S 46. *The Liquid Dinitrogen Tetroxide Solvent System. Part I.*
General Introduction.

By C. C. Addison and R. Thompson.

On the basis of the ionic dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ reactions in liquid dinitrogen tetroxide show many points of analogy with corresponding reactions in aqueous, liquid ammonia, and liquid sulphur dioxide media. An introductory account of the scope, advantages, and limitations of the system is given. Acid–base reactions, liquid dinitrogen tetroxide–metal reactions, reactions between metals and solutions of nitrosyl chloride in liquid dinitrogen tetroxide, and amphoteric behaviour are co-ordinated from the point of view of this solvent system.

THE work to be described in this series was initiated with the object of studying predominantly inorganic and ionic reactions in which liquid dinitrogen tetroxide is involved. On the basis of the ionic dissociation
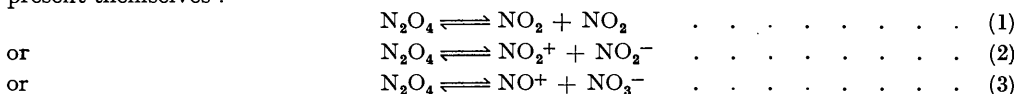
$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

(compare $2H_2O \rightleftharpoons H_3O^+ + OH^-$; $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$; $2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$)

many points of analogy with the well-known water, liquid ammonia, and liquid sulphur dioxide systems arise, and treatment of the chemistry of liquid dinitrogen tetroxide from the point of view of a solvent system has been found to provide a very satisfactory basis on which to classify (*a*) reactions in which the tetroxide serves as a medium for reaction and (*b*) reactions in which it features as a reactant.

Frankland and Farmer (*J.*, 1901, **79**, 1356) first considered liquid dinitrogen tetroxide as a medium for ionic reactions. They observed that some organic compounds and non-metallic elements were soluble with ease, but were unable to find any inorganic salts which dissolved to a considerable extent. In view of this, and of the low order of electrical conductivity (specific conductivity less than 2×10^{-8} ohm^{-1}), they concluded that the liquid was unable to behave as an ionising medium, and resembled closely in its general behaviour such organic solvents as benzene. A few reactions between liquid dinitrogen tetroxide and ionic compounds have since been reported; such reports have been quite disconnected, and no attempt has yet been made to systematise the chemistry of dinitrogen tetroxide in the liquid state.

Dissociation of the N_2O_4 *Molecule.*—All reactions in which this molecule takes part can be assumed to involve, as a first stage, the dissociation of the molecule. At least three possibilities present themselves :

$$N_2O_4 \rightleftharpoons NO_2 + NO_2 \qquad \qquad \qquad (1)$$
or
$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad \qquad \qquad (2)$$
or
$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad \qquad \qquad (3)$$

Dissociation occurs thermally according to equation (1) and is almost complete at the high temperatures at which many reactions of the gaseous oxide have been studied. However, it is undesirable to draw direct comparison between liquid and gaseous reactions for the following reasons. (*a*) Dissociation (1) occurs to a small extent only in the liquid state. Accurate values are not available for the extent of this dissociation, but the liquid at the boiling point (21·3°) will not be dissociated to a greater extent than the 15% which occurs in the gas at this temperature; the considerable diminution in colour intensity which accompanies the cooling of the liquid indicates that dissociation will not exceed about 5% at a temperature of 0°, which is convenient for the study of liquid reactions. (*b*) The initial products of reaction, such as the nitrate, may be unstable at elevated temperatures. (*c*) Mechanisms by which reactions can occur in the gaseous state at elevated temperatures may not be possible at low temperatures and in the liquid state. For instance, Bawn and Evans (*Trans. Faraday Soc.*, 1937, **33**, 1571) have shown that in the flame reaction with sodium, the primary reaction is $Na + NO_2 \longrightarrow NaO + NO$, and that the NaO then reacts with free sodium atoms to form Na_2O. A similar mechanism may interpret the results of Sabatier and Senderens (*Ann. Chim. Phys.*, 1896, **7**, 348), who observed the formation of nitrate and nitric oxide under somewhat different conditions. Now metallic sodium reacts also with liquid dinitrogen tetroxide; again nitric oxide is evolved and sodium nitrate is formed, but the liquid reaction is more satisfactorily interpreted on the basis of dissociation of N_2O_4 into NO^+ and NO_3^- ions (equation 3) when the reaction $Na + N_2O_4 \longrightarrow NaNO_3 + NO$ proceeds by the transfer of an electron from the sodium atom to the nitrosyl ion, giving the resonance-stabilised nitric oxide molecule.

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That dissociation according to equation (2) can occur has been illustrated by the work of Levy and Scaife (*J.*, 1946, 1093 *et seq.*) on the preparation of aliphatic nitro-compounds in liquid dinitrogen tetroxide; this confirmed that addition of the tetroxide to the olefinic double bond gives either dinitro-compounds or nitro-nitrites, and that, except where dinitrogen trioxide is deliberately used, nitroso-compounds are not formed. These authors did not postulate the free existence of NO_2^+ and NO_2^- in the medium, but considered that such dissociation took place during reaction, and that the NO_2^+ group was responsible for the initial attack. Ingold *et al.* (*Nature*, 1946, **158**, 480) have shown that in concentrated sulphuric acid the NO_2^+ ion is capable of separate existence, and Bennett *et al.* (*J.*, 1946, 869 *et seq.*) consider this nitronium ion to be the active species in aromatic nitrations employing nitric–sulphuric acid mixtures. Riebsomer (*Chem. Reviews*, 1945, **36**, 157) has listed a large number of aliphatic and aromatic compounds which give nitro-derivatives by reaction with liquid dinitrogen tetroxide, and in these nitrations also the NO_2^+ group may well be significant.

In view of the fact that Exner (*J.*, 1872, 1072) established the reaction $NO_2Cl + AgNO_2 \longrightarrow AgCl + N_2O_4$, it seemed feasible that ionic dissociation of N_2O_4 according to equation (2) might be important in purely inorganic reactions also, and therefore our postulate that dissociation into nitrosyl and nitrate ions is fundamental in inorganic reactions may appear to be at variance with considerable evidence to the contrary. This is not so; the liquid dinitrogen tetroxide reactions above involve nitration of covalent compounds, and there is much evidence to indicate that the mode of its dissociation, and thus the nature of the reaction products, depends upon whether the reacting molecules are covalent or ionic compounds. For example, aniline reacts explosively with liquid dinitrogen tetroxide, yet aniline hydrochloride is scarcely attacked; diethylamine reacts, yet the hydrochloride undergoes only simple ion exchange to give the nitrate (see below); ammonia reacts explosively, yet most simple ammonium salts are stable in contact with the liquid tetroxide. Thus, the conversion of a covalent molecule into ionic form provides some, and in many cases complete, protection from attack by the liquid tetroxide, and the following general statements are in agreement with available experimental evidence :
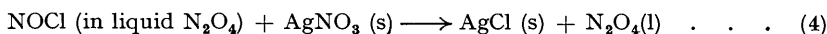
(1) When liquid dinitrogen tetroxide reacts with covalent molecules, dissociation into NO_2^+ and NO_2^- occurs during the course of the reaction. It is unlikely that these groups are present as free ions in the liquid tetroxide, since nitrites are not obtained as products in ionic reactions.

(2) When liquid dinitrogen tetroxide reacts with ionic compounds, dissociation into NO^+ and NO_3^- occurs, and the readiness with which ionic reactions proceed is consistent with the assumption that these ions are present in the liquid tetroxide in small concentration.

" *Acid–Base* " *Reactions*.—A formal analogy being employed with the water, ammonia, and sulphur dioxide solvent systems, nitrosyl compounds in which the nitrosyl group features as a cation may be regarded as acids, and nitrates as bases in this solvent system, and the reactions between nitrosyl compounds and nitrates (which are fundamentally $NO^+ + NO_3^- \longrightarrow N_2O_4$) may be termed neutralisation processes. As Bell (*Quart. Reviews*, 1947, **1**, 113) has stated, it is inconvenient, in a study of acid–base systems, to use the terms " acid " and " base " in a sense which varies with change of solvent, but as this is a matter of definition only, the terms acid and base are retained here for lack of more appropriate terms and in order to maintain the formal analogy with other established solvent systems. Since proton transfer is not involved, the Brönsted–Lowry definitions (*Rec. Trav. chim.*, 1923, **42**, 718; *Chem. and Ind.*, 1923, **42**, 43) are clearly inapplicable. The system may be considered, as may the liquid sulphur dioxide system, as falling within Lewis's broader acid–base definitions (*J. Franklin Inst.*, 1938, **226**, 293), but for present purposes it is adequate to use Cady and Elsey's definitions (*J. Chem. Educ.*, 1928, **5**, 1425), when the nitrosyl compounds are acidic, and the nitrates basic, in the dinitrogen tetroxide system because they give rise respectively to cations and anions characteristic of the solvent.

Of the available nitrosyl compounds, the chloride is amongst the most stable. Its dissociation into nitric oxide and chlorine, even in the gaseous state at room temperature, is only about 0·5% (Beeson and Yost, *J. Chem. Physics*, 1939, **7**, 44), and it has been found to be miscible with liquid dinitrogen tetroxide in all proportions. The investigation of acid–base reactions is restricted by the low solubility of the simple metal nitrates. In the nature of its solvent powers, the liquid tetroxide appears to resemble liquid sulphur dioxide more closely than it resembles water or liquid ammonia, and the low stability of its addition compounds with inorganic salts is of the same order as those of the corresponding sulphur dioxide compounds. Although liquid dinitrogen tetroxide is a good solvent for some non-metallic elements and certain classes of organic compound (*e.g.*, nitro-compounds and carboxylic acids), Frankland and Farmer (*loc. cit.*) were unable to find any readily soluble inorganic salt; we have examined a wider range of metal salts, but have found no instance of appreciable solubility, and co-ordination of the metal

ion does not seem to assist solution. It is of interest that the solubility in liquid sulphur dioxide of the corresponding bases, the metal sulphites, is of the order of only 0·02—0·05% ; in both systems conductimetric methods are necessary for following acid–base reactions involving metal salts in solution. However, solutions of nitrosyl chloride in liquid dinitrogen tetroxide have been found to react with solid metal nitrates. The reaction

$$\text{NOCl (in liquid } N_2O_4) + \text{AgNO}_3 \text{ (s)} \longrightarrow \text{AgCl (s)} + N_2O_4(l) \quad . \quad . \quad . \quad (4)$$

proceeds to completion, in the direction indicated, within a few minutes at 0—10°, the velocity of the reaction being limited only by the surface area of the powdered silver nitrate. Pure silver chloride and liquid dinitrogen tetroxide were found to be unchanged after contact for several days. The ease with which this reaction proceeds does not necessarily imply that the medium is strongly ionising with respect to nitrosyl chloride; indeed, this appears unlikely (see below). Perrot (*Compt. rend.*, 1935, **201**, 275) has shown that the same reaction can proceed in the absence of N_2O_4 as a medium, and Söderbäck (*Annalen*, 1919, **419**, 217) found a similar reaction, NOCl + AgCNS = AgCl + NO·CNS, to take place in carbon tetrachloride medium. However, these reactions clearly involve the NO^+ ion, and provided that N_2O_4 is a reaction product, reaction (4) can be considered as falling formally within this acid–base system irrespective of whether the ionic dissociation of nitrosyl chloride is enhanced in liquid dinitrogen tetroxide.

Although alkali-metal sulphites are only slightly soluble in liquid sulphur dioxide, certain substituted ammonium sulphites (*e.g.*, tetra-methylammonium sulphite) are readily soluble. Similarly, ammonium nitrate neither reacts with nor dissolves appreciably in liquid dinitrogen tetroxide at temperatures up to its boiling point, although decomposition into nitrogen and nitric acid occurs in a sealed tube at 100° (Besson and Rosset, *Compt. rend.*, 1906, **142**, 633). When the hydrogen atoms in the NH_4^+ group are replaced by organic radicals the substituted salts become more soluble. Depending on the nature and number of substituent groups, decomposition may occur, or the salt may dissolve unchanged. For example, diethylammonium nitrate is readily soluble in liquid dinitrogen tetroxide, and when diethylammonium chloride is added to the liquid at 0° the reaction

$$[\text{Et}_2\text{NH}_2]^+\text{Cl}^- + N_2O_4 = \text{NOCl} + [\text{Et}_2\text{NH}_2]^+\text{NO}_3^- \quad . \quad . \quad . \quad (5)$$
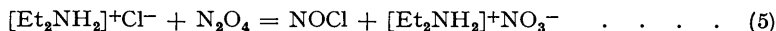
proceeds readily. As the chloride dissolves, the solution is coloured red by the nitrosyl chloride produced. On gentle warming (immersing the reaction vessel in a water-bath at 20—30°) under slightly reduced pressure, the nitrosyl chloride is removed from the system, and from the resulting solution the diethylammonium nitrate may be crystallised in quantitative yield. The process is analogous to that of hydrolysis in aqueous medium. If the reaction mixture is heated further, without preliminary removal of the nitrosyl chloride, the products undergo further mutual interaction in the accepted manner (Sidgwick, " The Organic Chemistry of Nitrogen ", Oxford Univ. Press, 1937, p. 24) to give *N*-nitrosodiethylamine. This technique provides a convenient and attractive method for the direct preparation of nitrosoamines which will be discussed in detail at a later stage.

The method of Whittaker, Lundstrom, and Merz (*Ind. Eng. Chem.*, 1931, **23**, 1410) which was employed for the preparation of nitrosyl chloride involves the reaction $\text{KCl} + N_2O_4 = \text{KNO}_3 + \text{NOCl}$. This reaction does not take place if the reactants are perfectly dry, but reaction is rapid at room temperature if the gaseous tetroxide is passed over solid potassium chloride moistened with about 2·5% of water. Noyes (*ibid.*, 1932, **24**, 1084) has postulated the mechanism

$$N_2O_4 + H_2O \longrightarrow \boxed{NO^+} + OH^- + H^+ + \boxed{NO_3^-}$$
$$\text{KCl} \longrightarrow \boxed{Cl^-} \qquad\qquad\qquad \boxed{K^+}$$
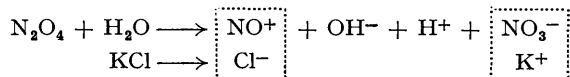
Reaction must clearly take place in the film of aqueous potassium chloride solution covering the crystals. Since at room temperature the nitrosyl ion is continuously removed from the system as nitrosyl chloride (b. p. $-5\cdot5°$), ionisation of the amphoteric nitrous acid in the aqueous film proceeds entirely as $HNO_2 \rightleftharpoons NO^+ + OH^-$, and the water may be regarded as providing a liquid medium in which the ionisation of both KCl and N_2O_4 molecules occurs. It is significant that solid potassium chloride does not react with liquid dinitrogen tetroxide. These reactions point to the conclusion that the acid–base reaction $\text{MCl} + N_2O_4 \rightleftharpoons \text{MNO}_3 + \text{NOCl}$ (where M is a metal or substituted ammonium ion) is fully reversible in liquid media. When the salts can dissolve readily and ionise in the medium, an equilibrium is set up and the forward reaction goes

to completion on removal of the nitrosyl chloride. When the salts are insoluble in the medium no forward reaction occurs, but the reverse reaction proceeds to completion.

Liquid Dinitrogen Tetroxide as an Ionising Medium.—The reactions discussed here suggest that the behaviour of nitrosyl chloride in liquid dinitrogen tetroxide differs little from its behaviour in other " inert " media such as carbon tetrachloride. Conductimetric studies of these solutions will be reported later, but it is relevant here to draw comparison with other solvent systems. In the water and the liquid ammonia system the strong proton-acceptor properties of the H_2O and NH_3 molecules are responsible for the breaking of the H–Cl bond in dissolved hydrochloric acid to give Cl^- and H_3O^+ or NH_4^+ respectively. For example, the specific conductivity of water is changed from the order of 10^{-7} to 10^{-2} ohm^{-1} by addition of hydrochloric acid in 0·05M-concentration. However, in the liquid sulphur dioxide system there are no properties characteristic of the sulphur dioxide molecule which are likely to bring about any considerable ionisation of dissolved $SOCl_2$ molecules. Consequently, when thionyl chloride is added to liquid sulphur dioxide in 0·05M-concentration, the changes in specific conductivity are relatively small, from $0·1 \times 10^{-6}$ to $6·8 \times 10^{-6}$ ohm^{-1} (Jander and Wickert, *Z. physikal. Chem.,* 1936, **178**, 57), and although experimental evidence is not at present available, the ionisation of thionyl chloride in other inert media may well be of the same order. Similar considerations apply to solutions of nitrosyl chloride in liquid dinitrogen tetroxide and it is not to be anticipated, therefore, that the liquid tetroxide will serve as a strongly ionising medium with respect to nitrosyl chloride. The results are, however, consistent with the belief that liquid nitrosyl chloride itself undergoes some ionic dissociation into NO^+ and Cl^- ions, but that this dissociation is not considerably influenced by dilution of the nitrosyl chloride with liquid dinitrogen tetroxide. That nitrosyl chloride should itself undergo ionic dissociation irrespective of the medium is consistent with physical measurements on the nitrosyl chloride molecule. The N–Cl bond distance is 1·95 A. compared with 1·69 A. for the sum of the covalent single-bond radii. The view that the bond has about 50% ionic character is supported by dipole-moment measurements (Ketelaar and Palmer, *J. Amer. Chem. Soc.,* 1937, **59**, 2629) and the ionic structure $:N{\equiv}O:^+ \; :\!\ddot{C}\!\ddot{l}:^-$ is accepted as one of the limiting states of resonance of the molecule. Angus and Leckie (*Trans. Faraday Soc.,* 1935, **31**, 958) have shown the NO^+ ion to be present in conducting media; Hantzsch and Berger (*Z. anorg. Chem.,* 1930, **190**, 321) have demonstrated its presence in solutions of nitrosyl perchlorate in the non-conductor nitromethane, and cryoscopic measurements (to be reported later) indicate that nitrosyl chloride is ionised in liquid dinitrogen tetroxide. It would appear, however, that the presence of the NO^+ ion in this solution is to be attributed rather to the nature of the nitrosyl chloride molecule than to the ionising power of the dinitrogen tetroxide medium.

The Structure of Dinitrogen Tetroxide.—The reactions already referred to, together with the dinitrogen tetroxide–metal reactions discussed below, suggest that the ionic dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ proceeds readily in either direction, although the dissociation constant is small. As evidence for this mode of dissociation accumulates, it becomes appropriate to consider the structure of the N_2O_4 molecule in this light. Ingold (*Nature,* 1947, **159**, 743) considers structure (I) to be confirmed by the olefinic reactions studied by Levy and Scaife
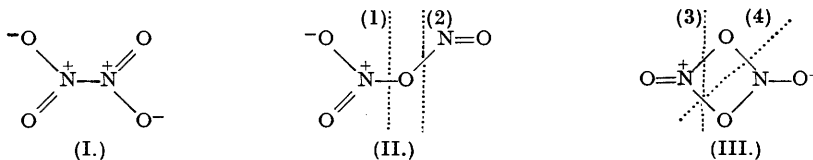
(*loc. cit.*) since it was not necessary to assume dissociation other than into NO_2^+ and NO_2^- to explain these reactions. Assuming this structure, dissociation into NO^+ and NO_3^- could only occur as a result of transfer of an oxygen atom, whereas this dissociation appears to arise in reactions involving electron transfer only; it should be noted, however, that such atom transfer in the dissociation $2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$ is envisaged by Jander and Wickert (*loc. cit.*) as a basis of the sulphur dioxide solvent system. It has already been emphasised that the ionic or covalent character of the reacting molecules has a pronounced influence on the nature of dissociation of N_2O_4; structure (II), favoured by Pauling (" The Nature of the Chemical Bond ", Cornell Univ. Press, 1945, p. 271), appears capable of dissociation at either position (1) or (2). The resonance state of this molecule, the strength of bonds (1) and (2), and thus the point of fission, may well be influenced by the ionic character of the molecules with which it reacts, but

this structure is at variance with the requirements regarding symmetry (Sutherland, *Proc. Roy. Soc.*, 1933, *A*, **141**, 342). However, structure (III) (Longuet-Higgins, *Nature*, 1944, **153**, 408) appears to be similarly capable of dissociation into either NO_2^+ and NO_2^- [at (4)], or NO^+ and NO_3^- [at (3)], without atom transfer, and is supported by available physical data.

Liquid Dinitrogen Tetroxide–Metal Reactions.—Experimental evidence on this aspect is at present limited. The alkali metals, including lithium, react readily; magnesium shows no sign of attack after 3 days' contact with the liquid, and reaction with calcium is slight. Some of the metals of the transition series undergo slow reaction; thus, zinc develops a coating of nitrate after about 20 hours, mercury reacts (Divers and Shimidzu, *J.*, 1885, **47**, 630) to form a mixture of mercuric and mercurous nitrates, and finely-divided copper gives a mixture of cuprous and cupric nitrates. Although the rate of reaction depends upon many factors, including the physical state of the metal, the scheme

$$\text{Metal} + N_2O_4(l) \longrightarrow \text{Metal nitrate} + NO \quad \ldots \ldots \quad (6)$$
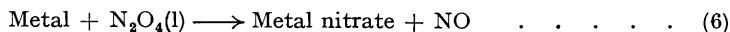
satisfies all reactions yet studied, and in no case has the formation of nitrate been found or reported. In contact with the liquid, sodium metal rapidly becomes coated with a white layer of sodium nitrate (free from nitrite), and if this loosely attached layer is removed by agitation of the reaction tube, the reaction quickly proceeds to completion. At room temperatures the nitric oxide is evolved, although at lower temperatures or under pressure some of the nitric oxide remains associated with the medium as green-blue dinitrogen trioxide. The above metal–medium reactions can, therefore, readily be explained on ionic equation (3), and the following equations illustrate the direct analogy with the water and liquid ammonia systems :
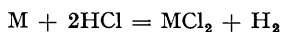
$$2Na + 2H_2O = 2NaOH + H_2$$
$$Na + N_2O_4 = NaNO_3 + NO$$
$$2Na + 2NH_3 = 2NaNH_2 + H_2 \text{ (using catalyst)}$$
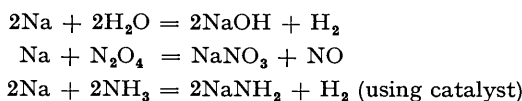
In each case the solvent cations (*i.e.*, H^+ or NO^+ ions) can be regarded as ready electron-acceptors in view of the stability of the H_2 and NO molecules, so that each reaction can be considered as involving the transfer of an electron from the metal to the solvent cation. In the liquid sulphur dioxide system, the low order of stability of sulphur monoxide implies that the SO^{2+} cation accepts electrons much less readily; this is in accord with the experimental observation that sodium does not dissolve in or react with liquid sulphur dioxide.

In some of their experiments on the addition of liquid dinitrogen tetroxide to olefins, Levy and Scaife (*loc. cit.*) employed the reagent diluted with organic solvents. The possibility that this dilution may itself influence the mode of dissociation could not be dismissed on theoretical grounds alone. However, when sodium is immersed in benzene solutions of the tetroxide, reaction (6) again proceeds, and is not influenced except in velocity by the benzene content of the medium. Any attempt to explain these metal reactions on the basis of dissociation into NO_2^+ and NO_2^- would involve the intermediate formation of sodium nitrite, which we have found to be stable in contact with the liquid.

Nitrosyl Chloride–Metal Reactions.—Because of the low concentration of the solvent cation NO^+ in pure liquid dinitrogen tetroxide, ready reaction with this medium is restricted to the more electropositive metals. However, increase in concentration of the solvent cation by the addition of nitrosyl chloride gives rise to a solution which is capable of reacting with a wide range of metals inert to liquid dinitrogen tetroxide alone. For example, zinc, iron, and tin are attacked by such solutions, although we have found that attack of certain other metals such as bismuth, chromium, and tungsten is negligible even by solutions containing 50% of nitrosyl chloride. The reactions follow the general course

$$\text{(metal)} \ M + 2NOCl = MCl_2 + 2NO \quad \ldots \ldots \quad (7)$$
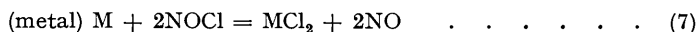
which is comparable with $\qquad M + 2HCl = MCl_2 + H_2$

and $\qquad M + 2NH_4Cl = MCl_2 + H_2 + 2NH_3$

and it is of interest that, although liquid sulphur dioxide is inert to such metals as sodium and potassium, thionyl chloride reacts with sodium and even tin and antimony, to give sulphur monoxide as the initial product (Schenk and Platz, *Z. anorg. Chem.*, 1933, **215**, 113), $M + SOCl_2 = MCl_2 + SO$, and it is to be anticipated (Luder, *Chem. Reviews*, 1940, **27**, 547) that the same reaction will proceed in liquid sulphur dioxide medium, particularly since sulphur dioxide is one of the decomposition products of the monoxide. The insoluble metal chloride

produced by reaction (7) is usually combined with nitrosyl chloride. Many metal chlorides are known to form double salts when treated with nitrosyl chloride alone (Sudborough, *J.*, 1891, **59**, 655) or in carbon tetrachloride (Rheinboldt and Wasserfuhr, *Ber.*, 1927, **60**, 732), and preliminary experiments indicate that the complexes formed as a result of nitrosyl chloride–metal reactions in liquid dinitrogen tetroxide are similar in character. These salts are either unstable addition compounds (*e.g.*, $ZnCl_2,NOCl$) or more stable complex salts of the nitrosyl radical (Asmussen, *Z. anorg. Chem.*, 1939, **243**, 127) $\{e.g., (NO^+)_2 [SnCl_6]^{2-}\}$. The nitrosyl complexes are acids in this solvent system, and their method of preparation is similar in principle to that of the corresponding acids (*e.g.*, $H_2[SnCl_6]$) in the aqueous system.

Although acid–base reactions in liquid dinitrogen tetroxide are clearly ionic, the significance of the NO^+ ion in reactions between metals and nitrosyl chloride in this medium merits further consideration. In order to compare the behaviour of nitrosyl chloride in liquid dinitrogen tetroxide with its behaviour when dissolved in other solvents, solutions were prepared containing the same concentration of nitrosyl chloride (11.6%) in pure dinitrogen tetroxide and in pure carbon tetrachloride. A small rectangular plate of " AnalaR " zinc weighing approximately
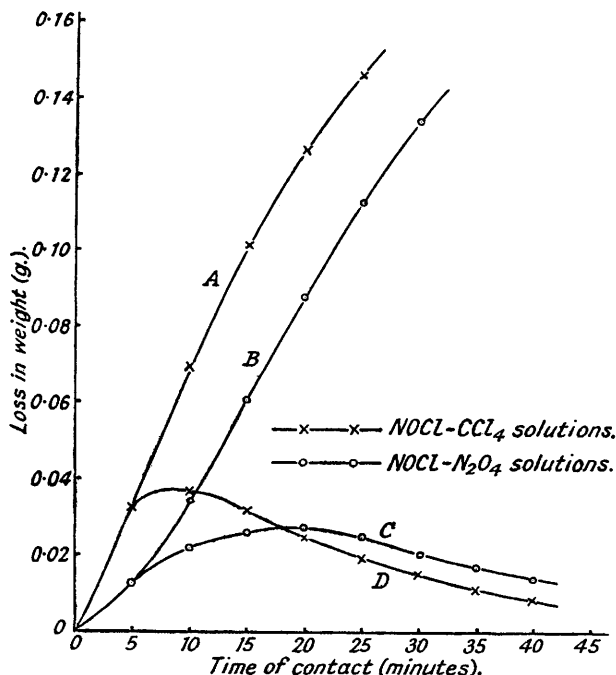

3 g. and of surface area 3.5 cm.^{2} was immersed in 10 g. of NOCl–N_2O_4 solution. The reaction proceeded readily at first but the rate decreased as the metal surface became covered with a layer of zinc chloride–nitrosyl chloride complex. After 5 minutes' contact the zinc plate was removed from the liquid and dropped into a large volume of water. The layer of yellow chloride complex dissolved immediately; the dried metal was then re-weighed and returned to the solution, the process being repeated several times. A parallel experiment was carried out using the solution in carbon tetrachloride, and the results are shown graphically in the figure. Except for a higher rate of reaction with the carbon tetrachloride solution on initial immersion, the cumulative-loss curves *A* and *B* follow an almost parallel course for the two media. The fall away in the successive-loss curves *C* and *D* is to be attributed to decreasing nitrosyl chloride concentration, and the somewhat lower values of successive loss in the carbon tetrachloride solutions in later experiments follows from the greater decrease in nitrosyl chloride concentration on initial immersion of the metal. It is clear that nitrosyl chloride is not more reactive with zinc when dissolved in dinitrogen tetroxide than when dissolved in carbon tetrachloride.

A study of the influence of nitrosyl chloride also supports the belief that its ionisation is influenced but little by solution in dinitrogen tetroxide. Where electron transfer takes place between the metal and solvent cations in a strongly ionising medium, as with aqueous solutions of mineral acids, the rate of solution of a metal passes through a maximum with increasing
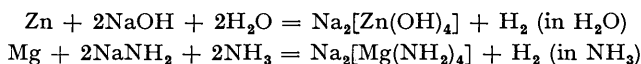
acid concentration and decreases considerably as ionisation diminishes at very high acid concentrations. In general, where an acid which is itself capable of slight ionic dissociation is dissolved in a non-ionising medium, the rate of reaction should increase with concentration throughout the whole concentration range. This has been found to be the case with solutions of nitrosyl chloride in dinitrogen tetroxide. For example, pure iron when placed in a 10% solution of nitrosyl chloride suffered negligible attack; at 50% the attack was rapid, and pure liquid nitrosyl chloride attacks iron violently (Sudborough, *loc. cit.*). Again, we have found that bismuth is but slightly attacked by a 50% solution, although it is readily attacked by pure liquid nitrosyl chloride. Magnesium, which does not react with pure nitrosyl chloride, is also unattacked by solutions of nitrosyl chloride in liquid dinitrogen tetroxide, and we have observed no cases where a metal is attacked by a $NOCl-N_2O_4$ solution more readily than by nitrosyl chloride alone.

However, while the reaction between nitrosyl chloride and metals can be explained at least qualitatively on the above ionisation hypothesis, the possibility of direct reaction between the metals and the nitrosyl chloride molecules cannot yet be dismissed. The reactions occur at the metal surface, and in the case of those metals (*e.g.*, zinc) which do not react very readily with dinitrogen tetroxide alone, reaction can be considered as occurring as a result of collision between (*a*) NO^+ ions and (*b*) $NOCl$ molecules with the metal surface. Because of the stability of the nitric oxide molecule, electron transfer to the NO^+ ion will clearly be the more ready process, but in view of the ionic character of the N–Cl bond, collision between an $NOCl$ molecule and an electropositive metal atom may well result in dissociation of the $NOCl$ to produce an insoluble ionic chloride at the metal surface, with the evolution of nitric oxide. The metal reactions outlined above are thus capable of interpretation by either of the two mechanisms; it seems possible that both occur, and the topic will be treated quantitatively in later papers in this series.

Amphoteric Behaviour.—The existence of amphoteric behaviour in the liquid dinitrogen tetroxide system further enhances the analogy with the aqueous, liquid ammonia and liquid sulphur dioxide systems. For example, zinc metal reacts very slowly with the liquid tetroxide, but the reaction is vigorous in the presence of nitrosyl chloride (v. supra). However, if the liquid tetroxide is rendered basic by the addition of diethylammonium nitrate, a vigorous reaction again occurs :
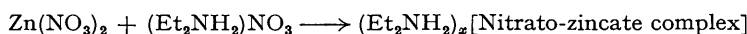
$$Zn + (Et_2NH_2)NO_3 + N_2O_4 \longrightarrow (Et_2NH_2)_x[\text{Nitrato-zincate complex}] + NO \qquad (8)$$
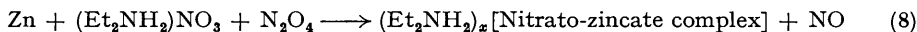
Nitric oxide is rapidly evolved, and the zinc complex dissolves in the medium. The reaction is directly comparable with

$$Zn + 2NaOH + 2H_2O = Na_2[Zn(OH)_4] + H_2 \text{ (in } H_2O)$$
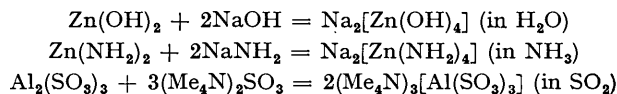$$Mg + 2NaNH_2 + 2NH_3 = Na_2[Mg(NH_2)_4] + H_2 \text{ (in } NH_3)$$

The nitrato-zincate complex (equation 8), solvated with several molecules of dinitrogen tetroxide, may be crystallised from the solution. Its composition depends upon conditions of crystallisation, and will be discussed in detail in a later part.

Zinc nitrate can be obtained in the anhydrous state by allowing zinc metal to stand for some hours in contact with liquid dinitrogen tetroxide, when the salt is formed as a white coating on the metal. When diethylammonium nitrate is added to the liquid, the white solid quickly dissolves. Thus zinc nitrate may be regarded as an amphoteric base in the dinitrogen tetroxide system.

The reaction

$$Zn(NO_3)_2 + (Et_2NH_2)NO_3 \longrightarrow (Et_2NH_2)_x[\text{Nitrato-zincate complex}]$$

is then analogous to reactions in other systems, viz.

$$Zn(OH)_2 + 2NaOH = Na_2[Zn(OH)_4] \text{ (in } H_2O)$$
$$Zn(NH_2)_2 + 2NaNH_2 = Na_2[Zn(NH_2)_4] \text{ (in } NH_3)$$
$$Al_2(SO_3)_3 + 3(Me_4N)_2SO_3 = 2(Me_4N)_3[Al(SO_3)_3] \text{ (in } SO_2)$$

The nitrato-zincate complex is soluble in diethylammonium nitrate–dinitrogen tetroxide mixtures, and no precipitation of zinc nitrate takes place when this solution is treated with nitrosyl chloride. The complex is almost insoluble, though stable, in the presence of tetroxide alone. In this respect it resembles the ammonozincate, which is stable in liquid ammonia, rather than the aquozincate complex, which is only stable in an aqueous solution containing excess of hydroxyl ions.

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