Mössbauer Study of the Thermal Decomposition of Dinitrogen Tetroxide Solvates of Iron(III) Nitrate

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The thermal decomposition of the 1·5 N_2O_4 solvate of iron(III) nitrate, $[N_4O_6]^{2+}2[Fe(NO_3)_4]^-$, has been investigated. Four isolable intermediates, $[NO]^+[Fe(NO_3)_4]^-$, $[NO_2]^+[Fe(NO_3)_4]^-$, $[Fe_2O(NO_3)_4]$, and $[FeO(NO_3)]$, have been characterised, the ultimate product being Fe_2O_3. $[Fe_2O(NO_3)_4]$ and $[FeO(NO_3)]$ both exhibit room temperature Mössbauer effects characteristic of polymeric lattices. The Mössbauer spectra of the complexes $M^+[Fe(NO_3)_4]^-$[M = Me_4N, Et_nNH_{4-n} (n = 1—4), $N_4O_6^+$, or NO_2^+] and $M^+[FeCl_4]^-$[M = Et_nNH_{4-n} (n = 1—4)] all consist of a single resonance with isomeric shifts in the ranges 0·54—0·61 mm s^{-1} and 0·30—0·31 mm s^{-1}, respectively. The two nitrosonium salts, $[NO]^+[FeX_4]^-$ (X = Cl, NO_3), however, exhibit small quadrupole splittings (Δ = 0·36 mm s^{-1}, X = Cl; Δ = 0·45 mm s^{-1}, X = NO_3), which are attributed to the interaction of the highly polarising nitrosonium cation with one of the ligands X.

THE nature of the intermediates formed in the thermal decomposition of anhydrous metal nitrates and their dinitrogen tetroxide solvates has aroused much interest, but has been little studied. Basic nitrato-derivatives of the composition $[M_2O(NO_3)_4]$ (M = tripositive metal) have been discerned as intermediates in the thermal decompositions of $Sc(NO_3)_3$,[1] $[Al_2O(NO_3)_4]{\cdot}2N_2O_4$,[2] $Bi(NO_3)_3{\cdot}N_2O_4$,[3] and $Au(NO_3)_3{\cdot}N_2O_5$,[4] but the structures of such compounds have yet to be fully elucidated.

In recent years Mössbauer spectroscopy has been employed as a useful probe into solid-state reactions. Among the systems which have been successfully investigated by this technique are the thermal decompositions of europium(III) [5] and iron(III) [6] oxalates, potassium, strontium and barium tris(oxalato)ferrate(III) hydrates,[7] $[K_2FeO_4]$,[8] and $[SrFeO_4]$.[9] Here we report Mössbauer and i.r. studies of the thermal decomposition of the compound $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ as a possible route to anhydrous iron(III) nitrate, $Fe(NO_3)_3$. This latter compound has been reported by Lovejoy and Vosper [10] to be the product of the reaction between $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$ and excess N_2O_4 at 0 °C, but the low thermal stability of the material inhibited its complete characterisation.

RESULTS

The recent X-ray diffraction study [11] of the iron(III) compound, $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$, has shown that the asymmetric unit incorporates $[N_4O_6]^{2+}$ cations (formed by the association of one $[NO_3]^-$ and three $[NO]^+$ ions) and two $[Fe(NO_3)_4]^-$ anions. The latter has been found, from a crystal-structure determination on its tetraphenylarsonium salt,[12] to consist of four bidentate nitrate groups tetrahedrally disposed around iron in such a way that the overall symmetry of the anion approximates to D_{2d}. Not unexpectedly therefore the ^{57}Fe Mössbauer spectrum of the solvate $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ exhibits a single resonance due to the near cubic electric field at the iron nucleus. Isomer-shift data for this and other compounds known to contain the $[Fe(NO_3)_4]^-$ anion are listed in the Table. All fall in the range 0·54—0·61 mm s^{-1}, but show some dependence on the gegenion employed, presumably due to the effect on local site symmetry of crystal packing forces. These isomer shift values are among the highest observed for high spin iron(III) compounds, and are much higher than corresponding $[FeCl_4]^-$ complexes (see Table). This difference may be ascribed to a much lower degree of covalency in the Fe–ONO_2 bond owing to the highly electronegative nitrate ligands. In the i.r. region, the solvate exhibits a broad band at 2230 cm^{-1} attributable to the perturbed $[NO]^+$ components of the complex $[N_4O_6]^{2+}$ cation.

Prolonged heat treatment *in vacuo* (30 °C, several days, 10^{-2} mmHg) of the $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ results in its conversion into $Fe(NO_3)_3{\cdot}N_2O_4$, which exhibits a sharp band, characteristic of the unperturbed NO^+ cation, consistent with its formulation as $[NO]^+[Fe(NO_3)_4]^-$. The Mössbauer spectrum, however, consists of a finely split doublet with δ = 0·52 mm s^{-1} and Δ = 0·45 mm s^{-1}, in contrast to other

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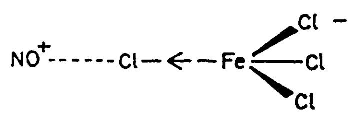
salts containing the $[Fe(NO_3)_4]^-$ anion. We have also observed a similar inducement of an electric-field gradient at iron in the corresponding tetrachloroferrate(III) salts. The series of ammonium salts $[Et_nNH_{4-n}]^+[FeCl_4]^-$ (n = 1—4) all exhibit a single resonance with isomer shift 0·30 mm s^{-1}. In the nitrosonium salt, however, a slight increase in isomer shift is accompanied by the appearance of a small quadrupole splitting (0·36 mm s^{-1}). An even smaller quadrupole splitting has been discerned for $[Ph_4As]^+$-$[FeCl_4]^-$ (Δ = 0·2 mm s^{-1}),[13] but in this case the solid-state structure is known,[14] and the quadrupole splitting may be ascribed to the distortion of the electric field around the iron from T_d symmetry, as a result of the tetragonal distortion of the anion due to crystal-packing forces. In the case of the nitrosonium salt, such effects should be at a minimum because of the small size of the cation. An alternative rationalisation may however be proposed in terms of the strongly polarising nature of the cation. Interaction of the $[NO]^+$ cation with one of the chlorine atoms of the $[FeCl_4]^-$ anion would induce an electron drift away from the iron nucleus along one of the iron–chlorine axes, *viz.*



thus creating an asymmetry in the electric field at iron. The increase in isomer shift is also consistent with this rationalisation. For iron $\delta R/R$ is negative, so that an increase in isomer shift corresponds to a *decrease* in *s* electron density at the iron nucleus. Interaction of the nitrosonium cation with the $[Fe(NO_3)_4]^-$ anion, in contrast, causes a small reduction in isomer shift. Apparently in this compound, where the interaction of the cation and metal takes place *via* a series of bonds of the nitrate–metal system, the *s* electron density at iron is actually increased.

Mössbauer parameters

(A) Products of thermal decomposition of $Fe(NO_3)_3$·1·5N_2O_4

Temp. of heat treatment (t/°C)	δ/mm s^{-1}	Δ/mm s^{-1} [a]	Species
42	0·49	0·51	$[NO]^+[Fe(NO_3)_4]^-$
76	0·52	0·88	$[NO]^+[Fe(NO_3)_4]^-$ $[Fe_2O(NO_3)_4]$
88	0·50	0·93	$[Fe_2O(NO_3)_4]$
106	0·49	0·93	$[Fe_2O(NO_3)_4]$
140	0·47	0·97	$[FeO(NO_3)]$ [b]
160	0·47	1·06	$[FeO(NO_3)]$ [b]
206	0·47	1·05	$[FeO(NO_3)]$ [b]

(B) Complexes containing the $[Fe(NO_3)_4]^-$ anion

Complex	δ/mm s^{-1}	Δ/mm s^{-1}
$Fe(NO_3)_3$·1·5N_2O_4≡$[N_4O_6]^{2+}2[Fe(NO_3)_4]^-$ [d]	0·57	
$Fe(NO_3)_3$·N_2O_4≡$[NO]^+[Fe(NO_3)_4]^-$	0·52	0·45
$[NO_2]^+[Fe(NO_3)_4]^-$ [d]	0·57	
$[Me_4N]^+[Fe(NO_3)_4]^-$ [d]	0·59	
$[Et_4N]^+[Fe(NO_3)_4]^-$ [d]	0·54	
$[Et_3NH]^+[Fe(NO_3)_4]^-$ [d]	0·57	
$[Et_2NH_2]^+[Fe(NO_3)_4]^-$ [d]	0·61	
$[EtNH_3]^+[Fe(NO_3)_4]^-$ [d]	0·60	

(C) Complexes containing the $[FeCl_4]^-$ anion

Complex	δ/mm s^{-1}	Δ/mm s^{-1}
$[Et_4N]^+[FeCl_4]^-$ [c,e]	0·31	
$[Et_3NH]^+[FeCl_4]^-$ [e]	0·31	
$[Et_2NH_2]^+[FeCl_4]^-$ [e]	0·31	
$[EtNH_3]^+[FeCl_4]^-$ [e]	0·30	
$[NO]^+[FeCl_4]^-$	0·33	0·36
$[Ph_4As]^+[FeCl_4]^-$	0·3	0·2

[a] Considered accurate to at least ±0·03 mm s^{-1} (δ) and ±0·06 mm s^{-1} (Δ). [b] Parameters for $[FeO(NO_3)]$ from gas-phase reaction between $[Fe(CO)_5]$ and N_2O_4: δ = 0·45 mm s^{-1}, Δ = 1·01 mm s^{-1}. [c] Ref. 13: δ = 0·29 mm s^{-1}, Δ = 0. Ref. 20: δ = 0·282 mm s^{-1}, Δ = 0. [d] Linewidth at half-peak height falls in the range 1·05—1·29 mm s^{-1}. [e] Linewidth at half-peak height falls in the range 0·65—0·81 mm s^{-1}.

It might also be expected that the value of the N–O stretching frequency of the cation in these two nitrosonium salts would move to lower energy compared with non-interacting $[NO]^+$ cations. Values of this vibration for the nitrosonium salts of non-polarisable anions, *e.g.* $[MF_6]^{n-}$ (M = Ge, V, Sb, P, Sn, As, U, Mo), fall in the range 2331—2391 cm^{-1}.[15] Observed values for the two compounds in question are $[NO]^+[FeCl_4]^-$, 2200 cm^{-1} and $[NO]^+$-$[Fe(NO_3)_4]^-$, 2298 cm^{-1}, values which are not inconsistent with the model formulated.

Differential thermal analysis thermograms[16] of $[NO]^+$-$[Fe(NO_3)_4]^+$ show plateaux at 85—102, 128—140, 195—210, and 254 °C. Minor features at 166—173 and 224 °C are also observed. In the present study, the sample of $Fe(NO_3)_4$·1·5N_2O_4 heat-treated at 30 °C was further heated, and samples removed at selected temperatures for i.r. and Mössbauer examination. After the sample had been treated to 76 °C, several new bands besides those due to $[NO]^+[Fe(NO_3)_4]^-$ appeared in the i.r. region. Those at 2350 and 570 cm^{-1} are readily assigned to vibrations associated with the $[NO_2]^+$ cation, whilst those at 720, 640, and 500 cm^{-1} are presumably metal–oxygen stretching frequencies. In addition, much sublimate, identified as $[NO_2]^+[Fe(NO_3)_4]^-$, appeared on the cooler parts of the apparatus. Heating to 88 °C and then 106 °C resulted in the total removal of $[NO_2]^+[Fe(NO_3)_4]^-$ from the system as indicated by the loss of the band at 2350 cm^{-1}. At 106 °C, the decomposition of the nitrosonium salt was complete, and the band at 720 cm^{-1} was observed to increase in intensity, whilst those bands due to co-ordinated nitrate diminished. Analysis showed the product formed at this temperature to have the composition $[Fe_2O(NO_3)_4]$, similar to the $[M_2O(NO_3)_4]$ species reported in the thermal decompositions of $Sc(NO_3)_3$,[1] $[Al_2O(NO_3)_4]$·$2N_2O_4$,[2] $Bi(NO_3)_3$·N_2O_4,[3] and $Au(NO_3)_3$·N_2O_5.[4] The structure of $[Fe_2O(NO_3)_4]$ has previously[17,18] been formulated as (i) $[FeONO_3]$·$Fe(NO_3)_2$ and (ii) $[FeO]^+[Fe(NO_3)_4]^-$, both containing two formally different types of iron. The Mössbauer spectrum of this compound however consists of two lines at +0·03 and +0·96 mm s^{-1} of equal intensity. Thus, formulation (ii) may be excluded since all other compounds containing the $[Fe(NO_3)_4]^-$ anion exhibit resonances in the range 0·52—0·61 mm s^{-1}. The spectrum of (i) is expected to be complex, consisting of three or four lines due to two (quadrupole split) resonances of the two types of iron atom. Neither of the possibilities (i) and (ii) are consistent with the observed spectrum. The alternative is that the observed spectrum is a single quadrupole split resonance, *i.e.* both iron atoms of $[Fe_2O(NO_3)_4]$ are in identical environments. On this basis, only the symmetrical formulation $[(NO_3)_2FeOFe(NO_3)_2]$ is consistent with the observed data. The band

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[18] D. H. Jones, Ph.D. Thesis, University of Nottingham, 1972.

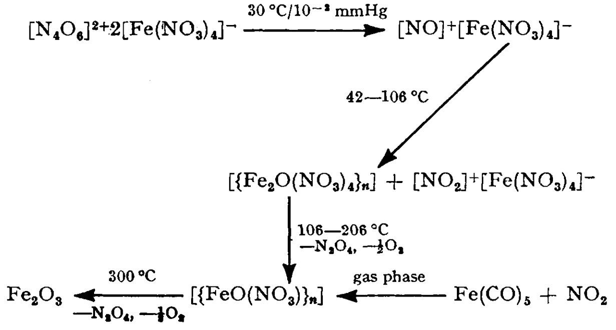
at 720 cm^{-1} is also observed in the i.r. spectrum of Fe_2O_3, suggesting its assignment as an antisymmetric Fe–O–Fe stretching vibration and corroborating the presence of such linkages in $[Fe_2O(NO_3)_4]$. The preservation of the Mössbauer spectrum at room temperature is indicative of the presence of a polymeric solid-state lattice, in which both oxygen atoms and nitrate groups presumably function as bridging groups towards iron atoms.

The spectra of samples heat-treated at temperatures above 140 °C also exhibit two resonances in the Mössbauer spectrum, corresponding to one type of iron with $\delta = 0{\cdot}47$ mm s^{-1} and $\Delta = 1{\cdot}03$ mm s^{-1}, identified by analysis as $[FeONO_3]$. An identical product ($\delta = 0{\cdot}45$ mm s^{-1}, $\Delta = 1{\cdot}01$ mm s^{-1}) has been obtained from the gas-phase reaction of pentacarbonyliron and nitrogen dioxide.[19] This compound exhibits bands in the infrared due to co-ordinated nitrate, and also a strong sharp band at 720 cm^{-1} indicating the presence of Fe–O–Fe linkages. The Mössbauer spectrum of $[FeO(NO_3)]$ is also preserved at room temperature, indicating a similar polymeric structure again containing both bridging nitrate and oxide ligands.

The differential thermal analysis thermogram shows that no further decomposition takes place after *ca.* 250 °C. Heating samples of $[FeO(NO_3)]$, prepared both by the thermal decomposition of $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ and the gas-phase reaction of iron pentacarbonyl and nitrogen dioxide, to 300 °C resulted in the evolution of nitrogen dioxide and the formation of Fe_2O_3, as indicated by its characteristic magnetically perturbed spectrum. Further heating to 400 °C and then 500 °C caused only minor changes in the spectrum, and no decomposition to either Fe_3O_4 or FeO_2 could be detected.

DISCUSSION

It is apparent from the above results that the thermal decomposition of the compound $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ proceeds by loss of N_2O_4 from the $[N_4O_6]^{2+}$ cation to give $[NO]^+$ cations, whilst $[Fe(NO_3)_4]^-$ remains unchanged. At moderate temperatures (76—100 °C), the nitrosonium salt, $[NO]^+[Fe(NO_3)_4]^-$, decomposes to afford the nitronium analogue, $[NO_2]^+[Fe(NO_3)_4]^-$, and polymeric $[\{Fe_2O(NO_3)_4\}_n]$. Addison *et al.*[17] have proposed a rather complex mechanism by which $[NO_2]^+$-$[Fe(NO_3)_4]^-$ could arise from the nitrosonium salt, *via* the intermediate formation of $Fe(NO_3)_3$ and $[FeO(NO_3)]$. The present study, however, demonstrates that the compound $[FeO(NO_3)]$ is formed by the thermal decomposition of $[Fe_2O(NO_3)_4]$ at temperatures of 106—206 °C. Further heating of $[FeO(NO_3)]$ at 300 °C results in the formation of Fe_2O_3. A summary of the decomposition is presented in the Scheme:



As already noted, the d.t.a. thermogram[16] shows small features at 166—173, 195—210, and 224 °C, indicating that the decomposition of $[\{Fe_2O(NO_3)_4\}_n]$ to $[\{FeO(NO_3)\}_n]$, and of $[\{FeO(NO_3)\}_n]$ to Fe_2O_3 do not take place directly, but rather *via* the formation of (metastable) intermediates, although some of these features could be attributed to phase changes.

The Mössbauer isomer shift decreases steadily as nitrate groups attached to iron condense to form Fe–O–Fe linkages: $[N_4O_6]^{2+}2[Fe(NO_3)_4]^-$, 0·57 mm s^{-1}; $[NO]^+[Fe(NO_3)_4]^-$, 0·52 mm s^{-1}; $[\{Fe_2O(NO_3)_4\}_n]$, 0·50 mm s^{-1}; $[\{FeO(NO_3)\}_n]$, 0·47 mm s^{-1}; Fe_2O_3, 0·38 mm s^{-1}. The spectra of the two polymeric intermediates, $[\{Fe_2O(NO_3)_4\}_n]$ and $[\{FeO(NO_3)\}_n]$, both exhibit quadrupole splittings of *ca.* 1 mm s^{-1} indicating significant distortion from cubic symmetry, in contrast to the near cubic environments in the $[Fe(NO_3)_4]^-$ anion and Fe_2O_3. This again is probably a reflection of the differing Fe–O bond distances and electronegativities of the oxide and nitrogen ligands, which create imbalances in the σ-framework of octahedrally co-ordinated iron, rather than the presence of five-co-ordinated iron(III).

EXPERIMENTAL

All nitrato-derivatives of iron were handled in an atmosphere of dry nitrogen.

Spectra.—I.r. spectra were recorded as Nujol mulls using a Perkin-Elmer 457 spectrophotometer calibrated with a polystyrene film. Mössbauer measurements were performed at 77 K *vs.* a Pd/^{57}Co source (The Radiochemical Centre, Amersham) using a Harwell system equipped with a 256 multichannel analyser. Calibration of the velocity scale was effected using iron foil enriched with 10% ^{57}Fe and sodium nitroprusside. The resultant data were then fitted to Lorentzian line shapes by least-squares methods. Isomer shifts in the Table are quoted with respect to iron metal.

Preparative Methods.—The compound $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ was prepared by the reaction of iron(III) chloride with dinitrogen tetroxide in the presence of ethyl acetate. $[FeO(NO_3)]$ was obtained by the gas-phase reaction of pentacarbonyliron and nitrogen dioxide.[19] The substituted ethylammonium tetrachloroferrates(III) were prepared by the reaction of stoicheiometric quantities of iron(III) chloride and the respective ethylammonium chloride in nitromethane. The ethylammonium tetranitratoferrates(III) were obtained by treating the corresponding tetrachloroferrates(III) with dinitrogen tetroxide. Nitrosonium tetrachloroferrate(III) was prepared by the reaction of iron(III) chloride and liquid nitrosyl chloride, followed by removal of excess of nitrosyl chloride *in vacuo*.

Thermal Decomposition of $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$.—The sample of $Fe(NO_3)_3{\cdot}1{\cdot}5N_2O_4$ was distributed evenly and thinly over the base of a flat-bottomed Schlenk tube. In this way it was ensured that no significant thermal gradient was present in the depth of the sample. The evacuated apparatus was then heated to the required temperature. After holding the sample at the temperature for 1 h, sufficient material was removed for Mössbauer and i.r.

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study. The bulk of the sample was then heated to the next selected temperature, and the process repeated.

Samples of [$FeO(NO_3)$], from both the gas-phase reaction of pentacarbonyliron and nitrogen dioxide and the thermal decomposition of $Fe(NO_3)_3 \cdot 1 \cdot 5N_2O_4$, were sealed in ampoules *in vacuo* and heated successively to 300, 400, and 500 °C using an electric furnace for 1 h during which time the formation of nitrogen dioxide was observed.

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