot}NO_2$
C, Copper	72 mol. % ,,
B, Copper	3·6 mol. % of $CH_3{\cdot}CN$
D, Zinc	77 mol. % ,,

FIG. 9. *Systems in which reaction rate becomes independent of stirring rate* (15°).



Metal	Mixture : N_2O_4 with
A, Uranium	62·6 mol. % of $CH_3{\cdot}NO_2$
B, Copper	60 mol. % of $CH_3{\cdot}CO_2Et$
F, Zinc	33 mol. % ,,
C, Zinc	3·2 mol. % of $Ph{\cdot}CH_2{\cdot}CN$
D, Zinc	9·7 mol. % ,,
E, Copper	33 mol. % of $Et_2N{\cdot}NO$
G, Zinc	8·2 mol. % of dioxan



to which must be added the possible side reaction

$$Cu(NO_3)_2 + 2CH_3{\cdot}CO_2H \rightleftharpoons Cu(CH_3{\cdot}CO_2)_2 + 2HNO_3$$

In each case nitric acid is produced, which may account for the lack of consistency in reaction rates.

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[13] Gray and Yoffe, *J.*, 1951, 1412; *Chem. Rev.*, 1955, **55**, 1069.

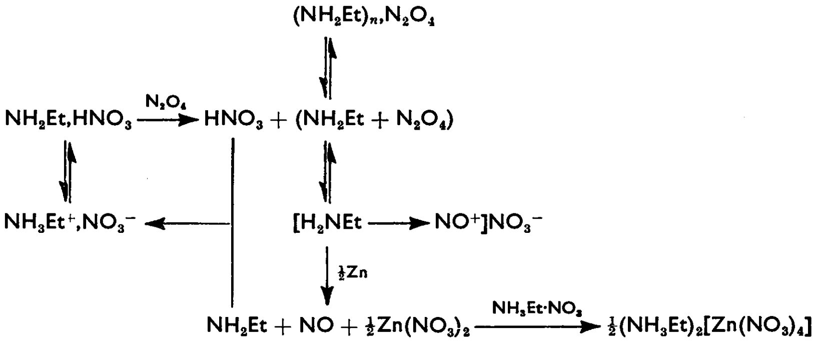
[14] Riebsomer, *Chem. Rev.*, 1945, **36**, 157.

Although metal–N_2O_4 reaction rates are increased by 'onium donor solvents, π-donor solvents have no such effect. Benzene and nitrobenzene are π-donors, forming solid 1 : 1 compounds with dinitrogen tetroxide.[1] Immersion of copper in tetroxide–benzene mixtures for 20 minutes gave a scarcely detectable weight change. Ionisation of dinitrogen tetroxide in nitrobenzene is enhanced by high dielectric constant, and might have been expected to lead to higher reaction rates with these mixtures. Zinc reacts with the pure tetroxide at the rate of $7{\cdot}5 \times 10^{-4}$ g./cm.^{2} in 15 minutes at 15° and 250 r.p.m. Over a wide composition range, reaction rates with nitrobenzene–tetroxide mixtures did not exceed 1×10^{-4}. This is attributed to the feeble solvating and desorbing powers of nitrobenzene, which are presumed to be less than those of the nitrate ion. Results with π-donors are therefore in accord with views already expressed.

Reactions of Metals with Solutions of Alkylammonium Nitrates in Dinitrogen Tetroxide.—The rate of reaction of metals with dinitrogen tetroxide is increased on addition of alkylammonium nitrates. Conditions and products of reaction with zinc have been described elsewhere.[7, 8] Such solutions have been regarded as " basic " in this solvent system, since the added solute introduces the anion (NO_3^-) characteristic of the medium, and reactions such as

$$Zn + 2N_2O_4 + 2NH_3Et{\cdot}NO_3 = (NH_3Et)_2[Zn(NO_3)_4] + 2NO$$

have been regarded as illustrating amphoteric behaviour in this system, being formally analogous to that between zinc and aqueous alkali. However, the simple introduction of R_4N^+ and NO_3^- ions into the solution should not in itself enhance reaction rates; no satisfactory reaction mechanism can be postulated on the basis of these ions alone, and the rates are much higher than would result from alteration in dielectric constant of the solution. The studies with solvent mixtures described above suggest that a similar mechanism accounts suitably for these reactions also; this is outlined for the zinc–ethylammonium nitrate solution reaction [7] in the following scheme :



The reactive species in alkylammonium nitrate solutions is therefore again considered to be the $(\text{Don})_n$,NO^+ ion. The amines are strong donors to dinitrogen tetroxides;[15, 16] they react explosively with the tetroxide when the pure liquids are mixed at room temperature, but addition compounds can be isolated at low temperatures. The presence of nitric acid stabilises the addition compound in some way, since dilute solutions of the alkylammonium nitrates are relatively stable. This may occur by ternary addition compound formation since compounds of empirical formula N_2O_4,Et_3N,HNO_3 and $N_2O_4,2Et_3N,2HNO_3$ have also been isolated.[17] Reaction rates with alkylammonium nitrate solutions are of the same order as with many donor-solvent mixtures. For example, in a 7·1 mol. % diethylammonium nitrate solution, unstirred, zinc reacts at the rate of 0·0016 g./cm.^{2} per min. at 15°. The reaction rate with a benzyl cyanide solution of the same concentration is 0·0018 unit (Fig. 5).

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[15] Comyns, *Nature*, 1953, **172**, 491; *J.*, 1955, 1557.

[16] Davenport, Burkhardt, and Sisler, *J. Amer. Chem. Soc.*, 1953, **75**, 4175.

[17] Addison and Hodge, *Chem. and Ind.*, 1953, 1315.

EXPERIMENTAL

Apparatus.—Copper and zinc were used in the form of rectangular blocks approx. 2·5 cm. long, and 0·5 cm. wide, with a hole of 0·2 cm. diameter drilled near one end. They were machined with precision so that the surface area could be determined accurately by micrometer. The blocks were suspended on a glass hook mounted in an aluminium stirring gland with B.24 cone. The gland was geared to a variable-speed electric motor. About 30 c.c. of the liquid mixture (made up by direct weighing, with precautions against contact with atmosphere) were transferred to a B.24 tube, which was coupled to the stirring gland at the start of the run and was immersed in a thermostat. At the end of the run the block was rapidly withdrawn and washed successively with dry carbon tetrachloride, alcohol, and ether, and its loss in weight determined. Uranium was used in the form of thin discs of approx. 1·4 cm. diameter, 3·5 cm.^{2} surface area, and 3·0 g. weight. The disc was suspended by a hole (1 mm. diameter) bored near its edge. The experiments were carried out as for copper and zinc, except that because of the longer immersion times it was desirable to fit the tube containing the liquid mixture with two side-arms—one, which served as a vent, carried a phosphoric oxide guard tube, and the other a thermometer whose bulb was immersed in the reaction liquid.

Purity of Materials.—Dinitrogen tetroxide was prepared and purified as already described,[18] and organic solvents were carefully purified by accepted methods. Spectroscopically pure copper (Johnson Matthey Ltd.) was used, and the zinc blocks were cast from " AnalaR " granulated zinc. Uranium of very high purity was kindly supplied by the Atomic Energy Research Establishment, Harwell.

Behaviour of Metals with Liquid Dinitrogen Tetroxide alone.—Reaction with zinc has already been described.[4] Copper showed only the slightest indication of attack during immersion for many days. A freshly filed disc of uranium retained its bright surface without tarnish, and no loss in weight could be detected after 7 days' immersion. Similarly, no reaction took place when uranium was left in contact with dinitrogen tetroxide diluted with carbon tetrachloride or chloroform for 3 weeks at 25°. (The reactivity of uranium with dinitrogen tetroxide vapour is low at temperatures up to 120°; the metal surface became covered by a very thin film of oxide, and prolonged exposure gave no further changes.)

Treatment of Metal Surfaces.—Before reaction the copper and zinc blocks were abraded with a clean file to produce a fresh surface, then degreased in dry alcohol and ether; thereafter during weighing and mounting they were handled with forceps only. With this treatment, reproducible results were obtained. Uranium discs were treated in various ways to examine the influence of surface condition on reaction rate with nitromethane mixtures, and results are shown in Table 2. Treatments 1, 4, and 5 gave a dull metal surface, owing to formation of uranium salt or oxide at the surface, and gave high values. The freshly filed surface again gave reproducible results.

TABLE 2.

Treatment of uranium discs	Loss in wt. in 60 mol. % nitromethane mixture (g./cm.^{2} in 2 hr. at 20° and 350 r.p.m.)
1. Acid washed with 2N-HCl	0·00281
2. Abraded with carborundum powder	0·00271
3. Filed	0·00271
4. Exposed to atmosphere for 7 days	0·00298
5. Heated at 200° for 1 hour	0·00371

Selection of Immersion Periods.—Long immersion of the metal in the liquid mixture can result in a change in reaction rate due to passivity effects or to the accumulation of soluble reaction products in the solution or of insoluble products at the metal surface. Preliminary measurements were therefore made to determine suitable immersion periods over which reaction rate was constant. Typical experiments for copper and zinc are shown in Table 3.

Over periods up to 4 min. the weight loss was proportional to immersion time for all solvents used (except acetic anhydride). In these measurements surface area suffered negligible change, and weight losses are given in g. rather than g./cm.^{2}. Immersion for 0·5 min. gave weight losses of suitable magnitude, and all results reported for copper and zinc in this paper are based on this immersion time. Uranium reaction rates are slower.

Reaction products are soluble in mixtures containing a large proportion of nitromethane,

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[18] Addison, Allen, Bolton, and Lewis, *J.*, 1951, 1289.

TABLE 3. *Influence of immersion time on copper and zinc reaction rates.*

Metal	Solvent	Solvent (mol. %)	Wt. loss (10^{-3} g.) from metal block for the following immersion times (min. at 15° and 400 r.p.m.)					
			0·25	0·5	1·0	2·0	2·5	4·0
Cu	$Me{\cdot}NO_2$	94	6	12	23	—	—	—
Cu *	Me·CN	12	14	28	56	—	—	—
Cu	$CH_3{\cdot}CO_2Et$	34	—	8	16	33	—	—
Cu	$Et_2N{\cdot}NO$	32	—	3	—	11	—	22
Zn	,,	3·9	—	4·5	—	18	—	39
Zn	$Ph{\cdot}CH_2{\cdot}CN$	39	—	2·1	4·2	—	10·5	—
Zn	,,	76	—	—	1·9	3·7	—	—

* At 640 r.p.m.

TABLE 4. *Influence of immersion time on uranium reaction rate in* N_2O_4–$CH_3{\cdot}NO_2$ *mixtures.*

Expt.	Nitromethane (mol. %)	Wt. loss (10^{-3} g./cm.^{2}) from uranium block for the following immersion times (hr. at 20° and 350 r.p.m.)					
		2	4	6	8	10	11
1	62·6	2·45	4·9	7·3	9·7	12·1	13·5
2	18·4	1·75	3·4	5·1	6·8	7·9	8·2

and weight loss is proportional to immersion time for at least 11 hr. (Expt. 1, Table 4). As the solubility of the reaction product diminishes (Expt. 2) it accumulates ultimately on the metal surface, so that reaction rates decrease after about 7 hr. The reaction rates for uranium given in Figs. 2, 6, and 9 are based on 2-hour immersion periods.

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