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Dinitrogen Tetroxide, Nitric Acid, and Their Mixtures as Media for Inorganic Reactions

C. CLIFFORD ADDISON

Department of Chemistry, Auburn University, Auburn, Alabama 36830

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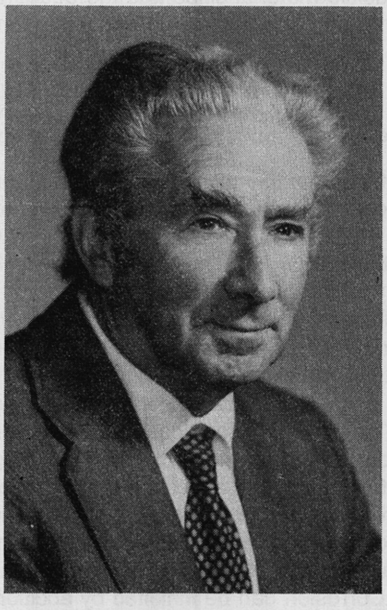
I. Introduction

In the early years of nonaqueous solvent chemistry (around 1900) the main emphasis lay in establishing formal analogies with water, identifying typical acids and typical bases, recognizing neutralization reactions, and so on. Such schemes have no more than a limited value as they cannot be applied to many liquids which are nevertheless useful solvents, and nowadays the interest arises from a quite different direction: new products can be isolated which would have been hydrolyzed in an aqueous medium, and are often related to the self-ionization of the medium involved. Liquid dinitrogen tetroxide provides a good example of this; consistent with its self-ionization into NO^+ and NO_3^- ions, many reactions yield anhydrous metal nitrates, or their N_2O_4 solvates, as pure crystalline products. Some of these anhydrous nitrates have been found to have a high volatility, which in turn led to much rethinking on the strength of the metal–nitrate coordinate bond and the recognition that this is only weak in an essentially aqueous environment. There are relevant reviews on "Chemistry in Liquid Dinitrogen Tetroxide" (1966, ref 1), "Anhydrous Metal Nitrates" (1964, ref 2), "Structural Aspects of Coordinated Nitrate Groups" (1971, ref 3), "The Use of Non-Aqueous Solvents in Inorganic Chemistry" (1960, ref 4), and "Complexes containing the Nitrate Ion" (1967, ref 5). It is not, therefore, necessary to attempt a full treatment of dinitrogen tetroxide chemistry here, and only those aspects which are relevant to the main theme of this Review will be referred to.



C. C. Addison took his B.Sc. and Ph.D. degrees at the University of Durham, England. After war service with the Ministry of Supply, he was appointed to the University of Nottingham, where he became Lecturer (1946), Reader (1950), Professor of Inorganic Chemistry (1960), and Dean of Science (1972). He was awarded the Liversidge Medal of the Chemical Society in 1976. On National bodies, he served as Vice-President of the Royal Institute of Chemistry (1958) and as President of the Chemical Society (1976-1977). He was elected to Fellowship of the Royal Society (FRS) in 1970 and has received Honorary Degrees of Doctor of Science from the Universities of Warwick and Durham. His research interests are in the general field of inorganic nonaqueous solvents, with particular reference to the use of the liquid alkali metals, and the liquid nitrogen oxides, as reaction media. Dr Addison spent the year 1979 at the Department of Chemistry, Auburn University, Auburn, Alabama, as Distinguished Visiting Professor.

An important extension to nonaqueous solvent chemistry involves the use of mixtures of two (or more) inorganic liquids, each of which is an inorganic nonaqueous solvent in its own right. The question then arises as to which liquid dominates the chemistry in that medium and whether the mixtures can be adjusted to take advantage of the specific properties of each liquid. The success of the dinitrogen tetroxide work can be attributed in large measure to the use of mixtures with organic solvents, whereby the reactivity as well as the solution properties of the medium can be controlled at will by selection of the appropriate organic diluent. This aspect is an important one in industry, where mixed solvents are probably more commonly encountered than single pure solvents, but it has not received a corresponding degree of attention in academic research.

The main purpose of this Review is to discuss reactions in, and precipitation from, mixtures of dinitrogen tetroxide with nitric acid. The choice is not an arbitrary one, since pure nitric acid is inherently unstable and eventually decomposes into an HNO_3–N_2O_4 mixture. Attention was originally focused on these

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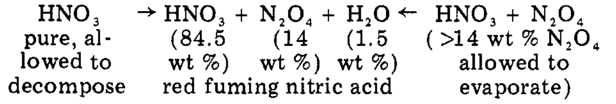
liquids following the decision of the U.S. Air Force to employ liquid nitrogen oxides as the oxidizer components in rocket propellant systems. Liquid N_2O_4 alone is well established as an efficient liquid oxidizer in rocket propulsion, e.g., in the upper stages of the Apollo-Saturn V space vehicles (Lunar, Command, and Service Modules), and is commonly used with dimethylhydrazine as fuel. "Pure" nitric acid (actually white fuming nitric acid, WFNA) is also established as an oxidizer in rocket engines. However, because of the instability of WFNA, its oxidizing power is rather unpredictable, and this prompted the use of "red fuming nitric acid" (RFNA) containing about 14 wt % N_2O_4. This is a more reproducible material since it is the equilibrium product attained from both extremes of the concentration range, i.e.



$$\begin{array}{ccccc} HNO_3 & \rightarrow HNO_3 & + N_2O_4 & + H_2O \leftarrow & HNO_3 + N_2O_4 \\ \text{pure, al-} & (84.5 & (14 & (1.5 & (>14\text{ wt \% }N_2O_4 \\ \text{lowed to} & \text{wt \%)} & \text{wt \%)} & \text{wt \%)} & \text{allowed to} \\ \text{decompose} & \multicolumn{3}{c}{\text{red fuming nitric acid}} & \text{evaporate)} \end{array}$$

As a result of the demand for greater propellant thrust (e.g., in the Agena rocket[6,7]), the N_2O_4 content of the oxidizer was increased to 44 wt %. Molecule for molecule, N_2O_4 provides more thrust than HNO_3, and the value of 44 wt % N_2O_4 represents the maximum convenient N_2O_4 content acceptable without modification of rocket engine design. (There is also an HNO_3-N_2O_4 immiscibility region which sets an upper limit to the N_2O_4 content.) This mixture is commonly termed "high density acid" (HDA), and many of the experiments referred to in this Review have employed this composition. However, variations in composition within the 14-44 wt % N_2O_4 range seem to involve little fundamental change in the basic chemistry.

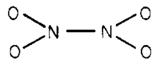
This mixture is highly corrosive and attacks containing vessels (usually steel or aluminum), setting up solutions of iron, chromium, nickel, and aluminum salts, which may remain in solution or precipitate. Corrosion can be inhibited by addition of fluorine compounds (notably HF or PF_5). The variety of chemical species involved in these processes have been discussed in unclassified reports to the U.S. Air Force (Rocket Propulsion Laboratory, California),[8-10] and the aim of this Review is to correlate these results with the chemistry of the liquid medium. The Review will first present relevant aspects of the chemistry of the separate liquids, followed by consideration of the chemical nature of the HNO_3-N_2O_4 mixture. The solution chemistry of the metal salts will then be discussed against this background.

II. Dinitrogen Tetroxide

A. Some Physical Properties and Structure

The liquid freezes at −11.2 °C and boils (under atmospheric pressure) at 21.15 °C. The liquid range is therefore narrow, but convenient. Supercooling readily occurs. Density is high (1.470-1.515 g/cm^3 between +10 and −10 °C) but viscosity is low (0.468-0.599 cP between +10 and −10 °C) so that the liquid is easily manipulated in large quantities. The surface tension is 26.5 dyn/cm at 20 °C, which is similar to many of the more volatile organic solvents. The specific conductivity (10^{-12} ohm^{-1} cm^{-1}) is the lowest value recorded for any of the common inorganic solvents.

The molecule may be represented by a single structure in the solid and gaseous states. Ignoring bond multiplicities, this may be represented as in **1**, and this is the main structure in the liquid



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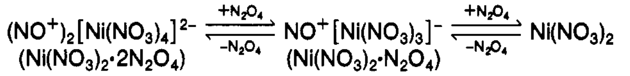
state also. X-ray evidence on the solid gives 1.17 Å for all N-O distances; the N-N distance is 1.64 Å and the O-N-O angles are 126°. The molecule is symmetrical and diamagnetic and the solid is colorless. The N-N bond must be of an unusual type which is not even yet fully understood, since in spite of its length, the two NO_2 units do not rotate with respect to one another. At liquid helium temperatures, other structures have been identified, but these are not considered to be significant at normal temperatures.

B. Dissociation in the Liquid State

Studies of the reactivity, or mechanisms of reactions, of liquid N_2O_4 have to take into account the relatively large number of species which are available by dissociation. There are three possible dissociation modes, given by reactions 1-3.



$$\underset{(Ni(NO_3)_2\cdot 2N_2O_4)}{(NO^+)_2[Ni(NO_3)_4]^{2-}} \underset{-N_2O_4}{\overset{+N_2O_4}{\rightleftharpoons}} \underset{(Ni(NO_3)_2\cdot N_2O_4)}{NO^+[Ni(NO_3)_3]^-} \underset{-N_2O_4}{\overset{+N_2O_4}{\rightleftharpoons}} Ni(NO_3)_2 \qquad (1)$$

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad (2)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (3)$$

The homolytic dissociation (eq 1) is always present in the liquid. The NO_2 radical absorbs strongly throughout the visible range; as a result, the liquid is very pale yellow at the freezing point, but darkens to a deep red-brown color at the boiling point. This reflects any increase in the NO_2 concentration from about 0.01% to 0.1% NO_2. There is evidence (summarized in ref 1, p 8) that the NO_2 radical is important in reactions of dinitrogen tetroxide with unsaturated organic compounds.

The species NO_2^+ and NO_2^- formed by heterolytic dissociation (eq 2) have not been identified as free ions in liquid N_2O_4. To produce these ions on breaking the N-N bond, the bonding electrons are shared unequally, giving in the first instance the ion pair $[NO_2^+][NO_2^-]$. Nitrites have never been produced in reactions of metals with liquid N_2O_4, and it is considered that the oxygen exchange reaction (eq 4) must follow immediately

$$NO_2^+ + NO_2^- \rightarrow NO^+ + NO_3^- \qquad (4)$$

on the heterolytic dissociation and must be irreversible. It seems, however, that strong electron-pair acceptors such as BF_3 can stop the process at the $[NO_2^+][NO_2^-]$ stage. NO_2^- is a stronger electron donor than is NO_3^- (compare the covalent properties of HNO_2 and HNO_3), and it is reasonable that in the presence of a strong electron-pair acceptor the formation of an NO_2^--acceptor complex is preferred to oxygen atom exchange. Thus, BF_3 reacts with liquid N_2O_4 to give $N_2O_4\cdot BF_3$[11,12] or $N_2O_4\cdot 2BF_3$[13] depending on conditions, and these have been shown to have the structures $NO_2^+[BF_3\cdot NO_2]^-$ and $NO_2^+[N(OBF_3)_2]^-$. However, when nitric acid (in which N_2O_4 is fully ionized into NO^+ and NO_3^-) is used as reaction medium, NO_2^+ compounds are no longer formed, and a different product, $NO\cdot BF_4$, is produced.[13]

With this exception, inorganic reactions in the liquid state are concerned almost entirely with equilibrium 3, and the dissociation products NO^+ and NO_3^- (or species derived from them) are the only significant ones.

C. Solution Properties of the Pure Liquid

The dielectric constant of liquid N_2O_4 is 2.42; this is very close to the value for benzene (2.28), and the solution properties are similar. Thus, no metal salts are soluble in the pure liquid. When the liquid is used industrially on a large scale, traces of water are present as impurity, and the liquid then has slight solvent properties for metal salts. This would not be important were it not for the phenomenon of "flow decay". Liquid N_2O_4 which has been stored for some time in iron or iron-containing vessels accumulates several parts per million of iron in the form of dissolved iron nitrate salts. When the liquid is then passed through fine gauze, or fine orifices (as in the charging or operation of a rocket engine), this minute concentration of iron salts may separate at the points of highest shear in the orifice, restricting the flow of liquid oxidizer. For this reason, studies have been made on solutions so dilute that they would not normally have merited attention.[8]

It should be emphasized, however, that the low dielectric constant is not the disadvantage it would appear to be, since N_2O_4 can be diluted with many other solvents to give stable mixtures in which dissociation into NO^+ and NO_3^- remains unchanged, except in extent. For example, the rate of reaction of liquid N_2O_4 with many metals (e.g., Zn, U) is greatly enhanced by dilution with nitromethane; the latter is chemically inert toward the tetroxide, but its dielectric constant is 37. The products of reaction are the same, but they are now soluble in the liquid mixture.

Following the analogy with benzene, many organic compounds are miscible with liquid N_2O_4; they include aliphatic and aromatic hydrocarbons, halogen compounds, nitro compounds, nitrophenols, quinones, carboxylic acids, esters, ketones, anhydrides, and nitriles. Some nonmetallic elements (e.g., chlorine, bromine, iodine, sulfur) are soluble, but there is a negligible amount of data in this area. Ammonium nitrate is insoluble, but the alkyl-substituted ammonium nitrates dissolve readily.[14]

The process of solvolysis, in which the anion of a salt is replaced by NO_3^- (the anion characteristic of the medium), is a common experience. Trimethylammonium chloride reacts immediately on addition to N_2O_4:

$$Me_3NHCl + N_2O_4 \rightarrow Me_3NHNO_3 + NOCl \quad (5)$$

The deep-red color of nitrosyl chloride appears, and the pure nitrate crystallizes from the solution. Simple metal halides are insoluble in the tetroxide, but may still undergo solvolysis on immersion, e.g.

$$ZnCl_2 + 3N_2O_4 \rightarrow Zn(NO_3)_2{\cdot}2N_2O_4 + 2NOCl^{15} \quad (6)$$

Uranium tetrachloride undergoes solvolysis:

$$UCl_4 + 4N_2O_4 \rightarrow UO_2(NO_3)_2{\cdot}N_2O_4 + 4NOCl \quad (7)$$

but the reaction is slow due to the insolubility of the tetrachloride. The reaction is fast if a mixture of nitromethane with N_2O_4 (in which UCl_4 is soluble) is used instead.[16] Many chlorides (e.g., $FeCl_3$, $CrCl_3$) resist solvolysis even in the presence of inert, high dielectric solvents such as nitromethane. In this case, electron-donor solvents (see below) may be used; if anhydrous ferric chloride is added to an ethyl acetate-N_2O_4 mixture, nitrosyl chloride is immediately evolved[17] (eq 8). It will be noted that

$$FeCl_3 + N_2O_4 \text{ (in EtOAc)} \rightarrow Fe(NO_3)_3{\cdot}1.5N_2O_4 + NOCl \quad (8)$$

the metal nitrates produced usually separate as adducts with N_2O_4. These adducts (and particularly the iron compound in (8)) are important corrosion products formed by N_2O_4–HNO_3 mixtures and feature prominently later in the Review.

The behavior of metal nitrites is important in this context. If the dissociation represented by eq 2 was significant in metal–N_2O_4 systems, nitrites might be expected as reaction products, and the fact that they are never observed could be attributed to subsequent oxidation, or solvolysis by the tetroxide. Although this hypothesis is not considered to be true, it is nevertheless difficult to test fully since very few anhydrous metal nitrites are known. Thus, samples of sodium nitrite[18] and calcium nitrite[19] (which are ionic nitrites) have been immersed in N_2O_4 for 7 days at 20 °C, after which the samples were found to contain no trace of nitrate. In contrast,[20] anhydrous nickel nitrite, which is covalently bonded, undergoes rapid conversion to the nitrate on immersion in N_2O_4.

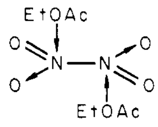
D. Mixtures with Other Solvents

Published information on mixtures of N_2O_4 with inorganic solvents is very limited. The variety of species produced in solutions of N_2O_4 in sulfuric[21,22] and hydrofluoric acids[23] have been studied because of their potential as nitrating agents. Simpler systems are provided by mixtures with nitrosyl chloride,[24] dinitrogen trioxide,[25] and sulfur dioxide.[26] The mixtures with nitric acid (see later) are probably the most important. A full discussion of the extensive literature on mixtures of N_2O_4 with organic solvents, and of the oxidizing powers of the tetroxide in these systems, is outside the scope of this Review. Brief reference should be made, however, because of the use of these mixtures in the preparation of anhydrous metal nitrates and their N_2O_4 adducts and because of the possible use of organic additives in oxidant rocket fuels.

1. Molecular Interactions

Liquid N_2O_4 is almost unique in the way in which its reactivity can be predetermined by the choice of diluting solvents. The types of reactivity which have been studied include oxidation,[27] nitration,[28] and reaction with metals;[29] illustrations will emphasize the effect of molecular interactions in the liquid on its reactivity with metals. As a result of studies on as many as 50 organic diluents, it has now been possible to divide diluents into three classes: (a) onium donor solvents, (b) π-donor solvents, and (c) inert solvents.[30]

The N_2O_4 molecule is electron deficient and acts as an electron acceptor. In diluents of class a, molecular addition compounds can be formed with almost all compounds which contain an atom which has one or more lone pairs of electrons available in s or p orbitals. Ethyl acetate is the most commonly used electron donor, but many other common solvents behave in this way. In the N_2O_4 molecule, each atom possesses a p-atomic orbital perpendicular to the plane of the molecule, and these combine to give a system of six π-molecular orbitals, embracing the whole molecule. These orbitals can be occupied by a maximum of 12 electrons; the N_2O_4 molecule has 8 electrons in the molecular orbital system, and hence up to two pairs of electrons can be accepted in adduct formation. The compound may be represented as in **2**. The NO^+ ion formed by self-ionization of N_2O_4 is also electron deficient to the extent of two electron pairs. The formation of a 2:1 ion, as in **3**, involves completion of the electron octet of both N and O atoms in the NO^+ ion. If we represent an electron donor solvent by the term (Don), then the equilibria in liquid dinitrogen tetroxide in the presence of such solvents can be expressed as shown by eq 9, where n is usually 2, except where there are unusual steric factors in the donor solvent or where (as with the dialkyl sulfoxides) the solvent molecule possesses two donor atoms.



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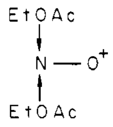

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$$(Don)_n{\cdot}N_2O_4 \overset{a}{\rightleftharpoons} n(Don) + N_2O_4 \overset{b}{\rightleftharpoons} [(Don)_n{\cdot}NO]^+NO_3^- \quad (9)$$

These molecular interactions in the solution can be recognized from the changes in physical properties such as electrical conductivity,[14] freezing point,[29] and viscosity,[31] but as most organic solvents are weak electron donors, the adducts are not present in sufficient quantity to be readily detected by infrared or Raman spectroscopy. Since the formation of the coordinated NO^+ ion requires preliminary ionization of N_2O_4, equilibrium a normally predominates over equilibrium b. Although the concentration of $[(Don)_nNO]^+$ ions is small with most diluents, dilution of N_2O_4 with a donor solvent has its most profound and obvious effect on the reaction rate of the liquid with metals. Rates are increased often by many factors of 10, and metals (e.g., Fe) which are apparently not attacked by N_2O_4 alone react readily on addition of ethyl acetate.

Dinitrogen tetroxide also forms addition compounds with aromatic hydrocarbons; compound formation is considered to arise as a result of plane-to-plane overlap of the molecular π orbitals of the aromatic ring and the N_2O_4 molecule, hence the term "π donors". Benzene is a typical example.[30] However, these compounds become significant in the solid state (the crystals are often highly colored), and there is no evidence for distinct molecules of adduct in the liquid mixtures. Dilution of N_2O_4 with π donors does not enhance the NO^+ concentration; in consequence, π donors do not increase the reactivity of N_2O_4 toward metals, nor do they enhance the solvolysis of salts.

With "inert" solvents, there is no molecular association with N_2O_4, but these solvents nevertheless have their uses. *n*-Hexane and *n*-heptane may be used to reduce the speed of a vigorous reaction or to reduce the overall volatility of the liquid. Nitromethane is used to increase the dielectric constant of the liquid, and hence the NO^+ concentration.

2. Oxidation by N_2O_4

It is true, as an early review by Riebsomer[32] shows, that N_2O_4 oxidizes many organic compounds rapidly. What is surprising is the wide range of organic compounds which appear to be quite stable when dissolved in, or mixed with, liquid N_2O_4.[30] When oxidation does occur, a unique feature is the ability of N_2O_4 to restrict oxidation to a single stage only, when further oxidation would appear to be possible. Thus, the preparation of substituted aromatic aldehydes RC_6H_4CHO by N_2O_4 oxidation of the corresponding alcohols is superior to many methods in simplicity.[33] When dialkyl sulfides are added to N_2O_4 at −70 °C, a red color is obtained due to the formation of an onium donor adduct. When the mixture is warmed to room temperature, nitric oxide is evolved and the sulfide R_2S is converted completely to the sulfoxide R_2SO. Further oxidation to the sulfone R_2SO_2 is negligible. This is believed to be due to the formation of an onium donor adduct $R_2SO{\cdot}N_2O_4$ which has high stability since both the S and O atoms of the sulfoxide form donor bonds to the N–N atoms of the tetroxide.[34] Trialkyl- and triarylphosphines are similarly oxidized to the phosphine oxides.[34]

The aliphatic and aromatic amines are amongst the strongest onium donors known, and the formation of adducts with N_2O_4 probably contributes to their ready oxidation. Thus, dimethylaniline has been found[35] to form a 1:1 complex with N_2O_4 in pentane solution at −78 °C, which can be represented in the completely ionic form $[PhMe_2NNO]^+NO_3^-$. On warming to room temperature the compound decomposes. The closely related compound methylphenylnitrosamine, MePhNNO, is also rapidly attacked by N_2O_4 at room temperature. The most sensitive group to N_2O_4 attack is the NH or NH_2 group, irrespective of whether this group is bonded to an aromatic ring; aniline itself reacts with N_2O_4 with the vigor of a rocket fuel, and the unsymmetrical dimethylhydrazine, Me_2NNH_2, was used in conjunction with N_2O_4 as fuel during the Apollo program. Many heterocyclic amines also give adducts at low temperature which decompose on warming.[36]

Oxidative properties toward inorganic compounds are selective in that they involve the donation of oxygen atoms rather than the removal of electrons from metal atoms. Metal ions retain their usual oxidation state in compounds separated from N_2O_4 or its mixtures (e.g., iron and chromium separate as Fe^{3+} and Cr^{3+} compounds, and the product of reaction with cobalt metal is a Co^{2+} rather than a Co^{3+} compound). Where a metal has a wide range of available oxidation states, oxidation by N_2O_4 from the lower oxidation states can be quite slow. When uranium dissolves in an N_2O_4–nitromethane mixture, the solution becomes green due to U^{4+} compounds in solution, and remains so, so long as metal is present. Sodium hyponitrite, $Na_2N_2O_2$, takes up one atom of oxygen rapidly in N_2O_4 to give the oxyhyponitrite $Na_2N_2O_3$.[38]

TABLE I. Reaction of N_2O_4 with Metals

reaction with N_2O_4 alone	reaction with N_2O_4-ethyl acetate mixtures	no reaction in N_2O_4-solvent mixtures
alkali metals	metals in column 1 plus:	iron
silver	uranium	nickel
zinc	manganese	chromium
mercury	cobalt	platinum
	copper	gold
	cadmium	(many other transition metals)
	indium	beryllium
		aluminum

E. Reaction with Metals

Liquid dinitrogen tetroxide resembles water in that it attacks only a limited number of metals. The initial reaction is the formation of nitrates, with liberation of nitric oxide, e.g.

$$Na + N_2O_4 \rightarrow NaNO_3 + NO \qquad (10)$$

which may be considered as a simple electron transfer from the metal atom to the NO^+ ion:

$$Na + NO^+ \rightarrow Na^+ + NO \qquad (11)$$

At room temperature the nitric oxide is evolved, but at lower temperatures, or under slight pressure, some of the nitric oxide remains associated with the medium as green-blue N_2O_3. The alkali and alkaline earth metals are somewhat less electropositive on the N_2O_4 scale than in water, and calcium, strontium, or barium do not react with pure, dry liquid tetroxide when in the massive state.[39] Table I lists some of the metals which have been examined.

The above concept of metal reactions is supported by a typical experiment in which a zinc metal specimen was stirred in the liquid tetroxide. In most heterogeneous (usually aqueous) systems cited in the literature, reaction products accumulate at the metal surface, hindering access of the active species to the metal surface. Stirring tends to remove these, so that reaction rate increases with the rate at which the specimen is stirred. In N_2O_4 the reverse is the case. Using zinc, the solid product, $Zn(NO_3)_2{\cdot}2N_2O_4$, is insoluble and noncohesive, and so does not interfere with the reaction. Some of the NO evolved combines with the medium to give N_2O_3 near the surface; this has a higher dielectric constant than has N_2O_4, and the NO^+ concentration is therefore enhanced. Stirring of the specimen at 40 rpm reduces the reaction rate to little more than one-half of the rate for an unstirred specimen.[40]

Nitromethane is a useful inert diluent in that it gives stable mixtures of higher dielectric constant, and most anhydrous metal nitrates dissolve in the mixture. Figure 1 (broken line) traces the variation in electrical conductivity of the mixture with composition. The conductivity reaches a maximum near 90% nitromethane owing to enhanced dissociation of the tetroxide; thereafter the dielectric constant of the medium does not change appreciably, the N_2O_4 dissociation is not further increased, and the fall in conductivity represents dilution of the ions. The reaction rate curve A (full line) for copper (which does not react with N_2O_4 alone) follows the same form as the conductivity curve, and its peak coincides with the conductivity maximum.[41] This is further support for the basic reaction

$$Cu + NO^+ \rightarrow Cu^+ + NO \qquad (12)$$

The direct correlation between conductivity and reaction rate holds because copper has a stable monovalent state. With other metals which do not possess a stable monovalent state (e.g., Zn, U) the reaction rate still passes through a maximum but at

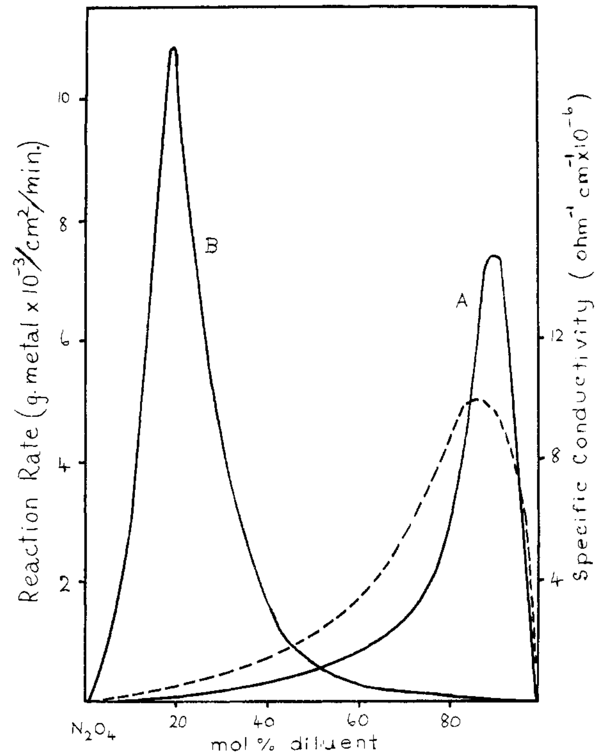


Figure 1. Reaction rates of copper with N_2O_4-solvent mixtures. (A) N_2O_4-nitromethane mixtures; (B) N_2O_4-ethyl acetate mixtures. Conductivity of N_2O_4-CH_3NO_2 mixtures (- - -).

a different composition since the dissolution rate cannot so readily reflect the transfer of a single electron.

The rate curves for onium donor solvents (e.g., curve B, Figure 1) also pass through sharp maxima, but the increase in rate occurs on addition of even small amounts of solvent. This is because on addition of onium donor solvents, the complex cation is formed immediately; electron transfer occurs from the metal to the complex with evolution of nitric oxide (eq 13).

$$M + (Don)_nNO^+ \rightarrow M^+ + n(Don) + NO \qquad (13)$$

The reaction of a metal with a nonaqueous solvent depends on two main factors. First, there is electron transfer, as discussed above. Second, the metal ion so formed must be able to leave the surface, and this process is assisted if species are present which can coordinate with the metal ion. In the tetroxide alone, the nitrate ion performs this function, but many donor solvents are also good ligands. Methyl cyanide combines all the qualities desirable for high reaction rate,[41] and the full curve A (Figure 2) shows the reaction rates of copper with mixtures of N_2O_4 and methyl cyanide. These rates are the sum of two effects, i.e., the high $(Don)_nNO^+$ concentration throughout the composition range (curve B) and the effect of dielectric constant (curve C), which for methyl cyanide is 37. This solvent is also an excellent ligand which is known to form complexes with Cu^+, with the result that the reaction rates of this mixture with copper metal are higher than with any other solvent studied.

F. Metal Nitrate-N_2O_4 Adducts

1. Structural Aspects

When reaction occurs between a metal (or its compounds) and N_2O_4 (alone or mixed with an organic solvent), the product is almost invariably the metal nitrate, combined with N_2O_4 in stoichiometric ratio. Table II gives a comprehensive list of known compounds. Many of the metals not included (e.g., most of the second- and third-row transition metals) are those which are capable of high oxidation states and yield oxide nitrates in the oxidizing N_2O_4 environment. The compounds listed in Table II vary widely in their thermal stability; some (e.g., the Zn and Ni compounds) evolve N_2O_4 on gentle warming, whereas others (e.g., the Fe and Cr compounds) are so stable that they undergo decomposition to the oxides on heating, and the anhydrous nitrates cannot be obtained from the adducts. For most of the 25 years during which these compounds have been investigated, it has been assumed that N_2O_4 molecules were bound in the metal nitrate lattice, hence the widely used term "adducts". Recently, however, the structures of a number of these compounds have been determined by X-ray crystallography and include both "strong" and "weak" adducts. Surprisingly, no single case has been found in which the N_2O_4 molecule occurs in the lattice; instead, all the compounds are found to be nitrosonium salts of nitrato complexes. For example, the compound represented as $Cr(NO_3)_3{\cdot}2N_2O_4$ is in fact the ionic compound $(NO^+)_2[Cr(NO_3)_5]^{2-}$. The stability of the compounds is therefore an indication of the stability of the particular nitrato complexes formed, and it is possible to interpret the properties of these compounds on this basis with much greater success than when they were considered to be N_2O_4 solvates.

Figure 3 shows the main modes of coordination of the nitrate group. (A full treatment of the bonding of nitrate groups is given in ref 3.) Symmetrical bidentate bonding is common and is probably the preferred bonding mode in the absence of external

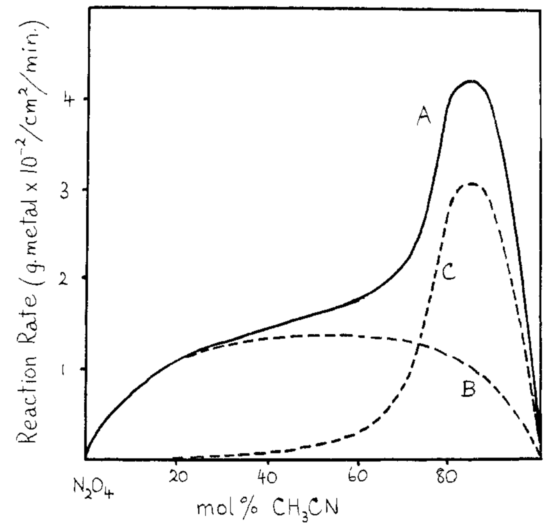


Figure 2. Reaction rates of copper with N_2O_4-methyl cyanide mixtures (see text for A, B, and C).

TABLE II. Metal Nitrate-N_2O_4 Adducts

main group elements	ref	transition elements	ref
$Be(NO_3)_2{\cdot}2N_2O_4$	39	$Sc(NO_3)_3{\cdot}2N_2O_4$	49
$Be(NO_3)_2{\cdot}N_2O_4$	39	$Y(NO_3)_3{\cdot}2N_2O_4$	49
$Mg(NO_3)_2{\cdot}N_2O_4$	39, 42	$La(NO_3)_3{\cdot}1.5N_2O_4$	50
$Al_2O(NO_3)_4{\cdot}2N_2O_4$	42, 73	$Cr(NO_3)_3{\cdot}2N_2O_4$	50, 51
$In(NO_3)_3{\cdot}2N_2O_4$	44	$Mn(NO_3)_2{\cdot}N_2O_4$	52
$In(NO_3)_3{\cdot}N_2O_4$	45	$Fe(NO_3)_3{\cdot}1.5N_2O_4$	53-55
$Tl(NO_3)_3{\cdot}N_2O_4$	46	$Fe(NO_3)_3{\cdot}N_2O_4$	17
$Bi(NO_3)_3{\cdot}0.8N_2O_4$	47	$Co(NO_3)_2{\cdot}2N_2O_4$	56
$Po(NO_3)_4{\cdot}N_2O_4$	48	$Co(NO_3)_2{\cdot}N_2O_4$	52, 56
		$Ni(NO_3)_2{\cdot}N_2O_4$	57, 58
		$Ni(NO_3)_2{\cdot}0.5N_2O_4$	59
		$Pd(NO_3)_2{\cdot}2N_2O_4$	57, 60
		$Cu(NO_3)_2{\cdot}N_2O_4$	61, 62
		$Au(NO_3)_3{\cdot}N_2O_4$	63
		$Zn(NO_3)_2{\cdot}2N_2O_4$	64
		$Zn(NO_3)_2{\cdot}N_2O_4$	65
		$Hg(NO_3)_2{\cdot}N_2O_4$	66
		$Ho(NO_3)_3{\cdot}2N_2O_4$	67
		$UO_2(NO_3)_2{\cdot}N_2O_4$	37
		$Th(NO_3)_4{\cdot}2N_2O_4$	68

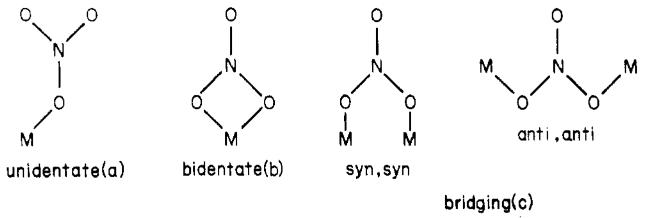


Figure 3. Modes of coordination of the nitrate group. (a) The M-O-N angle varies, depending on the metal and steric interactions with other ligands. (b) This ideal structure is often distorted, so that the two M-O distances differ. (c) Syn,anti bonding also occurs.

influences. However, the nitrate group does show remakable versatility as a ligand, and the coordination number in a nitrato complex is not directly related to the number of nitrate ligands present.

For instance, the scandium and yttrium complexes (Table II) have the structure $(NO^+)_2[M(NO_3)_5]^{2-}$. The Y atom is 10-coordinated (by five bidentate NO_3^- groups) whereas the Sc atom is 9-coordinated (by four bidentate and one unidentate NO_3^- group). Again, consider the family of compounds $NO^+[M(NO_3)_3]^-$, where M is Co, Ni, Cu, and Zn. These complexes contain polymeric nitrato anions, due to the preponderence of bridging nitrate groups. The Co atom is 6-coordinated by four bridging and one bidentate NO_3^- groups; the Cu atom is 6-coordinated by six bridging ligands, and the Zn atom is 5-coordinated by four bridging and one unidentate NO_3^- groups. The structure of the Ni complex has not been determined. It is expected to be 6-coordinate, but it is obviously difficult to anticipate the number of NO_3^- groups which will be involved.

The chemical nature of these compounds will be illustrated by reference to compounds of the four metals which are especially relevant to this Review, i.e., Fe, Cr, Al, and Ni.

2. Iron

This compound has the greatest practical significance since it is the compound formed as a corrosion product when N_2O_4 is stored in iron-containing vessels and was the compound which separated from the liquid N_2O_4 in rockets used in the Apollo space missions. The 1:1 product was the first to be studied.[17] Anhydrous iron(III) chloride is insoluble in, and unattacked by, liquid N_2O_4, but when sufficient dry ethyl acetate is added to bring the chloride into solution, solvolysis is rapid:

$$FeCl_3 + N_2O_4 \text{ (in EtOAc)} \rightarrow NOCl + NO^+[Fe(NO_3)_4]^- \quad (14)$$

On addition of excess tetroxide, a sticky solid separates, and when this is submitted to extensive vacuum treatment, a brown powder remains which has the composition $Fe(NO_3)_3 \cdot N_2O_4$. An infrared band at 2300 cm^{-1} shows the presence of the NO^+ ion; vibrations characteristic of covalently bonded NO_3^- groups are seen, but ionic NO_3^- vibrations are absent. Such evidence justified the ionic structure for the compound as shown in eq 14. The $[Fe(NO_3)_4]^-$ ion is one of the most stable known; on heating the compound, it is not possible to remove N_2O_4 without breakdown to an oxide nitrate, and as a result, the simple, anhydrous nitrate $Fe(NO_3)_3$ has not yet been isolated. The compound shows no visible evidence of an N_2O_4 vapor pressure when contained in a sealed glass tube for long periods.

When the practical importance of the iron compound was realized about 1970, it was reexamined. The compound was prepared as before, but without extensive vacuum treatment. It was then immersed in an excess of liquid N_2O_4, and the vapor pressure of the system was measured as aliquots of the tetroxide were progressively removed. By this means, it became clear that the product first separating from, and in equilibrium with, liquid N_2O_4 was an adduct of empirical formula $Fe(NO_3)_3 \cdot 1.5N_2O_4$. The 1:1.5 ratio is highly unusual, and the pale yellow-brown crystals were submitted to X-ray crystallographic examination.

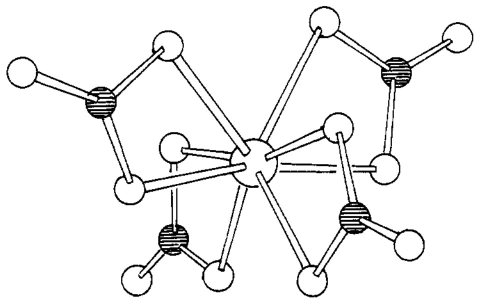


Figure 4. Structure of the tetranitratoferrate(III) ion.[69]

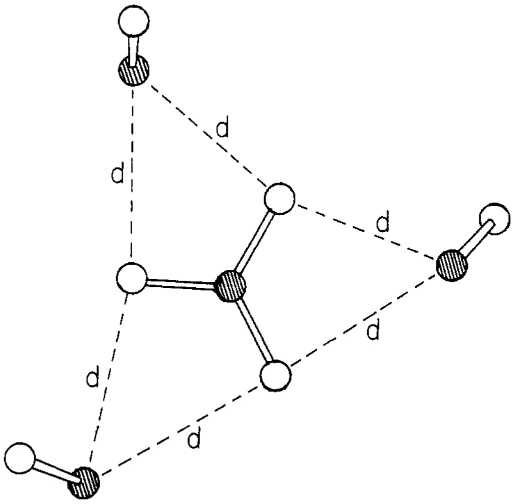


Figure 5. Structure of the $N_4O_6^{2+}$ group.

Since this 1.5 compound has an N_2O_4 vapor pressure of 6 cmHg, the X-ray data were obtained from crystals sealed into capillaries which contained liquid N_2O_4. The first feature in the structure to be recognized was the tetranitratoferrate (III) anions; these had the same flattened tetrahedral structure[69] as had been found in $(Ph_4As^+)[Fe(NO_3)_4]^-$. The structure is shown in Figure 4, which illustrates how the Fe^{3+} ion becomes 8-coordinate, as a result of the presence of four symmetrically bidentate nitrate groups. When the rest of the light atom positions became apparent, it was recognized that the compound should be given the formulation $(3NO^+ \cdot NO_3^-)[Fe(NO_3)_4^-]_2$. The relative positions of the three NO^+ and the NO_3^- ions are shown in Figure 5. One end of each NO^+ ion (presumably nitrogen) lies on the bisector of each nitrate ONO angle, and both the crystallographic symmetry and the vibrational spectroscopy suggest that we may think in terms of a weakly bonded $N_4O_6^{2+}$ group.[53,54] Thus, although the distances marked d in Figure 5 are around 2.6 Å, some of the vibrational characteristics of the nitrate ion are not observed, and the vibrational mode of NO^+ (which is 2300 cm^{-1} in the free ion) moves to 2235 cm^{-1} in the $N_4O_6^{2+}$ group.

3. Chromium

Both chromium metal and its chloride are unreactive, and the chromium compound of empirical formula $Cr(NO_3)_3 \cdot 2N_2O_4$ is best obtained from the reaction of chromium carbonyl or chromyl chloride with N_2O_4. When chromyl chloride is passed into a N_2O_4–CH_3NO_2 mixture, reaction is vigorous and green crystals separate.[51] These crystals have now been examined by X-ray crystallography and the compound has been shown to have the structure $(NO^+)_2[Cr(NO_3)_5]^{2-}$. The structure of the anion is shown in Figure 6; the 6-coordination of Cr^{3+} is achieved by four unidentate and one bidentate NO_3^- ions. Like the iron compound, this compound has a high thermal stability. The anhydrous $Cr(NO_3)_3$ cannot be obtained by thermal decomposition of the adduct, though it can be prepared by reaction of chromium

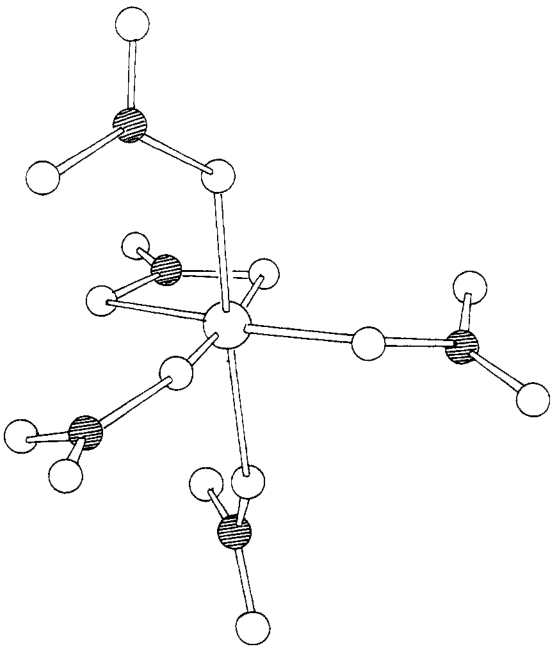


Figure 6. Structure of the $[Cr(NO_3)_5]^{2-}$ ion.

carbonyl with N_2O_5 in carbon tetrachloride solution.[70]

4. *Aluminum*

This metal resembles iron and chromium in its ability to form nitrato complexes but differs because of the readiness with which it forms oxide nitrates in the solid state. The compound $Al(NO_3)_3\cdot 0.38N_2O_4$ has been claimed,[42] but on reexamination[43,73] it seems that this solid product is better represented as the oxide nitrate $Al_2O(NO_3)_4\cdot 2N_2O_4$; this decomposes further at 70 °C to $Al_2O(NO_3)_4\cdot N_2O_4$, which itself undergoes further decomposition at 120 °C. It seems unlikely that products corresponding to the simple formula $Al(NO_3)_3\cdot nN_2O_4$ can be prepared; the anhydrous nitrate $Al(NO_3)_3$ can be prepared by sublimation of these adducts, and there is an unsupported statement that this compound can be obtained by reaction of aluminum bromide with chlorine nitrate in bromine solution.[71]

These results suggest that the NO^+ group is unable to stabilize a nitrato–aluminum complex in the solid state. It may well do so in solution, however, and a number of reasonably stable nitrato–aluminum complexes have been prepared using larger cations. For example:

$$AlBr_3 + CsNO_3 \text{ (in } HNO_3 + N_2O_5) \rightarrow Cs^+[Al(NO_3)_4]^- \quad (15)$$

$$AlCl_3 + Et_4NCl \text{ (in } N_2O_4) \rightarrow Et_4N^+[Al(NO_3)_4]^- \quad (16)$$

$$KAlCl_4 + AlBr_3 + KNO_3 \text{ (in } HNO_3 + N_2O_5) \rightarrow K_2{}^+[Al(NO_3)_5]^{2-} \text{ and } K_3{}^+[Al(NO_3)_6]^{3-} \quad (17)$$

$$AlBr_3 + CsNO_3 \text{ (in } HNO_3 + N_2O_5) \rightarrow Cs_2{}^+[Al(NO_3)_5]^{2-} \quad (18)$$

The conditions under which these reactions are carried out are described in ref 72 (eq 15 and 18), ref 73 (eq 16), and ref 74 (eq 17). Aluminum can, therefore, form tetra-, penta-, and hexanitrato complexes, and it is likely that in all these complexes the Al^{3+} ion retains 6-coordination by varying the number of unidentate and bidentate nitrate groups. The X-ray structure of the complex $Cs_2[Al(NO_3)_5]$ has been found to be almost identical with that of the corresponding chromium complex $[Cr(NO_3)_5]^{2-}$ discussed above.[75]

5. *Nickel*

The nickel adduct $Ni(NO_3)_2\cdot N_2O_4$ has been mentioned briefly above (Section F.1). The compound is prepared by reaction of anhydrous $NiCl_2$ with an N_2O_4–EtOAc mixture, followed by evacuation which leaves the 1:1 adduct as a pale green powder.[57,58] Its infrared and Raman spectrum[44] give clear evidence that the structure is $NO^+[Ni(NO_3)_3]^-$, and the magnetic moment[58] (2.98 μ_B) is consistent with a 6-coordinate, octahedral Ni^{2+} ion, which is achieved as a result of the presence of some bridging NO_3^- groups.

At one time a given metal nitrate–N_2O_4 adduct was considered as possessing a single nitrate–N_2O_4 ratio. It is now coming to be realized that if an adduct does indeed show clear evidence of existing in one ratio only, it is because of the high stability of the complex involved, and that a number of ratios, of widely differing stability, can often exist. Thus, the iron adduct owes its stability to the high stability of the $[Fe(NO_3)_4]^-$ species, and the two ratios which are found (1:1 and 1:1.5) involve change in the cation only. This is a discrete ion; it is, therefore, the species present when the compound is in solution, and it persists into the solid. Similarly, the 6-coordinate $[Cr(NO_3)_5]^{2-}$ is a stable species which occurs in solution and persists in the solid. Against this background, the position regarding the nickel compounds is an interesting one. The full equilibria can be represented as in eq 19. The $[Ni(NO_3)_4]^{2-}$ ion is well established in the compound $(Ph_4As)_2[Ni(NO_3)_4]$, and X-ray crystallography shows that the Ni^{2+} ion is 6-coordinate, by virtue of two unidentate and two bidentate nitrate groups.[65] When nickel nitrate dissolves in a medium in which NO_3^- is the only available ligand, this is the species which is assumed to exist in solution. However, this species does not appear to have any detectable stability as the nitrosonium salt, in the solid state. Vapor-pressure studies analogous to those for the iron compounds have not been carried out, but only limited vacuum treatment is necessary to produce the 1:1 compound. This could be attributed to an inherent instability of the $[Ni(NO_3)_4]^{2-}$ complex, which requires the presence of a large cation for its existence.[140] This may be true, but there is an additional factor: in producing a solid from a solution, it is easy for unidentate nitrate groups to become bridging, and this process is aided by the availability of the NO^+ group, which can carry away the surplus NO_3^- groups as N_2O_4. Similar chemistry applies to the Co, Cu, and Zn compounds. Each can give rise to the $[M(NO_3)_4]^{2-}$ species in solution; in the solid state Co and Zn give both 1:2 and 1:1 compounds, and Cu the 1:1 product only.

$$\underset{(Ni(NO_3)_2\cdot 2N_2O_4)}{(NO^+)_2[Ni(NO_3)_4]^{2-}} \underset{-N_2O_4}{\overset{+N_2O_4}{\rightleftharpoons}} \underset{(Ni(NO_3)_2\cdot N_2O_4)}{NO^+[Ni(NO_3)_3]^-} \underset{-N_2O_4}{\overset{+N_2O_4}{\rightleftharpoons}} Ni(NO_3)_2 \quad (19)$$

The 1:1 nickel adduct has a relatively low thermal stability, and dissociation to the anhydrous nitrate and N_2O_4 begins at 120 °C; this process is reversible.[58]

6. *Dissociation in Solution*

Since the solid compound $Fe(NO_3)_3\cdot N_2O_4$ can be formulated precisely as $NO^+[Fe(NO_3)_4]^-$, it might be expected that in solution in high dielectric solvents only the ions NO^+ and $[Fe(NO_3)_4]^-$ would be present. Conductivity measurements indicate, however, that this does not represent the whole case.[17] Figure 7 shows the molar conductivity–concentration curves for this compound in nitromethane and methyl cyanide. At higher concentrations curve A lies close to that (B) for the compound $(Et_4N)^+[Fe(NO_3)_4]^-$, which represents normal 1:1 electrolyte behavior in nitromethane. At lower concentrations, however, molar conductivity decreases with dilution. N_2O_4 has a relatively small conductivity in these solvents, and the conductivities of anhydrous, covalent metal nitrates are also small. The decrease in conductivity can, therefore, be attributed to the onset of an equilibrium

$$NO^+ + [Fe(NO_3)_4]^- \rightleftharpoons Fe(NO_3)_3 + N_2O_4 \quad (20)$$

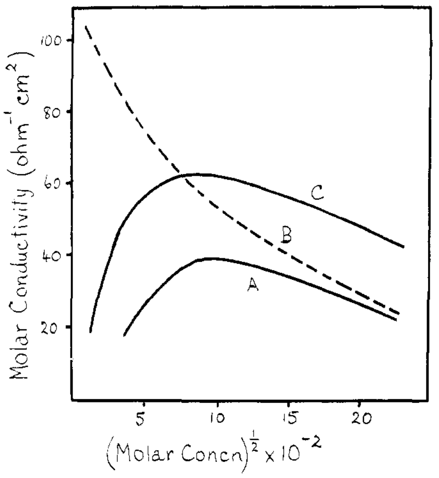


Figure 7. Molar conductivities at 25 °C: (A) $(NO^+)[Fe(NO_3)_4]^-$ in CH_3NO_2; (B) $(Et_4N^+)[Fe(NO_3)_4]^-$ in CH_3NO_2; (C) $(NO^+)[Fe(NO_3)_4]^-$ in CH_3CN.

which moves to the right on dilution. This type of behavior has been noted for other adducts (e.g., $Cu(NO_3)_2{\cdot}N_2O_4$[61]) and may well be a characteristic property. The effect must presumably be brought about by solvent participation, so that 20 can be expanded to eq 21, where S = solvent. Methyl cyanide is a

$$NO^+[Fe(NO_3)_4]^- + S \rightleftharpoons NO^+ + [Fe(NO_3)_3S] + NO_3^- \rightleftharpoons N_2O_4 + [Fe(NO_3)_3S] \qquad (21)$$

stronger ligand than is nitromethane; curve C falls at higher conductivity values than curve A, but the decrease in conductivity on dilution is even more pronounced.

G. Anhydrous Metal Nitrates

The simple anhydrous nitrates merit brief comment here, since most compounds discussed in the Review are derivatives or adducts of the anhydrous nitrates. They have been described in detail in earlier reviews.[2,3] Before about 1950, the known anhydrous metal nitrates (restricted to those of the alkali and alkaline earth metals, silver, thallium(I), and lead) were all ionic compounds. Nitrates of other metals were known only in the form of their hydrates, and attempts to dehydrate these usually resulted in the formation of hydroxide nitrates or oxides, with evolution of nitric acid. However, many of the anhydrous nitrates, once prepared using such nonaqueous solvents as N_2O_4, HNO_3-N_2O_5, or $ClNO_3$, have proved to possess high thermal stability. In the absence of water, covalent bonding of the nitrate group to many metals is remarkably strong, and can lead to volatility in some cases. The first example was anhydrous $Cu(NO_3)_2$, which develops a vapor pressure of 3.6 mmHg at 222 °C and is monomeric in the vapor state.[76,77] The stability in the vapor state is indeed greater than in the solid; decomposition of the vapor takes place sharply at 226 °C whereas decomposition of the solid can be detected at 100 °C. $Ti(NO_3)_4$,[78,79,88] $Sn(NO_3)_4$,[80] and $Co(NO_3)_3$[81] are very volatile and can be sublimed in vacuum at 40 °C. In each case the nitrate groups are symmetrically bidentate, and the Ti and Sn compounds have an 8-coordinate metal atom. The structures resemble closely that shown for the $[Fe(NO_3)_4]^-$ ion in Figure 4. Although the anhydrous nitrate $Fe(NO_3)_3$ has not been isolated, it is probably involved in the sublimation of the adduct $Fe(NO_3)_3{\cdot}N_2O_4$. It is unlikely that the whole adduct molecule will vaporize, and there is reason to believe that dissociation into the separate components occurs.[17] The anhydrous nitrate and nitrogen oxides are then present in the vapor phase and recombine on a cold finger. No volatility has been detected in either $Cr(NO_3)_3$[70] or $Ni(NO_3)_2$, but $Al(NO_3)_3$ is volatile.[73]

The oxidizing properties of some of these covalent nitrates is in sharp contrast to those of ionic nitrates. Thus, $Sn(NO_3)_4$, $Ti(NO_3)_4$, and $Co(NO_3)_3$[82,83] explode or inflame with organic compounds such as ethers or aniline, and the former oxidizes aliphatic hydrocarbons immediately on contact whereas $Mn(NO_3)_2$, $Ni(NO_3)_2$, and $Zn(NO_3)_2$ are inert. High reactivity is observed in those cases where the NO_3^- group is bonded as a symmetrical bidentate ligand. It is believed[79] that the species responsible for the vigorous oxidation is the NO_3 radical, which can be released in cases where the metal atom has sufficient electron-withdrawing power. Thus,

$$Ti^{IV}(NO_3)_4 \rightarrow Ti^{III}(NO_3)_3 + NO_3 \qquad (22)$$

Release of an NO_3 radical involves a decrease of one in the oxidation state of the metal, and strong oxidizing powers have been found only with nitrates of metals (e.g., Sn^{4+}, Ti^{4+}, Zr^{4+}, Co^{3+}, Cu^{2+}) for which a lower oxidation state is available. Loss of reactivity occurs when the nitrate bonding is changed from bidentate to unidentate; the adduct of $Sn(NO_3)_4$ with pyridine, $Sn(NO_3)_4{\cdot}2py$ in which the nitrate groups are unidentate, is no longer reactive.[80] Similar chemistry is observed for $Co(NO_3)_3$, which has three bidentate ligands.[82] The reactivity is lost on formation of the complex $Co(NO_3)_3{\cdot}2py$, in which all nitrates are unidentate.[83] An alternative interpretation of the reactivity of bidentate nitrates, based on the electron affinity of compounds such as $Ti(NO_3)_4$, has recently been put forward.[84]

III. Nitric Acid

Much of the work on the physical properties of nitric acid has been carried out in connection with the classical studies on aromatic nitration and has been reviewed by W. H. Lee.[85] The inorganic chemistry of the acid (and in the acid) has been largely avoided by chemists, perhaps because of its natural tendency to decompose.

A. Some Physical Properties and Structure

Acid of sufficient purity for most chemical purposes is prepared by distillation from a mixture of concentrated nitric acid and concentrated sulfuric acid (1:3 v/v) in a glass apparatus under reduced pressure and at room temperature. The acid condenses in a receiver at −78 °C as a white crystalline solid, mp −41.6 °C. The pure liquid boils at 82.6 °C. The density is very similar to the N_2O_4 value (1.549 g/cm^3 at 0 °C), but both the viscosity (10.92 cP at 0 °C) and surface tension (43.5 dyn/cm at 0 °C) are higher, due to hydrogen bonding in the liquid. In sharp contrast to N_2O_4 (which has probably the lowest conductivity), HNO_3 is one of the most highly conducting solvents, with a specific conductivity of 3.77×10^{-2} ohm^{-1} cm^{-1}. This makes measurement of the dielectric constant difficult, but a value of 50 (±10) at 14 °C, measured by the Furth force method,[86] is generally accepted. The structure of the nitric acid molecule has been studied by many spectroscopic techniques on both the vapor and the liquid.[87] HNO_3 is a rigid, planar molecule, and basic features of the structure are shown in Figure 8.

B. Dissociation in the Liquid State

The overall self-dissociation of nitric acid (eq 23) has been

$$\underset{0.4}{2HNO_3 \rightleftharpoons H_2O} + \underset{1.1}{NO_2^+} + \underset{1.5\ \text{wt}\ \%}{NO_3^-} \qquad (23)$$

well established by a number of classical studies.[89-95] Raman spectra[91] show that N_2O_5 is absent and that dissociation gives rise to approximately 0.25 *m* of the species produced. This work and the elegant cryoscopy by Gillespie et al.[89] show that a little over 3% by weight of the acid is dissociated, giving rise to quantities of the separate species shown in eq 23. Solvation

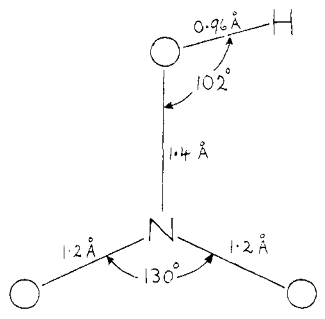


Figure 8. Structure of the nitric acid molecule.

TABLE III. Products of Reaction of Anhydrous Metal Salts with Pure Nitric Acid

reactant	product
$CrCl_3$	$Cr(NO_3)_3 \cdot 2H_2O$
$MnCl_2$	$Mn(NO_3)_2 \cdot 2H_2O$
$FeCl_3$	$Fe(NO_3)_3 \cdot 2H_2O$
$CoCl_2$	$Co(NO_3)_2 \cdot 2H_2O$
$NiCl_2$	$Ni(NO_3)_2 \cdot 2H_2O$
$CuCl_2$	$Cu(NO_3)_2 \cdot 2H_2O$
$Cu(NO_3)_2$	$Cu(NO_3)_2 \cdot 1.67H_2O$

is strong,[99] and as much as 10% of the acid is involved in solvating the species produced on self-dissociation.[89]

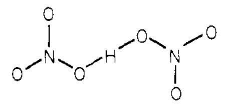
There is little direct evidence for the solvation of NO_2^+ by nitric acid, and any such solvate as $NO_2^+ \cdot HNO_3$ is coming very close to N_2O_5, which is known not to be present in the pure liquid. This 10% must, therefore, be employed largely in the solvation of the H_2O and NO_3^- species, for which there is plenty of evidence. Compounds showing NO_3^-–HNO_3 association will be discussed in Section IIIC.

Particular interest attaches to the state of the H_2O molecules formed by self-dissociation. Raman spectra confirm that molecular water is present in the anhydrous acid,[96] and cryoscopy[89] indicates that the H_2O molecules are un-ionized. Added H_2O up to 1.7 *m* (3.6 wt %) decreases the electrical conductivity of the acid,[97,98] so that up to this limit the added water is also un-ionized and suppresses the self-dissociation of the nitric acid. That water is available in pure nitric acid is obvious from the experiments of Hathaway and Underhill,[100] who treated anhydrous metal chlorides with pure nitric acid; the dihydrate rather than the anhydrous nitrate is produced, and hydrochloric acid is evolved (Table III). The fact that anhydrous copper nitrate yields the hydrate on solution and crystallization helps to confirm that water molecules are immediately available and are not produced in the course of any reaction between the acid and the anhydrous chloride.

Solvation, nevertheless, limits the chemical reactivity of the H_2O molecules, which are not capable of performing all the reactions characteristic of water alone. The best illustration lies in the self-dissociation species themselves, which are not normally compatible; NO_2^+ compounds are readily hydrolyzed by liquid water, yet H_2O and NO_2^+ groups exist together in nitric acid. Another example involves the hydrolysis of dissolved PF_5 which is not hydrolyzed in nitric acid to the extent to which water alone would be capable (see Section VII). Cryoscopy[89] shows that two molecules of nitric acid are employed in solvating each molecule of water, though by the nature of such experiments the value of 2 could be derived as an average of several species. Recently, the X-ray structures of the two main adducts $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$ have been determined.[101,102] The 1:1 compound has the ionic structure $H_3O^+NO_3^-$ in the solid, and in the 1:3 compound two additional molecules of water are attached to the H_3O^+ ion by short hydrogen bonds, giving the structure $H_7O_3^+NO_3^-$. However, the water molecules in nitric acid do not give rise to ions, and this case probably resembles that of N_2O_5 which is ionic $NO_2^+NO_3^-$ in the solid but a covalent molecule in solution. The state of H_2O molecules in the pure acid may well be as suggested in earlier papers,[103,104] where the respective covalent molecules were attached by strong hydrogen bonds as chains or rings. From the point of view of chemical reactivity, it seems adequate to consider the H_2O molecules as surrounded by a halo of nitric acid molecules, bonded by hydrogen bonds to a sufficient extent to limit, but not inhibit, their reactivity.

C. HNO_3 Adducts

These adducts have received much less attention than have the corresponding N_2O_4 adducts. They can be divided into two classes: (a) weak adducts, where the association is essentially by hydrogen bonding, and (b) strong adducts, which are really NO_2^+ compounds. Examples of weak adducts consist almost entirely of adducts with metal nitrates. The literature contains numerous examples in which nitrates, when crystallized from solutions containing nitric acid, carry with them "nitric acid of crystallization". In a number of cases these have now been recognized to be stoichiometric $NO_3^- \cdot HNO_3$ adducts, and their existence also provides evidence in support of the solvation of NO_3^- by HNO_3 in the pure acid. Examples of the 1:1 ratio predominate. The crystal structure of the compound $[Ph_4As]NO_3 \cdot HNO_3$ reveals a hydrogen dinitrate ion having structure **4** consisting of two coplanar unidentate nitrate groups linked across a center of symmetry by a short hydrogen bond,[106] and the infrared spectrum of this type of adduct has been defined.[105] The shape of the $H(NO_3^-)_2$ ion depends somewhat on the crystal lattice involved, and a structure for the ion has been reported where four oxygen atoms surround the hydrogen atom in a distorted tetrahedral arrangement.[107] In salts of the general type $[MA_4X_2]^+NO_3 \cdot HNO_3$, where M = Co or Rh, A = pyridine, and X = Cl^- or Br^-, the presence of $H(NO_3)_2^-$ ions has been confirmed by spectroscopy, conductivity, and pH measurements.[108] Solvent extraction studies often involve the extraction of aqueous nitric acid solutions by amines dissolved in an organic phase, and here also, $NO_3^- \cdot HNO_3$ adducts are commonly encountered.[109,110]



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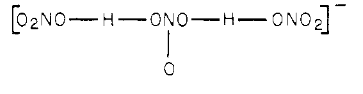
Other NO_3^-:HNO_3 ratios have been shown to exist. An X-ray analysis of the compound $NH_4NO_3 \cdot 2HNO_3$ reveals the presence of the dihydrogen trinitrate ion:



$$[O_2NO—H—\underset{\displaystyle O}{\underset{|}{ONO}}—H—ONO_2]^-$$

The complete structure[111] consists of layers of NH_4^+ and NO_3^- ions with intermediate layers of HNO_3 molecules, hydrogen bonded so as to link each NO_3^- group to $2HNO_3$. Again, it has been suggested[112] that solid adducts of the type $[M(NH_3)_6](NO_3)_3 \cdot HNO_3$ and $[M(NH_3)_5H_2O](NO_3)_3 \cdot HNO_3$ do not contain either $H(NO_3)_2^-$ or $H_2(NO_3)_3^-$ ions, but a further species $H(NO_3)_4^{3-}$, in which the protons are tetrahedrally coordinated by oxygen atoms.

The adduct with BF_3 provides a good example of a "strong" adduct. A stoichiometric compound, $HNO_3 \cdot 2BF_3$, is formed,[113] and this has now been shown, by Raman spectroscopy,[114] to have the structure $NO_2^+[(BF_3)_2OH]^-$. Adducts with sulfur trioxide,[115] formulated as $HNO_3 \cdot 2SO_3$, $2HNO_3 \cdot 3SO_3$, and $HNO_3 \cdot 3SO_3$, have been found, by X-ray crystallography, to be the NO_2^+ salts of the appropriate polymeric sulfate anion.[115,116]

D. Solution Properties of the Pure Liquid

As expected of a liquid of dielectric constant 50, nitric acid is a reasonably good solvent for ionic compounds. The only systematic study of nitric acid as a solvent system is by G. Jander.[117] This early study encompassed electrolytic behavior, solvate formation, acids and bases, solvolysis, and amphoteric behavior, on the basis of which Jander classified nitric acid as a "waterlike" solvent. Alkali metal nitrates (especially KNO_3) are readily soluble, while the alkaline earth nitrates are practically insoluble.[118] Results for the transition-metal nitrates[118] are of doubtful significance, since the only compounds available in 1948 would be the hydrated salts, but later work shows that many anhydrous nitrates do indeed dissolve readily in nitric acid. Crystallization as the hydrated salts[100] is sometimes prevented by addition of N_2O_5, and HNO_3 containing N_2O_5 has been used with success to prepare anhydrous nitrato complexes (e.g., $K_3^+[Al(NO_3)_6]^{3-}$)[74] which are difficult to isolate by other methods. Some nitrato complexes (e.g., $NO^+[Fe(NO_3)_4]^-$) are so soluble in HNO_3 that they eventually form a viscous gum, and in some cases (e.g., $NO_2^+[Au(NO_3)_4]^-$) nitric acid proves to be the only satisfactory medium for the study of physical properties and for recrystallization.[63]

A variety of other oxy salts give simple solutions (sulfates, phosphates, arsenates) provided the key element is in its highest oxidation state. Otherwise, oxidation (e.g., of chlorates, and elements P, S, Se, I) occurs. Iodine added to pure HNO_3 separates again as I_2O_5, and fluorine reacts smoothly to give FNO_3 and HF.

Nitric acid gives stable mixtures with several other inorganic acids, though the species formed in solution are often complex. Best known is the HNO_3–H_2SO_4 mixture, which has been reviewed elsewhere.[85,119] Solutions of HF have similar properties, due to reaction which has been confirmed by ^{14}N NMR spec-

$$HNO_3 + 2HF \rightarrow NO_2^+ + H_3O^+ + 2F^- \qquad (24)$$

troscopy.[120] Very few organic compounds give stable solutions, as they usually undergo nitration or oxidation. However, acetic acid is exceptional. Jander[118,121] made use of acetic acid and metal acetates in conductometric studies, and later work[122] has confirmed the stability of HOAc–HNO_3 mixtures. N_2O_5 is not detected in these mixtures, though it has been detected in mixtures of HNO_3 with the fully fluorinated CF_3COOH.[123,124]

E. Reaction with Metals

TABLE IV. Reaction of Pure HNO_3 with Metals

solution complete within			evidence of inhibition by film	no evidence of reaction
1 day (a)	1 week (b)	1 month (c)	(d)	(e)
Mg	Cr (powder)	Fe	Ca	Be
Sc		Mn	Cu	Al
V	Ni		Ag	Ti
Co	Cd		Bi	Pt
Zn	U			Sn
Hg				

As water is progressively removed from the aqueous acid, its chemistry changes, and beyond about 96–97% HNO_3 it becomes dominated by the NO_2^+ ion.[125,126] The acid undergoes no proton transfer to water molecules at the HNO_3 composition, and therefore it cannot be considered an acid, in the protonic sense, at this composition. The literature concerned with the reaction of metals (for the most part steels) with aqueous nitric acid is vast, but there is no published study, from the chemical point of view, of the reaction of steel or its constituent Fe, Cr, or Ni, with 100% HNO_3. The fact that the reactions which do occur are most likely attributable to NO_2^+ in the first instance has been postulated by two groups of workers.[74,127,128] D. M. Tallett[129] has recently carried out a survey to determine which metals are susceptible to attack by the pure acid, and this section will present his broad conclusions. A later section will then deal with the reactions of Fe, Cr, Ni, and Al[9,10] in more detail. In Tallett's experiments, 2-g specimens of the metal were immersed, without stirring, in HNO_3 at about 20 °C and observed over a period of 1 month. The results are summarized in Table IV. Of the 21 metals tested, about half of them showed little reactivity toward nitric acid, and the presence of, or formation of, surface films is the dominating factor. In this respect there are resemblances between liquid N_2O_4 and HNO_3. Sodium reacts immediately with liquid N_2O_4, but reaction soon ceases due to the cohesive film of $NaNO_3$ formed. The product with zinc, $Zn(NO_3)_2{\cdot}2N_2O_4$, is not cohesive, and has no influence on the reaction of the metal. In liquid nitric acid, the initial electron-transfer reaction:

$$M + NO_2^+ \rightarrow M^+ + NO_2 \qquad (25)$$

leads to the overall reaction:

$$M + 2HNO_3 \rightarrow MNO_3 + NO_2 + H_2O \qquad (26)$$

and nitrates are again produced at the metal surface. Those metals in columns a, b, and c of Table IV reacted steadily, with no evidence of film inhibition. Zinc showed the fastest reaction and is 10^3 times faster, at −20 °C, than is steel at +20 °C. The metals in column d showed visible evidence of the formation of a cohesive film, which quickly slowed the reaction. The metals in column e are either chemically inert toward HNO_3 in the true sense or possess oxide films before immersion which are stable in the liquid; these metals were added as bright specimens and retained their luster during long immersion. For the above reasons, it is not feasible to look for correlations between reactivity and the position of the metal in the periodic table. For instance, the series Be (no reaction), Mg (vigorous reaction), Ca (no reaction) is not consistent with the chemistry of these elements.

It is of interest that the metal nitrates which precipitated in the course of these experiments were those of the metals having M^{2+} as the highest oxidation state (Mg, Mn, Co, Cu, Zn, Cd, Hg), whereas those having higher available oxidation states (Sc^{3+}, Fe^{3+}, Cr^{3+}) gave stable solutions. The precipitates consist of lower hydrates of the metal nitrates, and these observations would suggest that the nitrato complexes of M^{2+} metals in solution, e.g., $[M(NO_3)_4]^{2-}$, are less resistant to attack by H_2O molecules than are those of metals in a higher oxidation state.

IV. *Dinitrogen Tetroxide–Nitric Acid Mixtures*

The significance of these mixtures has been discussed in the Introduction. Extensive thermodynamic[130,136] studies reveal that the thermal properties of N_2O_4, in solution in HNO_3, are similar to those of KNO_3. These and volumetric studies[131] were carried out from the standpoint, in recent years, of establishing engineering parameters in connection with the use of the mixtures as rocket oxidant fuels. They will not be reviewed here, but a reference to the phase system is necessary since this limits the available concentration ranges.

Since the mixture of these two liquids will be referred to repeatedly, the abbreviation "HNO_3–N_2O_4" will be used in the text and relative quantities specified only where they are chemically significant. Similarly, "HNO_3–N_2O_4–HF" and "HNO_3–N_2O_4–H_3PO_4" will be used to represent HNO_3–N_2O_4 to which a third solvent, HF or H_3PO_4, has been added.

A. *The Two-Phase System*

Suprisingly, the two liquids are not miscible in all proportions. The entire composition–temperature isobar has been covered down to −70 °C,[132,133] and the phase diagram is shown in Figure 9. The critical solution temperature is 60.9 °C, at a composition

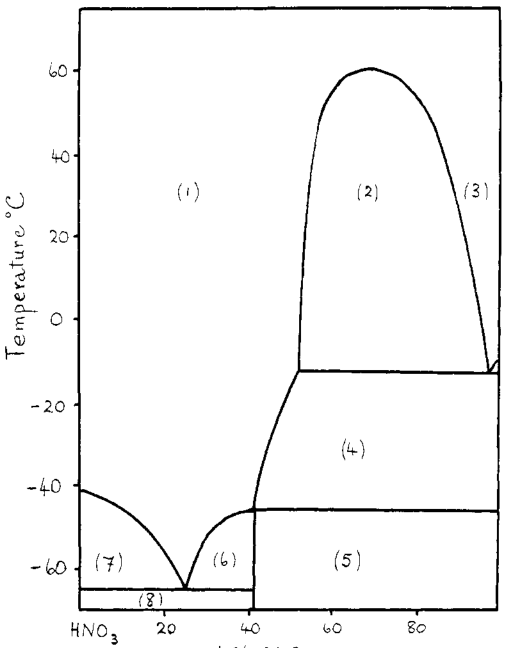


Figure 9. Phase system for HNO_3–N_2O_4 mixtures: (1) liquid A; (2) two liquids, A + B; (3) liquid B; (4) solid N_2O_4 + liquid A; (5) solid N_2O_4 + solid $N_2O_4 \cdot 2HNO_3$; (6) liquid A + solid $N_2O_4 \cdot 2HNO_3$; (7) liquid A + solid HNO_3; (8) solid HNO_3 + solid $N_2O_4 \cdot 2HNO_3$.

of 68.2 wt % N_2O_4. At room temperature (say 20 °C) an immiscibility region extends between about 54 wt % and 92 wt % N_2O_4, the system splitting into an upper N_2O_4-rich phase and a lower HNO_3-rich phase. (HDA contains 44 wt % N_2O_4.) These studies establish the existence of a solid compound, $(HNO_3)_2 \cdot N_2O_4$, which manifests itself as a eutectic of mp –65 °C at 25.6 wt % N_2O_4, confirming earlier data.[134] Values for the density and viscosity of the liquid mixtures[135] pass through a maximum at a composition corresponding to $(HNO_3)_2 \cdot N_2O_4$. These physical properties are not greatly influenced by the small degree of self-dissociation of the two liquids and reflect association in the liquid state between the large majority of covalent molecules present. This behavior is very reminiscent of the 2:1 association which takes place between electron-donor organic solvents when mixed with N_2O_4 (section IID,1).

B. *Species Present in the Liquid*

At concentrations up to about unit molarity, the dissociation of N_2O_4 in nitric acid solution ($N_2O_4 \rightarrow NO^+ + NO_3^-$) is virtually complete;[138] N_2O_4 behaves as a strong electrolyte, and the conductance–concentration curves for N_2O_4, NH_4NO_3, and KNO_3 solutions are almost identical.[137] Bands clearly attrubutable to NO^+ and NO^{3-} are seen in the Raman[138] and infrared spectra[139] of the dilute solutions. The 2300-cm^{-1} band characteristic of the free NO^+ ion is moved to 2240 cm^{-1}. This is close to the shift observed for the $N_4O_6^{2+}$ group in the compound $(N_4O_6)^{2+}[Fe(NO_3)_4]_2^-$ already discussed (Section IIF,2), and there is now every reason for believing that this association ($3NO^+ \text{-} NO_3^-$) occurs also in solutions of N_2O_4 in HNO_3.

The self-ionization of nitric acid (eq 23) appears to be suppressed appreciably by added nitrate ions, and thus by added N_2O_4. At concentrations as low as 1 wt % N_2O_4, the Raman and infrared bands associated with NO_2^+ could not be detected, though the chemistry of the mixtures indicates that this ion is present to some degree at all compositions. Suppression of the HNO_3 self-ionization will also, of course, reduce the concentration of H_2O molecules to a corresponding degree.

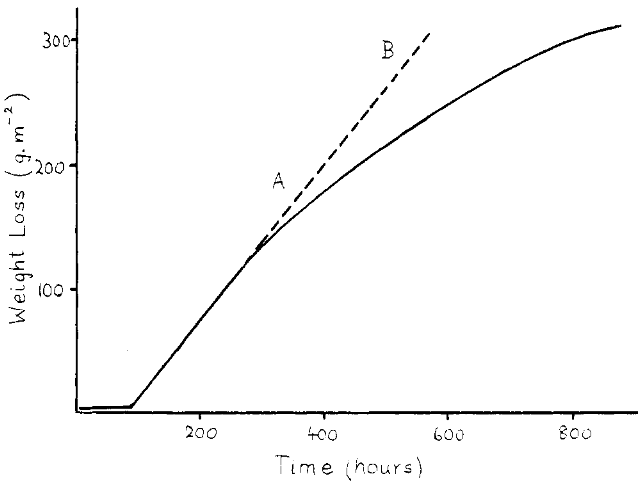


Figure 10. Rate of reaction of an unstirred specimen of 321 steel in 34 wt % N_2O_4 in HNO_3, at 20 °C.

The actual quantity of un-ionized N_2O_4 (and NO_2) present in dilute solution is still subject to some doubt. NO_2 absorbs only weakly in the Raman spectra,[138] and bands due to N_2O_4 or NO_2 were not observed in the infrared spectra of dilute solutions of N_2O_4.[139] Results based on optical absorbance measurements[126] are not precise, but the excellent agreement in the conductivities of solutions of N_2O_4, NH_4NO_3, and KNO_3 could not arise unless the quantity of N_2O_4 remaining un-ionized was very small. Nevertheless, even the most dilute solutions of N_2O_4 in HNO_3 show some yellow color. At higher concentrations, the quantities of N_2O_4 and NO_2 increase[139] as expected. The electrical conductivity of solutions containing more than 24 wt % N_2O_4 no longer increases with N_2O_4 concentration; indeed, a steady decrease is observed until phase separation begins (at 54 wt % N_2O_4). Over this range, much of the N_2O_4 is acting merely as an inert diluent of low dielectric constant.[97]

To summarize, it would seem that the important species present in HNO_3–N_2O_4 mixtures are as follows:

$$NO^+,\ NO_2^+,\ NO_3^-,\ H_2O,\ HNO_3,\ NO_2,\ N_2O_4$$

and these are the species most likely to appear in reaction products of the mixture with metals. A number of other species arise from the solvation of the first four of these species by the last three; these can be detected by spectroscopic methods, but are probably less significant in reaction chemistry.

C. Rates of Reaction with Metals

A typical weight loss–time curve for a metal immersed in HNO_3–N_2O_4 is shown in Figure 10. In this example the metal used was 321 steel (Cr 18%, Ni 8%),[173] but curves similar in shape are given also by the separate constituent metals Fe, Cr, and Ni.[9,10,129] The solution was analyzed periodically for each metal by atomic absorption and the values were converted to a total weight loss value. Each curve falls clearly into three parts, an induction period, then a steady reaction rate which is characteristic of the metal concerned and the composition of the medium (AB, Figure 10), followed by a levelling off of the rate curve. The induction period is not relevant here; it is concerned with surface condition and may vary from 0 to 10 days, depending on the metal used. All reaction curves tend to level off on long immersion, and this is more pronounced at high N_2O_4 concentrations. All results point to the conclusion that this is due largely to saturation of the liquid by corrosion products and that passivation by surface films plays a relatively minor role. Comparisons of reaction rates for different metals must always be carried out at the same ratio of liquid volume to metal surface area, as the shape of the reaction curve (particularly the stage at which the curve, Figure 10, levels off) varies with this ratio. The larger the available volume of liquid, the lower

SCHEME I. Reactions of Nickel with HNO_3-N_2O_4 Mixtures

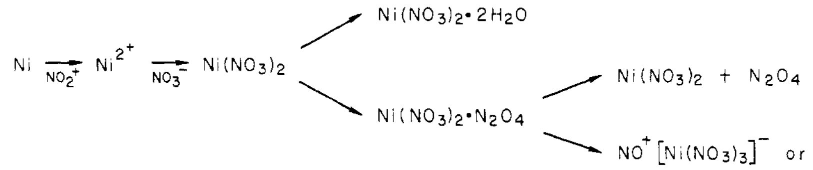


TABLE V. Influence of Temperature on Rate of Reaction of 321 Steel with 44% N_2O_4 in HNO_3

temp, °C	reaction rate, g m^{-2} h^{-1}
10	0.075
20	0.330
30	0.975

will be the concentration set up by solution of a given quantity of metal so that a higher reaction rate can be maintained for a longer period.

When an alloy (e.g., steel) is used, the component metals do not act independently, since the electrons occupy a conduction band which differs in energy range and profile from the conduction bands of the individual metals. Therefore, when one of the metals can no longer dissolve because its saturation limit has been reached, the other component metals also cease to react, no matter how high the solubility of their reaction products may be. This "Alloy Effect" is well illustrated in the reaction of steel; nickel reaction products have low solubility whereas the solubility of the iron and chromium products is high. During reaction, and up to the stage when reaction ceases, Fe, Cr, and Ni are present in solution in the same proportion as occurs in the solid metal, but the final quantities bear no relation to the respective solubilities. Reaction therefore becomes slow as the solution approaches saturation with respect to nickel. Again, when fresh metal samples are introduced to a solution already containing a high concentration of reaction products, the reaction rate is greatly reduced.

The characteristic reaction rate (AB, Figure 10) occurs over a period during which the concentration of products is too small to influence the reaction, and is readily measured. This rate increases considerably with temperature, and some values are given in Table V. The way in which this rate varies with liquid composition is shown in Figure 11, using similar metal samples as were used for Figure 10. The rate is highest with pure HNO_3 and falls dramatically as N_2O_4 is added. A satisfactory interpretation is to be found in terms of the equilibria discussed in section IVB, which indicate that the active species in the liquid is the NO_2^+ ion and that the basic reaction of (e.g.) nickel is:

$$Ni + 2NO_2^+ \rightarrow Ni^{2+} + 2NO_2 \qquad (27)$$

The NO_2^+ content of the liquid is highest in the pure acid, and the effect of added N_2O_4 is twofold. It can act as an inert diluent, but this alone does not explain the observation that the rate falls to $^1/_{50}$th of the pure acid value for a 50% dilution by N_2O_4. Much of the effect must, therefore, be attributed to the suppression of self-dissociation of HNO_3 (eq 23) by added N_2O_4, for which there is ample spectroscopic evidence (Section IVB). The NO_2^+ concentration is thereby reduced, and hence the reaction rate also.

These systems are remarkable in that stirring the specimen has no effect on the rate of attack on the metal, and this supports the above mechanism. With many (especially protonic) liquids, metal reaction rates have no significance unless the specimen is stirred rapidly to disperse all reaction products. Experiments on unstirred specimens (as in Figure 10) were continued until the characteristic rate range was reached, and then stirred at 250 rpm, without any effect on the reaction rate. In eq 27, the active species NO_2^+ is converted to NO_2, which merges with the medium.

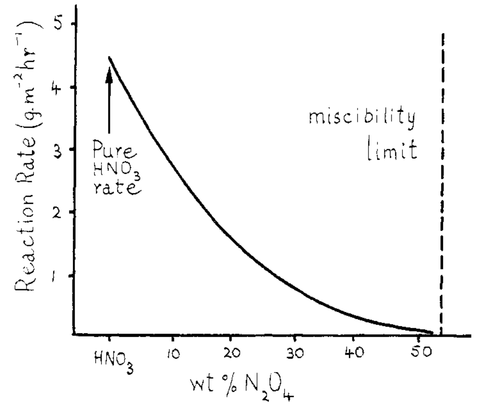


Figure 11. Variation in characteristic reaction rate of 321 steel with composition of HNO_3-N_2O_4 mixture (20 °C).

TABLE VI. Products of Reaction of Metals with HNO_3-N_2O_4 Mixtures

metal	probable species in solution	solid products
Ni	$[Ni(NO_3)_4]^{2-}$	$Ni(NO_3)_2 \cdot 2H_2O$
Fe	$[Fe(NO_3)_4]^-$	$Fe(NO_3)_3 \cdot 2H_2O$
Cr	$[Cr(NO_3)_5]^{2-}$	$Cr(NO_3)_3 \cdot 2HNO_3 \cdot 4H_2O$ $Cr(NO_3)_3 \cdot 2HNO_3$ $Cr(NO_3)_3 \cdot 5H_2O$
321 steel	all above species	$Ni(NO_3)_2 \cdot 2H_2O$
Al	$[Al(NO_3)_4]^-$	$Al_3O(NO_3)_7 \cdot 8H_2O$ $Al(NO_3)_3 \cdot 6H_2O$

V. Reaction Products of Ni, Fe, Cr, and Al with HNO_3-N_2O_4

Since metal salts in pure HNO_3 undergo solvolysis and are isolated as the metal nitrate hdyrates (Section IIIB and Table III), it might be assumed that reaction of metals with HNO_3 or its mixtures with N_2O_4 would yield similar products. In fact, the products quoted (Table III) are those which remain as solids when solvent is removed. During this process, the more volatile components of the liquid are removed first, and the concentration of the original product is then increased, in pure HNO_3, until separation of solid occurs. It follows that such solids are not necessarily the products first produced when a metal reacts with HNO_3-N_2O_4, and in order to understand the mechanism of corrosion of metals by these mixtures,[9,10,143] the reactions have been examined in more detail.

The compounds involved are summarized in Table VI. Using the chemistry discussed earlier, we may first consider the various possibilities which exist in the reactions of nickel with HNO_3-N_2O_4; these are correlated in Scheme I. The metal is attacked by NO_2^+, and the Ni^{2+} ion leaves the metal surface using NO_3^- ions as ligands. The covalent $Ni(NO_3)_2$ which then enters the solution has two alternatives; it may associate with the H_2O molecules present to form the dihydrate, or with N_2O_4 molecules to form an adduct, but will not remain as the simple covalent nitrate except in very dilute solution. The N_2O_4 adduct may be present in solution as either the $[Ni(NO_3)_3]^-$ or the $[Ni(NO_3)_4]^{2-}$ ion. The former involves bridging NO_3^- groups, and for this reason the $[Ni(NO_3)_4]^{2-}$ ion is the more likely. In this ion, 6-coordination of the metal is maintained by using bidentate and

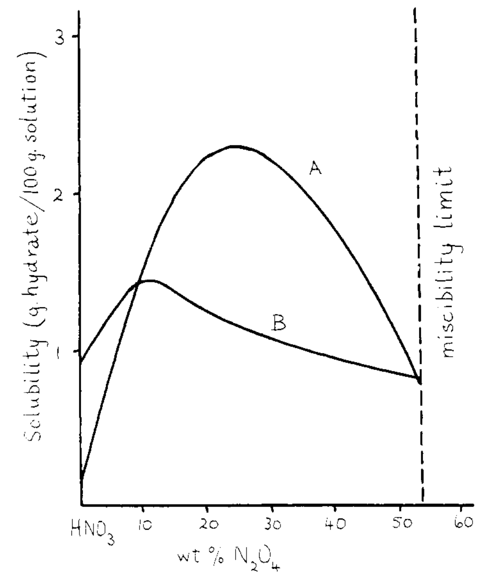


Figure 12. Solubilities of $Ni(NO_3)_2 \cdot 2H_2O$ (curve A) and $Al(NO_3)_3 \cdot 6H_2O$ (curve B) in HNO_3–N_2O_4 mixtures at 0 °C.

unidentate ligands. In the solid state, the ion requires a large cation for stability,[140] but this is probably irrelevant in this medium, especially in view of the high concentration of nitrate ions. The two most likely species are, therefore, the two closely similar complexes $[Ni(NO_3)_2 \cdot (H_2O)_2]$ and $[Ni(NO_3)_4]^{2-}$, in each of which Ni^{2+} is 6-coordinated by oxygen atoms.[140,142,144,145] In the event, an equilibrium exists between these species, the position of which varies with conditions, and the following are the determining factors: (a) H_2O and NO_3^- are in competition as ligands. In a high H_2O concentration (e.g., in aqueous solution) NO_3^- is extremely weak in ligand strength. However, analysis of the spectral data for $[Ni(NO_3)_4]^{2-}$ compounds shows that NO_3^- in nitromethane solution occupies a position only slightly lower than H_2O in the spectrochemical series,[141] i.e.

$$\begin{array}{lcccc} & H_2O > & NO_3^- > & Me_2SO > & Cl^- \\ Dq & 860 & 801 & 773 & 720 \end{array}$$

and in an HNO_3–N_2O_4 medium, H_2O and NO_3^- may be regarded as having comparable ligand strength. (b) In general, nitrate hydrates have low solubilities in HNO_3 and HNO_3–N_2O_4 mixtures, whereas nitrato complexes have high solubilities.

The general pattern set out in Scheme I applies to other metals also, but the route taken varies with the metal concerned. In the case of nickel, the low solubility of the dihydrate coupled with the instability of $[Ni(NO_3)_4]^{2-}$ leads to the ready formation of dihydrate. Thus when nickel foil is added to HNO_3, or a mixture containing up to about 50% N_2O_4, reaction is immediate. Nitrous oxide is evolved, and from a green solution, green crystals of $Ni(NO_3)_2 \cdot (H_2O)_2$ separate almost immediately. Reaction continues steadily until all metal is converted to the solid dihydrate. However, the operation of equilibrium 28 accounts

$$[Ni(NO_3)_2 \cdot (H_2O)_2] \underset{H_2O}{\overset{NO_3^-}{\rightleftharpoons}} [Ni(NO_3)_4]^{2-} \qquad (28)$$

satisfactorily for the unusual solubility changes shown in Figure 12. The solubility of nickel nitrate dihydrate in pure HNO_3 is very low, but on addition of N_2O_4 solubility increases rapidly. If N_2O_4 acted merely as an inert diluent of low dielectric constant, it should depress the solubility, so that the considerable increase must be related to a change in the dissolved species. Addition of N_2O_4 increased the NO_3^- content of the medium and at the same time suppresses the self-dissociation of HNO_3, and hence the H_2O content of the liquid. In consequence, equilibrium 28 moves to the right, giving rise to the more highly soluble nitrato complex. Solubility passes through a maximum at 25 wt % N_2O_4, after which the solubility of the nitrato complex diminishes in a medium of decreasing dielectric constant; it is zero, of course, in pure N_2O_4. Walker[143] has compared the effect of temperature on solubility at compositions on either side of the solubility maximum. In mixtures containing 15.7 and 32.5 wt % N_2O_4, the temperature coefficients (g of solute per 100 g of solution per degree) are 0.0035 and 0.066, giving values for ΔH_s, the molar heats of solution, of −1.2 and −5.8 kJ mol^{-1}, respectively. The appreciable difference observed is consistent with a change in species with composition.

In his survey of metal–HNO_3 reactions (Table IV), Tallett[129] found a group of metals (Mn, Co, Cu, Zn, Cd) where the reaction with HNO_3 responded similarly to N_2O_4 addition and whose chemistry may well resemble that of nickel. With these metals the reaction rate with HNO_3 was increased, or at least maintained on addition of N_2O_4, and precipitation of a hydrate was either retarded or prevented.

Iron takes the alternative route to that of nickel. The metal reacts steadily with HNO_3 or HNO_3–N_2O_4, and a brown solution develops which is identical with that formed on solution of $NO^+[Fe(NO_3)_4]^-$. No precipitation occurs, and the solubility is so high that the liquid eventually becomes viscous. Equilibrium 28 is clearly well to the right because of the high stability of $NO^+[Fe(NO_3)_4]^-$, but it does still operate. If the N_2O_4 is removed from the solution by evaporation (thus reducing the NO_3^- concentration and increasing the H_2O concentration) and the remaining solution submitted to 10^{-3} mmHg vacuum for 7–14 days, a light brown powder remains which is polymeric and has empirical formula $Fe(NO_3)_3 \cdot 2H_2O$. However, this compound is readily converted back to $NO^+[Fe(NO_3)_4]^-$ by treatment with N_2O_4, whereas $Ni(NO_3)_2 \cdot 2H_2O$ is unaffected by N_2O_4. Accurate values for the solubility of $NO^+[Fe(NO_3)_4]^-$ in nitric acid are difficult to obtain because of its magnitude, and a value of 33 g/100 g of solution[129] is probably an underestimate. The solubility is decreased on addition of N_2O_4, which is to be expected where no change in dissolved species is involved.

The corresponding chemistry of chromium is very similar in principle to that of iron. When chromium metal (or, more conveniently, chromium carbonyl) is added to HNO_3–N_2O_4, a stable green solution develops, which no doubt contains the highly stable complex $(NO^+)_2[Cr(NO_3)_5]^{2-}$ already described. No precipitation occurs, and the nitrate ligands in the complex are even more resistant to substitution by H_2O molecules than in the case of $[Fe(NO_3)_4]^-$. Thus, evacuation of the green solution at 10^{-3} mmHg for several days at 20 °C yields a green powder, $Cr(NO_3)_3 \cdot 2HNO_3 \cdot 4H_2O$, which may have the composition $H_2[Cr(NO_3)_5] \cdot 4H_2O$. Prolonged evacuation at −20 °C can give purple crystals of $Cr(NO_3)_3 \cdot 2HNO_3$ (or $H_2[Cr(NO_3)_5]$ anhydrous) and green crystals of the hydrate $Cr(NO_3)_3 \cdot 5H_2O$. The dihydrate obtained by Hathaway and Underhill[100] from the $CrCl_3$–HNO_3 reaction was not observed in these experiments.

It is of interest to compare the behavior of steel in HNO_3 and HNO_3–N_2O_4 with that of the separate components discussed above. After 20 days at 20 °C a green solution is obtained in HNO_3, which contains Fe, Cr, and some Ni, but the green precipitate which then begins to separate consists only of $Ni(NO_3)_2 \cdot 2H_2O$. In contrast, the reaction with a 44% N_2O_4 mixture, carried out under the same conditions, gave no precipitate even after 36 weeks. This is consistent with the solubility curve shown in Figure 12.

Aluminum resembles nickel much more than iron in its reactions with HNO_3–N_2O_4, and this is a reflection of its reluctance to form $Al(NO_3)_3$–N_2O_4 adducts and the relative instability of its nitrato complexes (section IIF,4). Thus, Al metal first dissolves in a 44% N_2O_4 mixture to give an apparently stable solution. If this is evaporated immediately, a precipitate of the oxide nitrate $Al_3O(NO_3)_7 \cdot 8H_2O$ is obtained as a pale yellow powder. However, if the solution is allowed to stand for 3 months in a closed vessel, pale yellow crystals of the hydrate $Al(NO_3)_3 \cdot 6H_2O$ separate. In this compound the Al^{3+} ions are octahedrally coordinated by six H_2O molecules, and the NO_3^- ions are not bonded to the metal ion. The solubility of this hydrate passes through a maximum with increasing N_2O_4 concentration and is shown in Figure 12. The variation in solubility is not so pronounced as for the nickel compound and passes through a maximum at a lower N_2O_4 concentration. A similar equilibrium in solution:

$$[Al(H_2O)_6]^{3+} \underset{H_2O}{\overset{NO_3^-}{\rightleftharpoons}} [Al(NO_3)_n]^{n-3} \qquad (29)$$

allows the Al^{3+} to retain its 6-coordination by oxygen atoms; the value of n (4, 5, or 6) is not yet known, but it seems that this equilibrium is moved to the right more readily than in the case of nickel (eq 28).

VI. Reactions in HNO_3-N_2O_4-HF Mixtures

The rate and extent of the reactions of HNO_3-N_2O_4 with the constructional metals Fe, Cr, Ni, and Al are such as to render these metals quite unacceptable as containing vessels for the mixture. It has been found in practice, however, that the addition of about 0.7 wt % of HF to the mixture reduces the corrosion rate by a factor of over 100, rendering these metals acceptable as containers, and the N_2O_4 (44%)-HNO_3 (56%) mixture with 0.7 to 1.0% HF added (termed "standard HDA") is in current use as a rocket oxidant fuel. Standard HDA comes into contact mainly with steel and aluminum, and the experiments reviewed below were carried out to determine to what extent and in what way the added HF influences the solution chemistry of these metals; higher concentrations of HF than the specification value quoted above were used when necessary, but this does not affect the chemistry involved.[9,10,146]

Steel samples remain bright throughout experiments of some weeks duration in the HF-inhibited mixture, and reaction rate measurements show no induction period (compare Figure 10). The way in which HF functions as a reaction inhibitor has been discussed for some years and is still not resolved; it may be a surface effect, a solubility effect, or both. Fluorine can be detected on the metal surface after immersion, by electron spectroscopy,[146] but there is no rigid physical barrier to chemical reaction; when steel samples which had been immersed in Hf-inhibited mixture for 800 h were transferred to the uninhibited mixture, they immediately reacted at the rapid rate characteristic of the simple HNO_3-N_2O_4 mixture. It can be argued that the low solubility of some of the fluorine-containing reaction products is largely responsible for reducing the reaction rate.

When HF is added to the mixture, the well-known reactions 30–33 will occur, so that the only important added species, which

$$2HF + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2F^- \qquad (30)$$

$$HF + F^- \rightarrow HF_2^- \qquad (31)$$

$$N_2O_4 + HF \rightarrow NOF + HNO_3 \qquad (32)$$

$$NOF + H_3O^+ \rightarrow NO^+ + HF + H_2O \qquad (33)$$

might be expected to occur in some of the reaction products, is the fluoride ion. However, at low N_2O_4 concentrations there is a small concentration of HF in the vapor over the mixture which is sufficient to be detectable in the infrared spectrum of the vapor by a characteristic band at 3861 cm^{-1}.

The reactions of metals with the inhibited liquid are so slow that reaction products are not available in sufficient quantity by direct reaction. The approach has, therefore, been to allow some of the metal to dissolve in the absence of HF; the solution was then cooled in liquid nitrogen, about 1% HF added, and the whole mixture then warmed to room temperature. These reactions are of particular interest in that the literature contains very few examples of reactions carried out in a mixture of three liquids, each of which is an established nonaqueous solvent in its own right. The medium now contains three potential ligands (NO_3^-, H_2O, and F^-) which compete for bonding with the metal ion, and their relative success varies with the particular metal used.

TABLE VII. Products of Reaction of Metals with HNO_3-N_2O_4-HF Mixtures

metal	probable species in solution	solid products
Cr	$[CrF_6]^{3-}$	$CrF_3 \cdot 3H_2O$
Fe	$[FeF_6]^{3-}$	$FeF_3 \cdot 3H_2O$
Ni	$[Ni(NO_3)_4]^{2-}$	$Ni(NO_3)_2 \cdot 2H_2O$
Al	$[AlF_6]^{3-}$	$Al_2OF_4 \cdot 5H_2O$

The compounds produced are collected in Table VII. The reactions which chromium solutions undergo are as follows:

$$[Cr(NO_3)_5]^{2-} \xrightarrow{a} [CrF_6]^{3-} \xrightarrow{b} CrF_3 \cdot 3H_2O \qquad (34)$$

Preparation of the original solution from chromium carbonyl and nitric acid involved the introduction of about 4% of N_2O_4 into the HNO_3, and this dilute N_2O_4 solution was used to facilitate detection of HF in the vapor. (Evidence for the presence of the $[Cr(NO_3)_5]^{2-}$ ion in the green solution so produced has been presented in section V.) HF vapor was then added, in aliquots, to the solution, and the infrared spectrum of the vapor was monitored. No HF whatsoever was detected until the $F^-:Cr^{3+}$ ratio reached 6:1, after which HF was immediately detectable in the vapor, indicating the appearance of uncomplexed F^- in solution. The identity of dissolved complexes is always difficult to establish in these highly reactive media, but this attractive experiment[147] leaves little doubt that step a involves the formation of the $[CrF_6]^{3-}$ ion, and also that F^- is a stronger ligand toward Cr^{3+} in the medium than is NO_3^-. In step b, the solution was placed under vacuum at 10^{-3} mmHg; this removed N_2O_4, the self-ionization of HNO_3 was no longer suppressed and so the H_2O concentration increased, and the hydrate $CrF_3 \cdot 3H_2O$ was deposited quickly as a green powder. This compound will dissolve in pure HNO_3 and recrystallize unchanged, with no evidence of HF formation in the vapor phase. In this medium, therefore, ligand strengths toward Cr^{3+} are in the order $H_2O > F^- > NO_3^-$, but there is so little difference between them that products can be varied by very small changes in conditions.

The chemistry of iron solutions is broadly similar, i.e., the reactions

$$[Fe(NO_3)_4]^- \xrightarrow{HF} [FeF_6]^{3-} \xrightarrow{10^{-3}\ mm} FeF_3 \cdot 3H_2O \qquad (35)$$

describe the behavior of dilute (<0.5 wt % Fe) iron solutions. Stronger solutions can be complicated by the formation of gels. Thus, when HF is added to a more concentrated solution of the iron complex in 44% N_2O_4 in HNO_3 at −196 °C and the whole raised to room temperature, a rigid gel is usually produced, and evacuation at 10^{-3} mm for 12 h is necessary to reduce this to green crystals of $FeF_3 \cdot 3H_2O$. It seems likely that some aquation commences as soon as the $[FeF_6]^{3-}$ ion is formed and that the rigid gel consists of a three-dimensional lattice held together by hydrogen bonds and fluorine bridges. The compound $FeF_3 \cdot 3H_2O$ has special importance as it is the least soluble product formed by corrosion of steel in standard HDA and therefore likely to be the reaction product which will control corrosion rate and separate from the liquid. The compound exists in two forms. The β form is obtained by crystallization at 50 °C from a solution of iron oxide hydrate in dilute aqueous HF. Crystals are pink, and a crystal structure determination shows that each Fe^{3+} ion is surrounded octahedrally by six ligands which consist of two bridging F^- ions, two F^- ions, and two H_2O molecules.[148] The

TABLE VIII. Influence of HF and PF_5 on Rates of Reaction with 321 Steel

medium	weight loss ($g\ m^{-2}$) after 28 days[a]
(a) N_2O_4 (44 wt %), HNO_3 (56 wt %)	330
(b) (a) + 0.7 wt % HF	2.85
(c) (a) + 0.7 wt % PF_5	0.64

[a] Identical metal samples, unstirred, in Teflon (polytetrafluoroethylene) vessel at 34 °C.

α form is white, and is isomorphous with α-$AlF_3 \cdot 3H_2O$. B. Mellor[10,146] has found that the trace of sediment formed in a steel vessel which had contained standard HDA for 10 months was indeed a hydrate of FeF_3, but the precise degree of hydration and the crystal form of this important sediment are not yet determined. Gel formation also has practical significance; blockages in the narrow tubes through which the oxidant liquid in a rocket engine is delivered to the burner can be caused by gel-like deposits.

The behavior of aluminum compounds in N_2O_4-HNO_3-HF mixtures parallels closely that of iron. The ion $[AlF_6]^{3-}$ is produced on initial addition of HF, and gel formation is a common feature. The solid obtained by removal of solvent under vacuum is the oxide fluoride $Al_2OF_4 \cdot 5H_2O$, which recalls the readiness with which Al forms oxide nitrates rather than simple nitrates (section V).

Chromium, iron, and aluminum therefore conform to the same pattern in which fluoro complexes are formed in the ternary mixture, and hydrated fluorides are the ultimate products. Nickel, however, provides a complete contrast. When $Ni(NO_3)_2 \cdot 2H_2O$ is dissolved in pure HNO_3, or any HNO_3-N_2O_4 mixture within the available composition range, and a few percent of HF added, the nitrate dihydrate separates unchanged on evaporation of the liquid. In fact, using solutions in pure HNO_3, it is necessary to add HF up to 70 mol % before the green color of the nitrate changes to the yellow color of nickel fluoride. $NiF_2 \cdot 2H_2O$ evolves HF vapor when added to nitric acid and is converted to $Ni(NO_3)_2 \cdot 2H_2O$. Similarly, $CuF_2 \cdot 2H_2O$ is converted to hydrated $Cu(NO_3)_2$ in nitric acid, and CdF_2 yields anhydrous $Cd(NO_3)_2$. In all these compounds, the solid or dissolved species normally consist of metal atoms which are 6-coordinated by oxygen atoms (from H_2O or NO_3^-) or F^- ions. It would seem that in contrast to the M^{3+} ion chemistry discussed above, there is a group of M^{2+} ions (Ni, Cu, Cd, and perhaps Mn, Co, and Zn also) where coordination by F^- is so weak by comparison with H_2O or NO_3^- that fluorides cannot be separated from the medium unless the HF content is extremely high. For these reasons, nickel will play no part in the HF inhibition of steel corrosion by HNO_3-N_2O_4.

VII. Solutions of PF_5 in HNO_3-N_2O_4 Mixtures

The literature contains few references to the properties of solutions of nonmetal compounds in N_2O_4 (section IIC), HNO_3 (section IIID), or their mixtures, so that a detailed study of PF_5 solutions has academic merit. The practical justification lies in Table VIII,[10,129,146] which shows that the corrosion rate of steel is reduced by a factor of over 500 by the addition of a very small amount of PF_5. As with HF addition, there is no rigid barrier to chemical reaction which is set up at the metal surface on addition of PF_5, although F, O, and P can be detected on the surface using electron microscopy.[146] The reaction rates will again be greatly influenced by the solubility of products formed by reaction of the metals with species in solution, and for this reason also it was necessary to identify these species. It should be noted, however, that the effect of PF_5 illustrated in Table VIII is not a universal one, since the reaction rate of N_2O_4-HNO_3 mixture with pure iron is actually increased on PF_5 addition.[149] When prepared on a large scale for use in rocketry, the solution of 0.7 wt % PF_5 in N_2O_4-HNO_3 mixtures is termed "modified HDA".

TABLE IX. ^{19}F and ^{31}P Chemical Shifts[a] (δ, ppm) and Coupling Constants (J, Hz)[153]

species	^{19}F δ	^{19}F J_{F-P}	^{31}P δ	^{31}P J_{F-P}
PF_6^-	+72.2	715	+118	710
PF_5	+77.9	930	+35.1	1010
POF_3	+95.7	1060	+35.5	1080
HPO_2F_2	+88.9	980	+20.1	985
H_2PO_3F	+76.1	955	+8.0	955
H_3PO_4	-	-	0.0	-
HF	+200.9	-	-	-
F^-	+126.1	-	-	-
PO_4^{3-} (154)	-	-	ca. −6	-
$P(OH)_4^+$ (155)	-	-	(−0.6 to −2.1)	-

[a] Chemical shifts referred to $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P) as external standards; the positive sign indicates a shift to higher magnetic field at a constant resonant frequency.

A. PF_5 Reaction with HNO_3

Two earlier papers made reference to this reaction. Kuhn and Olah[150] reacted HNO_3 with PF_5 in the presence of a small amount of HF to give nitronium hexafluorophosphate ($NO_2^+PF_6^-$) and a fluorophosphoric acid. In subsequent work[151] the products mentioned were $NO_2^+PF_6^-$, POF_3, and HF at ordinary pressures, with the appearance of orthophosphoric acid at higher pressures. Facilities are now available for the study of such reactions using ^{19}F NMR spectroscopy, and the potential of fast Fourier transform ^{31}P NMR spectroscopy has recently been demonstrated for solutions of phosphorus halides in strong acid media.[152] Both ^{19}F and ^{31}P NMR spectroscopy have, therefore, been employed in recent reinvestigation of this reaction.[10,149] Some values of chemical shifts and coupling constants for relevant P and F compounds are collected in Table IX, in order to illustrate the value of these techniques in differentiating between the various possible reaction products.

A sample of solid, pure HNO_3 was held at −196 °C, and 5 wt % PF_5 condensed on to it, using fluoroplastic equipment. When the mixture was warmed to room temperature a homogeneous liquid was obtained, from which a white crystalline solid separated. This was shown to be $NO_2^+PF_6^-$ by analysis, X-ray crystallography, and infrared and Raman spectroscopy. An infrared spectrum of the vapor phase over the liquid showed the presence of HNO_3, HF, PF_5, and POF_3, and the concentration of the latter two compounds decreased with time. The experiment was repeated in a Kel-F NMR tube, and the ^{19}F and ^{31}P NMR spectra of the "bulk liquid" were taken. These showed the presence of HF, HPO_2F_2, and PF_6^- in solution but also confirmed the absence of POF_3, orthophosphoric acid, and any other fluorophosphoric acid other than HPO_2F_2. Equation 36,

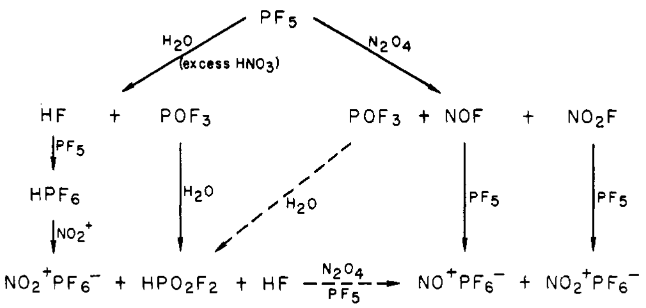
$$3PF_5 + 2HNO_3 \rightarrow 2NO_2PF_6 + HPO_2F_2 + HF \qquad (36)$$

therefore, represents the reaction in HNO_3 solution. This is basically a limited hydrolysis reaction, employing the H_2O produced by HNO_3 self-ionization.

B. PF_5 Reaction with N_2O_4

Hydrolysis is not possible in this reaction, and the basic step involves oxygen atom transfer (section IID,2). Peacock and Wilson[156] identified nitrosonium hexafluorophosphate ($NO^+PF_6^-$) as a reaction product and also discussed the reaction in terms of an unstable intermediate NO_2POF_4, which decomposed to yield POF_3 and NO_2F. This reaction has also been re-examined with the advantage of ^{19}F and ^{31}P NMR spectroscopy.[10,149] When PF_5 is added to liquid N_2O_4, the white solid which separates is a mixture of $NO^+PF_6^-$ and $NO_2^+PF_6^-$; being ionic salts, they are

SCHEME II. Reactions of PF_5 with HNO_3-N_2O_4 Mixtures



quite insoluble in N_2O_4. Using a range of concentrations, it was shown quite clearly that the only species remaining in solution was molecular POF_3 which did not diminish in quantity with time. The overall reaction is, therefore

$$3PF_5 + N_2O_4 \rightarrow NOPF_6 + NO_2PF_6 + POF_3 \quad (37)$$

C. PF_5 Reaction with HNO_3–N_2O_4 Mixtures

The various steps which lead to the final products of this reaction are set out in Scheme II. This scheme is known to apply to PF_5 concentrations up to 10%, and probably applies beyond this. At the higher concentrations, $NO_2^+PF_6^-$ and $NO^+PF_6^-$ crystallize from solution but remain soluble at the low concentrations (<1% PF_5) used in modified HDA. The scheme is also applicable over a wide N_2O_4–HNO_3 composition range. The overall reaction can be regarded as the sum of the separate reactions with HNO_3 and with N_2O_4 when allowance is made for the decomposition of HNO_3 products in N_2O_4, and vice versa. Thus, the HF produced by PF_5 in HNO_3 will react with N_2O_4 (eq 32), and the POF_3 which is a stable product of the N_2O_4 reaction will be hydrolyzed by H_2O molecules introduced with HNO_3. The ^{19}F and ^{31}P spectroscopy of solutions of up to 10% PF_5 in 44% N_2O_4 in HNO_3 showed the complete absence of HF or POF_3 in the solution, but confirmed the presence of PF_6^- and HPO_2F_2.

The reaction of PF_5 with excess HNO_3–N_2O_4 is, therefore, represented fully by eq 38. This implies that the PF_6^-:HPO_2F_2

$$4PF_5 + HNO_3 + N_2O_4 \rightarrow 2NO_2^+PF_6^- + NO^+PF_6^- + HPO_2F_2 \quad (38)$$

ratio in solution should be 3:1 for HNO_3–N_2O_4 and <3:1 for HNO_3 solutions. By integration of ^{19}F resonances, it has been shown that this is indeed the case.[149] The products of reaction shown in eq 36, 37, and 38 are stable on standing in the appropriate medium for 8 days, and probably for much longer periods.

The acid HPO_2F_2 can be substantially protonated only in very strong acids,[157] and HNO_3 will not be sufficiently strong for this purpose, especially when mixed with N_2O_4. Neither is it likely to be dissociated. ^{19}F and ^{31}P measurements confirm[149] that HF and H_3PO_4 exist in HNO_3–N_2O_4 solution as undissociated molecules, and since HNO_3 is itself present in molecular form, there seems no reason to assume that the stable compound HPO_2F_2 is other than in molecular form also. This is consistent with its high solubility in HNO_3–N_2O_4 and HNO_3, compared with the low solubility of the ionic compounds $NO_2^+PF_6^-$ and $NO^+PF_6^-$.

D. Hydrolysis in HNO_3 and HNO_3–N_2O_4

In dilute PF_5 solutions in HNO_3, sufficient H_2O molecules are present, from self-dissociation of the acid, to hydrolyze PF_5 completely to H_3PO_4, yet this does not occur. Reference has been made (section IIIB) to the solvation of H_2O molecules by HNO_3, and these PF_5 reactions provide excellent examples of the extent to which such solvation restricts the normal chemical reactivity of the H_2O molecules in solution. In pure HNO_3 (eq 36), two out of the three PF_5 molecules involved in the reaction become fixed in solution as PF_6^- complexes, and in HNO_3–N_2O_4 (eq 38) three out of four PF_5 molecules are stabilized in this way. This PF_6^- group is not resistant to hydrolysis in aqueous solution, so that the solvated H_2O molecules possess lower reactivity. Secondly, the PF_5 molecule which does undergo attack can in principle yield any of the products shown in eq 39. It is re-

$$PF_5 \underset{2HF}{\overset{H_2O}{\rightleftharpoons}} POF_3 \underset{HF}{\overset{H_2O}{\rightleftharpoons}} HPO_2F_2 \underset{HF}{\overset{H_2O}{\rightleftharpoons}} H_2PO_3F \underset{HF}{\overset{H_2O}{\rightleftharpoons}} H_3PO_4 \quad (39)$$

markable that the hydrolysis proceeds precisely to the difluorophosphate stage and that no other fluorophosphate has been observed. Studies of this sort could lead to a quantitative measure of the restriction imposed on the reactivity of the H_2O molecule by HNO_3 solvation.

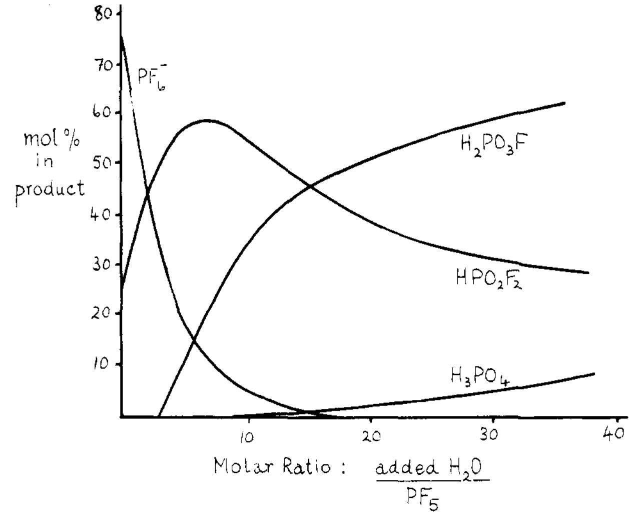


Figure 13. Effect of added H_2O on the reaction of PF_5 with HNO_3–N_2O_4 mixtures.

TABLE X. Products of Reaction of Metals with HNO_3-N_2O_4-PF_5 Mixtures

metal	possible species in solution	solid products
Fe	$[Fe(PO_2F_2)_4]^-$	$Fe_3O_2(PO_2F_2)_5 \cdot H_2O$
Cr	$[Cr(PO_2F_2)_5]^{2-}$	$Cr(PO_2F_2)_3 \cdot 2HPO_2F_2 \cdot 7H_2O$
Ni	$[Ni(NO_3)_4]^{2-}$	$Ni(NO_3)_2 \cdot 2H_2O$
Al	$[Al(PO_2F_2)_4]^-$	aluminum oxide–aluminum difluorophosphate

A small amount of water added to pure nitric acid may also be limited in chemical reactivity. This has not been established, but certainly in HNO_3–N_2O_4, it is only those H_2O molecules which form a natural part of the pure liquid medium which behave in this way. As soon as water is added to this mixture, the equilibrium is disturbed and the products shown in eq 36, 37, and 38 are decomposed. The effect of added water is demonstrated in Figure 13. The species PF_6^- is immediately attacked, yielding firstly HPO_2F_2, which then gives H_2PO_3F and eventually H_3PO_4 as the content of added water is increased. One of the major experimental difficulties in this work is to avoid the adventitious absorption of water; Figure 13 shows that with the specification amount of PF_5 (0.6 wt %), about 2% of added water is required before monofluorophosphoric acid appears in the liquid.

E. Reactions with Metals

Reference was made earlier in this section to the fact that addition of PF_5 to HNO_3–N_2O_4 decreased the reaction rate with steel, yet increased the reaction rate with, and the solubility of, pure Fe in HNO_3–N_2O_4. The reaction products of Fe, Cr, and Ni with this liquid must, therefore, have very different properties one from another. Some solid products have been identified;

the species formed in solution are difficult to identify, but the chemistry of PF_6^- and HPO_2F_2 gives some pointers to their nature.

The products formed are collected in Table X. The solution contains PF_6^- ions, and metals can react with HPO_2F_2 to give $PO_2F_2^-$ ions also. PF_6^- has very little coordinating ability, the only reported examples[158] of weak ligand behavior being in a few complexes such as $Cu(py)_4(PF_6)_2$. Iron is, therefore, unlikely to achieve high solubility in $HNO_3–N_2O_4$ in combination with PF_6^- in view of the clear tendency for metal ions to exist in solution as complexes. On the other hand, much of the chemistry of these solutions can be rationalized on the basis that the $PO_2F_2^-$ ion is a good ligand, resembling NO_3^- but with rather better ligand properties. This, for example, would facilitate the removal of Fe ions from the metal surface and increase the reaction rate. Published work on compounds of HPO_2F_2 with metals other than the alkali metals is limited,[159-162] and has been summarized.[163,164] Compounds with general formula $R_2Sn(PO_2F_2)_2$ have 6-coordinate Sn atoms, with $PO_2F_2^-$ acting as a bidentate ligand through the two O atoms.[165] $SnCl_2(PO_2F_2)_2$ has an 8-membered ring structure in which the $PO_2F_2^-$ ions act as bridging ligands,[166] and the corresponding Ti compound has similar features.[167] $Me_2Al(PO_2F_2)$ has a polymeric structure held together by $PO_2F_2^-$ bridges,[168,169] and the infrared, Raman, and Mossbauer spectra for $Fe(PO_2F_2)_3$ indicate that both the O and F atoms of $PO_2F_2^-$ may have ligand functions.[161,170] The analogous $Fe(PO_2Cl_2)_3$ is also polymeric, with the $(PO_2Cl_2)^-$ ligands acting as bidentate bridging groups.[171] It seems reasonable to suggest that the enhanced solubility of Fe in $HNO_3–N_2O_4$ on addition of PF_5 may be due to the formation of a complex $[Fe(PO_2F_2)_4]^-$, analogous to the complex $[Fe(NO_3)_4]^-$ which is responsible for the already high Fe solubility in untreated $HNO_3–N_2O_4$.

$PO_2F_2^-$ groups are also present in the solid which separates. This was prepared in three different ways. (1) A solution of HNO_3–44% N_2O_4 containing about 1 wt % Fe was treated with 8% PF_5. (2) Metallic Fe was added to $HNO_3–N_2O_4–PF_5$ mixtures containing 2% and 0.7% PF_5. (3) The Fe solution in (1) was mixed with the PF_5 solution in (2). In all cases the same amorphous, pale green powder quickly separated, leaving the bulk of the iron still in solution. Analysis corresponds with the formulation $Fe_3O_2(PO_2F_2)_5{\cdot}H_2O$; its infrared spectrum is identical with that for $Fe(PO_2F_2)_3$.[161] The separation of an oxide fluorophosphate resembles the readiness with which iron nitrate compounds form oxide nitrates, and is understandable remembering the oxidizing medium; the production of an amorphous polymer is encouraged by the ability of PO_2F_2 to act as a bidentate, bridging ligand. The low effective magnetic moment ($\mu_{eff} = 5.08\ \mu_B$/mol of Fe) is consistent with antiferromagnetic interaction between iron centers in a polymeric system.[172] This compound (like any compound which precipitates from $HNO_3–N_2O_4$) may be important in rocketry. Mellor sealed HNO_3–44% N_2O_4–0.6% PF_5 in a 321 steel vessel for 21 months. When the vessel was opened, minute quantities of an amorphous precipitate were separated; this contained iron, and its infrared spectrum showed the presence of $PO_2F_2^-$ also.[146]

The analogies between NO_3^- and $PO_2F_2^-$ chemistry are strong in the case of chromium compounds. $Cr(NO_3)_3$ is amorphous and involatile due to bridging, bidentate NO_3^- groups in the lattice (section IIG), and $Cr(PO_2F_2)_3$ is also amorphous and insoluble in organic solvents, for the same reasons.[162] The relationship between $CrO_2(PO_2F_2)_2$ and $Cr(PO_2F_2)_3$[162] resembles closely that between $CrO_2(NO_3)_2$ and $Cr(NO_3)_3$.[70] When HNO_3–44% N_2O_4 containing 0.8 wt % Cr was treated with 4% PF_5, a clear green solution was obtained. When the solution was allowed to stand for 24 h, a colloidal precipitate was observed, which was converted under vacuum to a green amorphous powder. Analysis and spectroscopy showed this to have the composition $Cr(PO_2F_2)_3{\cdot}2HPO_2F_2{\cdot}4H_2O$ and there is a direct analogy with the compound $Cr(NO_3)_3{\cdot}2HNO_3{\cdot}4H_2O$ obtained in the absence of PF_5 (section V). With the nitrate, there is evidence that the solid was obtained from a liquid containing the stable $[Cr(NO_3)_5]^{2-}$ ion, and it is tempting to believe that the $HNO_3–N_2O_4–PF_5$ solutions contain the corresponding ion $[Cr(PO_2F_2)_5]^{2-}$. In fact, the chemistry of chromium compounds in $HNO_3–N_2O_4$ is largely unchanged on addition of $PO_2F_2^-$ except that NO_3^- is replaced by the similar but stronger ligand $PO_2F_2^-$.

TABLE XI. Products of Reaction of Metals with HNO_3-N_2O_4-H_3PO_4 Mixtures[a]

metal	mole ratio H_3PO_4/metal	product	appearance
Fe	2.5	$FePO_4{\cdot}H_3PO_4$	pink powder
Cr	5	$CrPO_4{\cdot}6.5H_3PO_4$	green powder
Ni	5	$NiHPO_4{\cdot}H_3PO_4$	green powder
Al	1.0	$AlPO_4$	colorless crystals

[a] 5 wt % H_3PO_4 added to HNO_3 (56%)-N_2O_4 (44%).

Aluminum metal shows no sign of attack by PF_5 solutions in $HNO_3–N_2O_4$ over 2 months. Solutions of $Al(NO_3)_3{\cdot}6H_2O$ in HNO_3–44% N_2O_4 were, therefore, treated with 1% PF_5, and gelatinous precipitates were obtained. The general behavior resembles that of iron; the products are oxide difluorophosphates of aluminum, but are not readily reproducible.

Once again, nickel provides a sharp contrast. Its chemistry in $HNO_3–N_2O_4–PF_5$ is precisely the same as in the absence of PF_5 (section V), and $Ni(NO_3)_2{\cdot}2H_2O$ is precipitated. The relative ligand strengths of NO_3^- and F^- (section VI) and NO_3^- and $PO_2F_2^-$ are, therefore, greatly influenced by the charge (M^{3+} or M^{2+}) on the metal ion.

VIII. Reactions in HNO_3–N_2O_4–H_3PO_4 Mixtures

Phosphoric acid has widespread industrial use as a corrosion inhibitor in aqueous systems, although the literature gives no guidance on its efficiency in nonaqueous media. The mechanism of inhibition in aqueous media is generally ascribed to the formation of insoluble films of phosphate, or the formation of oxide films, depending on H_3PO_4 concentration.[174] In recognition of the widespread insolubility of heavy metal phosphates in many liquids, H_3PO_4 might be expected to cause precipitation of metals dissolved in $HNO_3–N_2O_4$.

Bruce[149] has carried out a few experiments with this mixture which show the nature of the products. H_3PO_4 gives stable solutions in $HNO_3–N_2O_4$, though in sufficiently strong dehydrating media (e.g., HSO_3Cl or $H_2SO_4–SO_3$)[155] H_3PO_4 can undergo dehydration and polymerization to give straight-chain or cyclic polyphosphates. However, the ^{31}P NMR spectrum of a 10% solution of H_3PO_4 in $HNO_3–N_2O_4$ was unchanged over several days, confirming that $HNO_3–N_2O_4$ has no dehydrating powers toward H_3PO_4, which exists as a stable solution of unprotonated H_3PO_4 molecules.

The same procedure was adopted for each metal. A solution of the metal was first prepared in $HNO_3–N_2O_4$ and mixed with an equal volume of a 5 wt % H_3PO_4 solution in $HNO_3–N_2O_4$. Results and relevant quantities are given in Table XI. It is remarkable, in comparison with the systems described earlier, that no hydrates are formed. Instead, H_3PO_4 solvates or the anhydrous phosphates are produced; the degree of solvation no doubt depends to some extent on the excess H_3PO_4 available. The Fe compound separates immediately as a dense gelatinous precipitate, shown by X-rays to be amorphous. Heavy metal phosphates generally exhibit amorphous, polymeric structures.[175] The simple 1:1 solvate is new, though the related compounds $FePO_4{\cdot}H_3PO_4{\cdot}H_2O$ and $FePO_4{\cdot}2H_3PO_4$ are known. Chromium produced a highly solvated product, which agrees with its behavior in the absence of H_3PO_4 (section V). The anhydrous

$CrPO_4$ is known, but H_3PO_4 solvates have not been reported.[177] The gelatinous precipitate from the aluminum solution will eventually turn crystalline, and was recognized as the D form of $AlPO_4$ by comparison with the published date.[178] The nickel product is exceptional in that it does not immediately precipitate; instead, a fine powder separates over a period of 24 h.

IX. References

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