917. *Adducts of Iron*(III) *Nitrate with Oxides of Nitrogen*

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The adduct $Fe(NO_3)_3,N_2O_4$ is prepared by reaction of iron(II) chloride, iron(III) chloride, or iron pentacarbonyl with dinitrogen tetroxide in an appropriate organic solvent. Formulation of the adduct as the nitrosonium salt $(NO^+)[Fe(NO_3)_4]^-$ is in accord with the infrared spectrum, magnetic properties, thermal decomposition, and the electrical conductivity and electronic spectra of solutions of the adduct in acetonitrile and nitromethane. When the adduct is heated *in vacuo*, sublimation occurs, but the sublimate has different properties; bands assignable to NO_2^+ replace those for NO^+ in the infrared spectrum, and on hydrolysis no nitrite is produced in solution. The sublimate is given the structure $(NO_2^+)[Fe(NO_3)_4]^-$, and this is supported by the electronic spectra and electrical conductivity of its solutions in organic solvents. A mechanism is suggested for the conversion of a nitrosonium to a nitronium salt during sublimation; attempts to prepare $(NO_2^+)[Fe(NO_3)_4]^-$ by reaction of iron carbonyl with dinitrogen pentoxide in carbon tetrachloride solution were not successful.

THE known chemistry of iron(III) nitrate is related almost entirely to hydrated systems. Naumann [1] discussed the formation of iron(III) nitrate in acetone solution by the reaction of iron(III) chloride solution with silver nitrate, but no solid product was isolated. This Paper is concerned with the structure and properties of adducts of anhydrous iron(III) nitrate with dinitrogen tetroxide and dinitrogen pentoxide; the preparation of the former have been reported briefly.[2]

EXPERIMENTAL

Preparation of $Fe(NO_3)_3,N_2O_4$.—(*a*) *From iron*(III) *chloride*. The observation that anhydrous iron(III) chloride is insoluble in, and unattacked by, liquid dinitrogen tetroxide was made as early as 1901 by Frankland and Farmer.[3] However, rapid solvolysis occurs on addition of ethyl acetate; the solution becomes red-brown, and nitrosyl chloride is evolved. Ethyl acetate, nitrosyl chloride, and excess of dinitrogen tetroxide were removed under vacuum at 70°, leaving

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[1] A. Naumann, *Ber.*, 1904, **37**, 4333.
[2] C. C. Addison, B. J. Hathaway, and N. Logan, *Proc. Chem. Soc.*, 1958, 51.
[3] P. F. Frankland and R. C. Farmer, *J.*, 1901, 1356.

a viscous, red-brown gum. On immersion in liquid dinitrogen tetroxide for some hours, this gum was transformed into yellow-brown crystals, which were collected on a sintered-glass filter, washed with liquid dinitrogen tetroxide, and dried under vacuum. The crystals were stable in a dry atmosphere, but immediately evolved brown fumes in moist air [Found: Fe, 16·5; total N, 21·4; N_2O_4, 30·2; $Fe(NO_3)_3,N_2O_4$ requires Fe, 16·7; total N, 21·0; N_2O_4, 27·6; and $Fe(NO_3)_3,1{\cdot}1N_2O_4$ requires Fe, 16·3; total N, 21·2; N_2O_4, 29·5%]. The product therefore contains dinitrogen tetroxide in slight excess of the 1 : 1 ratio. With adducts of this type, small departures from precise stoıcheiometry often occur, because of the volatile nature of the components, but experimental conditions can usually be designed to obtain exact stoichiometry if this is required.

The alternative procedure, in which iron(III) chloride is dissolved in ethyl acetate, and liquid dinitrogen tetroxide added to this solution, gives the same product.

(*b*) *From iron*(II) *chloride*. This reaction was examined in view of the possible formation of iron(II) nitrate, which is unknown. Iron(II) chloride does not react with liquid dinitrogen tetroxide, and is insoluble in ethyl acetate. On addition of dinitrogen tetroxide to the chloride immersed in ethyl acetate, a vigorous effervescence of nitric oxide and nitrosyl chloride occurred. The liquid showed a transitory green colour, due to dinitrogen trioxide and/or ferrous ion in solution. However, when reaction was complete the green colour disappeared, and on treatment of the solution as described above for iron(III) chloride, the same product $Fe(NO_3)_3,N_2O_4$ was obtained.

(*c*) *Reaction with metallic iron*. The pure metal does not react at room temperature with liquid dinitrogen tetroxide alone or in mixtures with ethyl acetate, acetonitrile, or dimethyl sulphoxide,[4] but the addition of very small quantities of iron(II) or iron(III) chloride to the ethyl acetate solutions gives rise to a steady reaction with iron. This is a general property, which no doubt applies also to systems involving other organic solvents, and arises from the production of nitrosyl chloride in solution. Pure nitrosyl chloride reacts with metallic iron [5-7] to give the adduct $FeCl_3,NOCl$; in dinitrogen tetroxide this undergoes solvolysis to give the corresponding compound in the tetroxide solvent system

$$FeCl_3,NOCl + 4N_2O_4 \rightleftharpoons Fe(NO_3)_3,N_2O_4 + 4NOCl$$

As with the corresponding uranyl compounds,[8] this equilibrium lies far to the right-hand side, so that nitrosyl chloride is regenerated to continue the cycle.

(*d*) *From iron pentacarbonyl*. The liquid pentacarbonyl and liquid dinitrogen tetroxide react at room temperature with explosive violence. The carbonyl was therefore solidified in liquid nitrogen and an excess of the tetroxide condensed on to it. By careful warming, the reaction could be controlled, and treatment of the resulting gum with excess of liquid dinitrogen tetroxide gave a product of composition $Fe(NO_3)_3,1{\cdot}5N_2O_4$, from which the 1 : 1 product could no doubt have been produced by prolonged vacuum treatment.

The reaction was carried out more conveniently at room temperature by using carbon tetrachloride as diluent for both reagents. A vigorous reaction occurred when a solution of the carbonyl was added to a stirred solution containing a seven-fold excess of the tetroxide. The brown gum formed was washed with carbon tetrachloride, and then immersed in liquid dinitrogen tetroxide; when the excess of tetroxide was removed, and the product kept under vacuum for some hours at room temperature, the adduct $Fe(NO_3)_3,N_2O_4$ was obtained as a free-flowing yellow powder [Found: Fe, 16·8; total N, 21·2; N_2O_4, 27·7%].

Materials.—Spectroscopically pure iron, and B.D.H. reagent grade iron(III) chloride were used as supplied. Anhydrous iron(II) chloride was prepared from metallic iron and gaseous hydrogen chloride at red heat, and purified by sublimation. Dinitrogen tetroxide was prepared and purified as described elsewhere.[9] Dinitrogen pentoxide was prepared by dehydration of fuming nitric acid with phosphoric oxide. The gas was treated with oxonised oxygen to oxidise traces of dinitrogen tetroxide, then passed through a column of phosphoric oxide to remove traces of nitric acid vapour. The gas so obtained gave a colourless solution in carbon tetrachloride. Reactions were carried out in vessels protected by phosphoric oxide guard-tubes,

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[4] D. K. Straub, H. H. Sisler, and G. E. Ryschkewitsch, *J. Inorg. Nuclear Chem.*, 1962, **24**, 919.

[5] J. J. Sudborough, *J.*, 1891, 655.

[6] J. R. Partington and A. L. Whynes, *J.*, 1948, 1952; 1949, 3135.

[7] C. C. Addison and J. Lewis, *J.*, 1951, 2843.

[8] C. C. Addison and N. Hodge, *J.*, 1961, 2490.

[9] C. C. Addison and R. Thompson, *J.*, 1949, S218.

and all transfers were conducted in a dry box. Solvents were scrupulously purified and dried by standard methods.

Physical Measurements.—Magnetic susceptibility was determined at room temperature by the Gouy method with a permanent magnet. Electical conductivities of solutions were measured in a cell of the type described by Groeneveld and Zuur.[10]

Analysis.—Iron was determined gravimetrically with 8-hydroxyquinoline, or volumetrically with mercurous nitrate; nitrite in solution was destroyed with sulphamic acid. Nitrogen analyses were carried out by hydrolysing a weighed quantity of the adduct in 2M-sodium hydroxide solution. Total nitrogen was determined by the Kjeldahl method and the dinitrogen tetroxide content of the adduct was calculated from the nitrite concentration of the solution, determined by titration with ceric sulphate.

Spectra.—Infrared spectra of mulls prepared with Nujol or Halocarbon Oil Series 11—14 were recorded with a Unicam S.P. 100 instrument fitted with potassium bromide windows protected with Polythene.[11] Ultraviolet and visible spectra were determined with Unicam S.P. 500 and 800 instruments, fitted with matched fused-silica cells.

RESULTS AND DISCUSSION

When the compound $Fe(NO_3)_3,N_2O_4$ is sublimed *in vacuo*, the sublimate resembles, but is not identical with, the original compound. A direct comparison of the infrared spectra of the sublimed and unsublimed compounds is given in the Table. The assignments employ the nomenclature normally adopted for unidentate bonding of nitrate groups (C_{2v} symmetry).[12]

Infrared spectra of $Fe(NO_3)_3$ adducts

$Fe(NO_3)_3,N_2O_4$ (unsublimed)				Sublimate from $Fe(NO_3)_3,N_2O_4$			
2298m, sp	(NO^+)	1018vs, sp	(ν_2)	2370vs, sp	(NO_2^+)	1030s	(ν_2)
1599vs	(ν_4)	796s, sp	(ν_6)	2350s, sp		1013s	
1570vs		763vs, sp	(ν_3)	1606vs	(ν_4)	1005s, sh	
1460s				1580vs		798s, sp	(ν_6)
1287vs	(ν_1)			1490b		795s, sh	
				1313vs	(ν_1)	767vs, sp	(ν_3)
				1280—1231s, b		583m, sp	(NO_2^+)
						575m, sp	
						571m, sp	

In our original Communication,[2] it was assumed that the sublimed and unsublimed compounds had the same empirical formulæ, $Fe(NO)(NO_3)_4$, and that the different behaviour on hydrolysis resulted from a change in the Fe–NO bond during sublimation. Field and Hardy,[13] who later prepared the same compound from iron powder and dinitrogen pentoxide, followed this assumption. However, careful comparison of the infrared spectra of the unsublimed and sublimed products leaves no doubt that two separate compounds, which can be represented by the formulæ $(NO^+)[Fe(NO_3)_4]^-$ and $(NO_2^+)[Fe(NO_3)_4]^-$, respectively, are involved.

The Compound $(NO^+)[Fe(NO_3)_4]^-$.—*Infrared spectrum.* The structure $(NO^+)[Fe(NO_3)_4]^-$ follows from (*a*) the definite NO^+ band at 2298 cm.$^{-1}$ (Table), (*b*) the absence of bands assignable to the N_2O_4 molecule or to the NO_3^- ion, and (*c*) the presence of bands characteristic of covalent nitrate groups. It is not possible to determine, on the basis of infrared spectra alone, the precise nature of the covalent bonding between the metal and nitrate groups. The position of the highest nitrate frequency depends upon the strength of the metal–nitrate bond, and on the orientation of the nitrate group with respect to the metal. In the tetranitratoferrate(III) anion, the nitrate groups may

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[10] W. L. Groeneveld and A. P. Zuur, *Rec. Trav. chim.*, 1953, **72**, 617.

[11] C. C. Addison and A. Walker, *J.*, 1963, 1220.

[12] G. Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, pp. 65, 179.

[13] B. O. Field and C. J. Hardy, *J.*, 1964, 4428.

be unidentate or bidentate; the splitting of the ν_4 band (Table 1) suggests that more than one type of bonding exists. Bidentate bonding does not necessarily require nitrate absorption above 1600 cm.$^{-1}$. For example, the compound $Ti(NO_3)_4$ absorbs at 1630 cm.$^{-1}$ largely because of the +4 charge on the metal ion and a bidentate bonding of the nitrate that is fully symmetrical [14] as a result of the absence of distorting *d* electrons; in contrast, in the complex $[Co(NO_3)_4]^{2-}$ the nitrate groups are bidentate, but unsymmetrically disposed towards the metal,[15] and the highest nitrate frequency [16] is at 1462 cm.$^{-1}$. Present evidence suggests that the structures of the complexes $[Fe(NO_3)_4]^-$ and $[Co(NO_3)_4]^{2-}$ may be quite similar.

Magnetic properties. The molar susceptibility χ_M is 14,520 × 10^{-6} c.g.s.u. at 16·5°; $\mu_{eff.} = 5{\cdot}83$ B.M., corresponding to the Fe^{3+} oxidation state with five unpaired electrons. This is consistent with the fact that co-ordination of the iron ion by oxygen ligands does not normally give rise to low-spin complexes, and in this case also, the ligand-field splitting Δ is obviously not related to the degree of covalency.

Solution properties. The compound dissolves readily in polar solvents (nitromethane, nitrobenzene, dioxan, ethyl acetate, acetonitrile) to give stable yellow-brown solutions. In these solutions, the tetranitratoferrate(III) anion is retained. Dimethyl sulphoxide, however, is sufficiently strong as a ligand to dissociate this complex. The sulphoxide was added dropwise to a solution of $(NO^+)[Fe(NO_3)_4]^-$ in ethyl acetate. Dinitrogen tetroxide was displaced, and an amorphous yellow powder of composition $Fe(NO_3)_3,6Me_2SO$ separated. The infrared spectrum of this product contained all the main bands characteristic of dimethyl sulphoxide co-ordinated to a metal through the oxygen atom.[17] The ν_1 and ν_4 bands of the co-ordinated nitrate group were replaced by the band at 1380 cm.$^{-1}$ typical of the nitrate ion, and the product is therefore the ionic compound $[Fe(Me_2SO)_6]^{3+}(NO_3^-)_3$.

The adduct is insoluble in the non-polar solvents carbon tetrachloride and light petroleum. As with many other metallic nitrate–N_2O_4 adducts, a vigorous reaction occurs with diethyl ether, giving acetaldehyde and a basic iron nitrate. The behaviour of the compound towards aromatic hydrocarbons, however, is unusual. On addition of crystals of the compound to benzene (or toluene), a deep red oil is formed immediately as a separate, lower, liquid phase. The oil slowly dissolves in the hydrocarbon, which then contains nitrobenzene, and a basic iron nitrate is precipitated. This behaviour is observed also [18] with the adduct $UO_2(NO_3)_2,N_2O_4$, but not with other adducts such as $Cu(NO_3)_2,N_2O_4$ or $Zn(NO_3)_2,2N_2O_4$. Since the iron and uranium compounds are the strongest adducts known, the red oil is probably associated with the release of a species (perhaps NO^+) that is more readily available in the strong adducts.

The red colour is produced when benzene is added to a solution of the iron nitrate adduct in nitromethane, but not when dioxan, ethyl acetate, or acetonitrile is used as solvent. Spectrophotometric and conductometric studies have shown that the intensity of colour does not involve any stoicheiometric relationship between the iron compound and benzene, since on addition of benzene to nitromethane solutions of the iron compound, colour intensity is still a function of benzene concentration at $Fe(NO_3)_3,N_2O_4$: benzene ratios as high as 1 : 50. These observations are reminiscent of experiments by Ingold and his co-workers,[19] who noted the formation of a deep red colour during nitration of benzene (or toluene) with anhydrous nitric acid in nitromethane. The coloured species was believed [20] to be formed from benzene and an oxide of nitrogen (NO, N_2O_3, or NO_2) in the presence of an " anhydrous condensing agent " (H_2SO_4, HNO_3, or P_4O_{10}); the anhydrous nitrate might well act as condensing agent in the present work.

[14] C. C. Addison, C. D. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.*, 1964, 367.

[15] F. A. Cotton and J. G. Bergman, *J. Amer. Chem. Soc.*, 1964, **86**, 2941.

[16] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1962, **1**, 848.

[17] F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.

[18] C. C. Addison and N. Hodge, unpublished results.

[19] C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *J.*, 1931, 1959.

[20] G. A. Benford and C. K. Ingold, *J.*, 1938, 929.

Conductivity of solutions. The formulation of the adduct $Fe(NO_3)_3,N_2O_4$ as the ionic compound $NO^+[Fe(NO_3)_4]^-$ receives direct support from the electrical conductivity of its solutions in nitromethane (dielectric constant 37) in which the nitrosonium ion is stable.[21] At the higher concentrations (Figure 1) the conductivity curve (C) lies close to that for the compound $(Et_4N)^+[Fe(NO_3)_4]^-$, which shows normal weak electrolyte behaviour[22] (curve A), and for which the molar conductivity at 0·001M is of the order expected for a 1 : 1 electrolyte in nitromethane.[23] Migration of iron into the anode compartment of a Hittorf type of cell during electrolysis of these solutions also supports the ionic structure. Below a concentration of about 0·01M, however, the conductivity decreases with dilution; this can be interpreted in terms an equilibrium

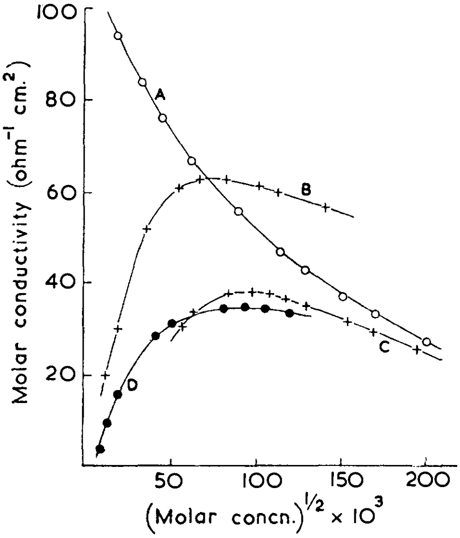

FIGURE 1. Electrical conductivity of solutions of $Fe(NO_3)_3$ adducts at 25°

(A) $(Et_4N^+)[Fe(NO_3)_4]^-$ in $MeNO_2$.
(B) $(NO^+)[Fe(NO_3)_4]^-$ in MeCN.
(C) $(NO^+)[Fe(NO_3)_4]^-$ in $MeNO_2$.
(D) $(NO_2^+)[Fe(NO_3)_4]^-$ in $MeNO_2$.

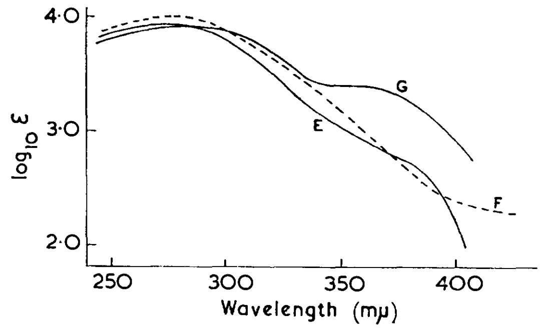

FIGURE 2. Ultraviolet spectra of $Fe(NO_3)_3$ adducts in acetonitrile

(E) $(NO^+)[Fe(NO_3)_4]^-$.
(F) $(Et_4N^+)[Fe(NO_3)_4]^-$.
(G) $(NO_2^+)[Fe(NO_3)_4]^-$.

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

The molar conductivity of dinitrogen tetroxide in nitromethane is relatively small.[24] We have not yet succeeded in isolating the simple nitrate $Fe(NO_3)_3$, but the molar conductivities of other covalent nitrates, *e.g.*, cupric nitrate[25] and zinc nitrate in nitromethane do not exceed 7 ohm^{-1} cm.^{2}. A displacement in the above equilibrium towards the right-hand side on dilution therefore accounts for the observed changes in conductivity. Since the effect is produced on dilution, it must presumably be brought about by solvent participation. The nitromethane molecule is known to act as an effective ligand in complexes of chromium(III) nitrate;[26] it may therefore displace a nitrate group from the $[Fe(NO_3)_4]^-$ complex at high dilution, so that an equilibrium of the type

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

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[21] A. Hantsch and K. Berger, *Z. anorg. Chem.*, 1930, **190**, 321.

[22] C. C. Addison, P. M. Boorman, and N. Logan, *J.*, 1965, 5146.

[23] J. E. Fergusson and R. S. Nyholm, *Nature*, 1959, **183**, 1039; R. S. Nyholm and R. V. Parish, *Chem. and Ind.*, 1956, 470.

[24] C. C. Addison, N. Hodge, and J. Lewis, *J.*, 1953, 2631.

[25] C. C. Addison and B. J. Hathaway, *J.*, 1960, 1468.

[26] C. C. Addison and H. Norbury, unpublished results.

(where S = solvent) provides an acceptable mechanism for the observed conductivity changes. Acetonitrile is a stronger ligand than nitromethane in these systems, and the more pronounced decrease in conductivity in acetonitrile solution (curve B, Figure 1) is consistent with this mechanism.

Ultraviolet spectra. The ultraviolet spectra of solutions of nitrates and nitrato-complexes in organic solvents fall generally into two classes, *i.e.*, those showing weak absorption (ε about 10 per nitrate group) in the 300 mμ region due to $np \longrightarrow \pi^{\pm}$ transitions within the nitrate group, and those showing intense absorption ($\varepsilon \sim 10^3$) in this region, which is usually attributed to electron transfer. The tetranitratoferrate(III) anion fulfils the requirements for the second class, in that the nitrate groups are covalently bonded to a metal that has partially filled *d* orbitals and a readily accessible lower oxidation state; conditions therefore favour electron transfer from ligand (or even solvent) to metal. The spectrum for the compound $(NO^+)[Fe(NO_3)_4]^-$ in acetonitrile is shown in Figure 2 (curve E). It shows a broad, intense maximum (ε = 8200) at 275—280 mμ, and the fact that it is very similar to the curve (F) for $(Et_4N^+)[Fe(NO_3)_4]^-$ is further evidence for the presence of the tetranitratoferrate(III) anion in the dinitrogen tetroxide adduct.

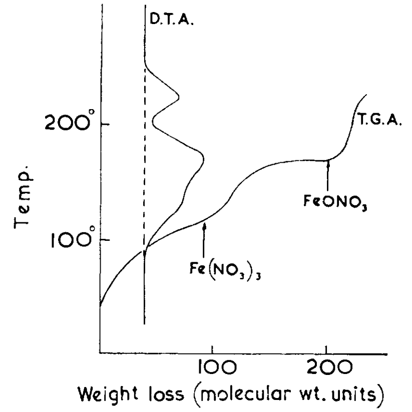

FIGURE 3. Differential thermal analysis (D.T.A.) and thermogravimetric analysis (T.G.A.) of the compound $(NO^+)[Fe(NO_3)_4]^-$

Thermal decomposition. The differential thermal analysis curve corresponding to a heating rate of 4° per minute in dry air at atmospheric pressure is shown in Figure 3. (The horizontal axis is arbitrary for this curve.) The shoulder in the curve at 130—140° represents melting of the compound with decomposition. The curve shows two distinct decomposition steps, the intermediate product being available over the narrow furnace temperature range of 195—210°. In a duplicate experiment, the product was removed at this stage and analysed (Found: Fe, 41·4; N, 10·5; $FeNO_4$ requires Fe, 41·7; N, 10·5%). This product, the properties of which indicate that it should be formulated as $FeO(NO_3)$, may also be prepared from the gas-phase reaction of iron pentacarbonyl and nitrogen dioxide,[27] and will be discussed elsewhere.

Thermal decomposition has also been studied by thermogravimetric analysis, partly because the heating rate necessary to obtain suitable instrument-response in differential analysis is too high to maintain thermal equilibrium, and also because all stages in the decomposition would not necessarily be detected by this technique. For the thermogravimetric analysis curve in Figure 3, the heating rate was reduced to 0·67°/min. and the weight changes are expressed in terms of 1 mole of the initial compound; there is a sharp fall in decomposition rate immediately following the composition $FeO(NO_3)$, but also at the stage corresponding to the anhydrous nitrate $Fe(NO_3)_3$. However, there is no plateau at this stage, so that the anhydrous nitrate cannot be prepared by thermal decomposition of the N_2O_4 adduct. In this respect, the nitrates $Fe(NO_3)_3$ and $Cr(NO_3)_3$ are probably

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[27] C. C. Addison, B. F. G. Johnson, and N. Logan, *J.*, 1965, 4490.

similar; in the latter,[28] the temperature required for the decomposition of the N_2O_4 adduct is higher than the decomposition temperature of the simple nitrate.

The Compound $(NO_2^+)[Fe(NO_3)_4]^-$.—When the compound $(NO^+)[Fe(NO_3)_4]^-$ is heated in a vacuum (10^{-2}—10^{-3} mm.) at 120° for several hours in a flask carrying a cold finger at 20°, a pale brown sublimate was obtained; about 20% of the original quantity of iron compound sublimes. This sublimate is even more deliquescent than the unsublimed material, and gives white fumes on contact with moist air (cf. the brown fumes of NO_2 from the nitrosonium compound). All available experimental evidence supports the formulation of the sublimate as the nitronium salt $(NO_2^+)[Fe(NO_3)_4]^-$. Apart from the much more extensive splitting of bands, the infrared spectrum of the sublimate (Table) differs from that of the unsublimed compound in two important respects. First, the 2298 cm.$^{-1}$ (NO^+) band is replaced by two more intense bands of higher frequency; secondly, new bands appear in the 580 cm.$^{-1}$ region. These are assigned to the asymmetric stretch ν_3 and the doubly degenerate bend ν_2 of the linear NO_2^+, which occur at the following positions in other nitronium salts:

Compound:	N_2O_5 (solid)	$NO_2^+ClO_4^-$	$NO_2^+BF_4^-$	$NO_2^+PF_6^-$	$NO_2^+SbF_6^-$
ν_3	2375	2360	2358	2364	2358
ν_2	538	570	—	—	—
Ref.	29	30	31	31	31

The electrical conductivity of nitromethane solutions is very similar to that for the nitrosonium salt [curves (C) and (D), Figure 1], and the mechanism suggested above for the unusual behaviour on dilution can apply equally well to either salt. The intense electron-transfer bands in the ultraviolet are almost identical for solutions of the nitrosonium and nitronium salts in acetonitrile (Figure 2, curves E and G), indicating that the $[Fe(NO_3)_4]^-$ ion occurs in each salt. The second peak in curve (G) is attributed to absorption by the NO_2^+ ion. The molar susceptibility χ_M is 14,378 × 10^{-6} c.g.s.u. at 19°; $\mu_{\text{eff.}} =$ 5·82 B.M., values that are in close agreement with those of the nitrosonium compound.

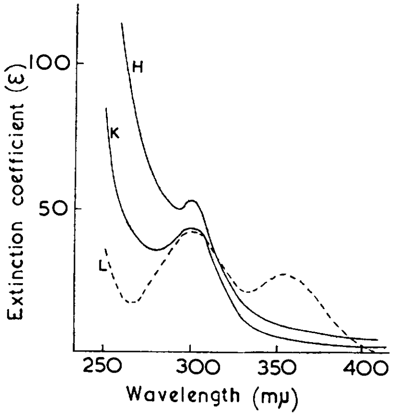

FIGURE 4. Hydrolysis of $Fe(NO_3)_3$ adducts
(H) $(NO_2^+)[Fe(NO_3)_4]^-$ in 1·0M-NaOH solution.
(K) $(NO_2^+)[Fe(NO_3)_4]^-$ in 0·1M-NaOH solution.
(L) $(NO^+)[Fe(NO_3)_4]^-$ in 0·1M-NaOH solution.

The two compounds are clearly distinguished by their modes of hydrolysis in alkaline solutions. On hydrolysis of $(NO^+)[Fe(NO_3)_4]^-$, iron(III) hydroxide is precipitated leaving a clear, colourless solution. The ultraviolet absorption spectrum of the solution (curve L, Figure 4) is independent of alkali concentration in the range up to 1-molar; there are peaks corresponding to nitrate and nitrite ions, and in all respects the curve is that expected from the reaction

$$(NO^+)[Fe(NO_3)_4]^- + 5OH^- \longrightarrow Fe(OH)_3 + NO_2^- + 4NO_3^- + H_2O$$

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[28] C. C. Addison and D. J. Chapman, *J.*, 1964, 539.
[29] R. Teranishi and J. C. Decius, *J. Chem. Phys.*, 1954, **22**, 896.
[30] J. R. Soulen and W. F. Schwartz, *J. Phys. Chem.*, 1962, **66**, 2066.
[31] D. Cook, S. J. Kuhn, and G. A. Olah, *J. Chem. Phys.*, 1960, **33**, 1669.

When allowance is made for nitrite absorption at the nitrate peak (302·5 mμ), the $NO_2^-:NO_3^-$ ratio is 1 : 4. The curve (K) obtained on hydrolysis of the sublimate $(NO_2^+)[Fe(NO_3)_4]^-$ shows a nitrate, but no nitrite, peak, which is consistent with the reaction

$$(NO_2^+)[Fe(NO_3)_4]^- + 5OH^- \longrightarrow Fe(OH)_3 + 5NO_3^- + H_2O$$

However, this equation does not appear to represent fully the hydrolysis process. Analyses of the solution for iron and nitrate (by means of "Nitron") gave an $Fe:NO_3^-$ ratio of 1 : 4·75 instead of 1 : 5. The solutions were pale yellow in colour, suggesting that a small part of the iron present remains in the alkaline solution as an anionic complex. The fact that the extinction coefficient at 302·5 mμ is almost identical in curves (K) and (L) is coincidental, and the contribution of the iron-containing complex in curve (K) must be similar in magnitude to the NO_2^- contribution in curve (L). Consistent with this, the spectrum of the solution obtained from the nitronium salt is influenced by alkali concentration (curve H).

Chemical analysis is in agreement with, but cannot be used to confirm, the suggested formula for the product obtained on sublimation; the nitrosonium and nitronium compounds differ by one oxygen atom only and the difference in the iron and nitrogen contents of the compounds is of the same order as the variation caused by slight deviations from stoicheiometry in the adducts. If the compounds are written as formal adducts, $Fe(NO_3)_3,N_2O_4$ and $Fe(NO_3)_3,N_2O_5$ require Fe, 16·7 and 16·0% and N, 21·0 and 20·0%, respectively. In nine separate sublimations, the iron content of the sublimate varied between 16·2 and 16·6%, and the nitrogen content between 19·7 and 20·5%. Since the only components of the sublimate are $Fe(NO_3)_3$ and N_2O_5, the product is best represented by the empirical formula $Fe(NO_3)_3,xN_2O_5$ where $0{\cdot}90 < x < 0{\cdot}95$.

The product almost certainly contains a very small amount of the simple anhydrous nitrate $Fe(NO_3)_3$. In our preliminary Communication[2] we referred to the nearly colourless crystals sometimes obtained on the walls of the sublimation flask (especially on rapid heating of the tetroxide adduct), having an $Fe:NO_3$ ratio of 1 : 3. This is the most deliquescent substance encountered in these laboratories, and we have not yet been able to confirm that the crystals are, in fact, the compound $Fe(NO_3)_3$. In considering the mechanism by which the nitronium compound is formed, however, it is reasonable to assume that anhydrous iron(III) nitrate is involved, and that this is volatile.

Mechanism of Reaction.—The essential step in the reactions that occur during sublimation is the conversion of N_2O_4 into N_2O_5. This normally requires an exceedingly strong oxidising agent (*e.g.*, ozone) capable of donating an atom of oxygen. In our experiments, we believe that the NO_3 radical performs this function. Evidence is accumulating that the violent oxidising properties associated with certain anhydrous metal nitrates [*e.g.*,[14] $Ti(NO_3)_4$] is due to the NO_3 radical, which can be released when a bidentate group is bonded to a metal having a readily accessible lower oxidation state. Anhydrous iron(III) nitrate may well satisfy these requirements, so that the reaction mechanism involves the following steps:

$$\begin{aligned}
(NO^+)[Fe(NO_3)_4]^- &\longrightarrow Fe(NO_3)_3 + 2NO_2 \\
Fe(NO_3)_3 &\longrightarrow Fe(NO_3)_2 + NO_3{\cdot} \\
Fe(NO_3)_2 &\longrightarrow FeO(NO_3) + NO_2 \\
NO_2 + NO_3{\cdot} &\longrightarrow N_2O_5 \\
Fe(NO_3)_3 + N_2O_5 &\longrightarrow (NO_2^+)[Fe(NO_3)_4]^-
\end{aligned}$$

This mechanism is consistent with the relatively low yield of sublimate, and the thermogravimetric analysis of the nitrosonium compound. The compound $FeO(NO_3)$ has already been recognised as the intermediate formed at ~170°; analysis of the residue after sublimation at 120° *in vacuo* corresponds to that of a compound $Fe(NO_3)_3,FeO(NO_3)$.

Attempts to Prepare $(NO_2^+)[Fe(NO_3)_4]^-$ *by Reactions in Solution.*—These reactions were carried out in order to compare the behaviour of chromium and iron carbonyls in solutions containing pure dinitrogen pentoxide. If analogous, these reactions should lead to the preparation of iron(III) nitrate or its dinitrogen pentoxide adduct. Chromium carbonyl reacts with both dinitrogen tetroxide and dinitrogen pentoxide. Whenenever the former is present, the compound $Cr(NO_3)_3,2N_2O_4$ is invariably obtained;[26] adducts with the pentoxide are generally much less stable than with the tetroxide [32] and, on reaction of chromium carbonyl with dinitrogen pentoxide in carbon tetrachloride solution, the simple nitrate $Cr(NO_3)_3$ separates.[28] A solution of iron pentacarbonyl (2·5 g.) in carbon tetrachloride (100 ml.) was added dropwise at $-10°$ to a stirred solution of dinitrogen pentoxide (7 g.) in carbon tetrachloride, and a stream of ozonised oxygen was bubbled throuth the solution. Reaction was vigorous, and the brown gum that first separated gave a free-flowing, pale brown powder on filtration and removal of solvent. Chemical analysis, infrared spectrum, and nature of products on hydrolysis indicated that the product had the composition $Fe(NO_3)_3,0{\cdot}5N_2O_4,0{\cdot}5N_2O_5$. The temperature and concentration of the reactants were modified, but no conditions were found under which the product was free from combined dinitrogen tetroxide.

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[32] C. C. Addison and N. Logan, " Preparative Inorganic Reactions," ed. W. Jolly, Interscience Publ., 1964, vol. I, p. 141.