830. *The Vapour-phase Reaction of Iron Pentacarbonyl with Nitrogen Dioxide; Iron(III) Oxide Nitrate*

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The reaction between iron pentacarbonyl and nitrogen dioxide vapours, using nitrogen as carrier gas, gives a yellow-brown powder of composition $FeNO_4$, in contrast to similar reactions using nickel and cobalt carbonyls, which give simple nitrites $M(NO_2)_2$. Infrared spectra and solution properties indicate that the product contains a covalent nitrate group, and should be formulated as $(FeNO_3)O$; a mechanism of reaction is suggested. Thermal decomposition at 400° gives an oxide FeO_2.

IN the reactions of dinitrogen tetroxide with metal carbonyls in the liquid phase, the self-ionisation $N_2O_4 \longrightarrow NO^+ + NO_3^-$ provides the active species, so that simple metal nitrates [*e.g.*, $Co(NO_3)_2,2N_2O_4$,[1] $Fe(NO_3)_3,N_2O_4$,[2]] or nitrato-derivatives [*e.g.*, $Mn(CO)_5NO_3$,[3]] are produced. In the vapour phase, the NO_2 molecule appears to be the active species, and reaction between nitrogen dioxide and the vapours of nickel carbonyl [4] and dicobalt octacarbonyl [5] give the pure nitrites $Ni(NO_2)_2$ and $Co(NO_2)_2$, respectively. The corresponding reaction of iron pentacarbonyl has special interest; several of the standard techniques for the preparation of nitric oxide involve reaction between the Fe^{2+} and NO_2^- ions, so that anhydrous iron nitrites may have much lower stability than those of nickel and cobalt.

EXPERIMENTAL

A portion ($\sim$10 ml.) of liquid dinitrogen tetroxide was transferred to tube A (Figure 1), and solidified in liquid nitrogen. The remainder of the apparatus was then flushed with dry nitrogen to exclude all air. With tap T_1 closed, iron pentacarbonyl (about 10 ml.) was then introduced into flask B, and the stream of dry nitrogen flowing into the flask carried the carbonyl vapour through the reaction vessel C and out at D. The tetroxide was allowed to warm to room temperature, all taps were opened, and a stream of nitrogen passed in at E then carried
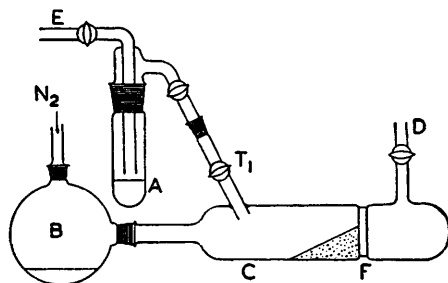

FIGURE 1. Apparatus used in reaction of NO_2 and $Fe(CO)_5$ vapours

the vapour into the reaction vessel. Immediately on mixing the two vapours a heavy yellow-brown smoke was formed, which was filtered out of the gas stream by the sintered-glass plate F. A plate of No. 2 porosity was not blocked by the product, which collected as shown. Provided that the carbonyl was always in excess a uniform product was obtained. With readily volatile carbonyls, this could easily be arranged by adjusting the flow rate of nitrogen over each liquid. Unless the carbonyl was in large excess, the initial yellow product reacted with nitrogen dioxide to form a brown deposit of the compound $Fe(NO_3)_3,N_2O_4$ round the mouth of the tube through which the dioxide entered the reaction vessel.

Analysis gave an empirical formula of $FeNO_4$ for the product (Found Fe, 42·0; N, 10·5. $FeNO_4$ requires Fe, 41·8; N, 10·5%). Absence of carbon was confirmed by analysis, and no

[1] C. C. Addison and D. Sutton, *J.*, 1964, 5553.
[2] C. C. Addison, B. J. Hathaway, and N. Logan, *Proc. Chem. Soc.*, 1958, 51.
[3] C. C. Addison, M. Kilner, and A. Wojcicki, *J.*, 1961, 4839.
[4] C. C. Addison, B. F. G. Johnson, N. Logan, and A. Wojcicki, *Proc. Chem. Soc.*, 1961, 306.
[5] C. C. Addison and D. Sutton, *Inorg. Chem.*, 1963, **2**, 228.

carbonyl bands were present in the infrared spectrum. The same product was formed when the temperature of the reaction vessel was varied between -20 and $20°$.

RESULTS AND DISCUSSION

The reaction of iron carbonyl with nitrogen dioxide resembles the reactions of nickel and cobalt carbonyls in that all carbonyl groups are removed, but differs in that the product cannot be formulated as a simple nitrite of iron. However, the compound $FeNO_4$ obtained in this way is the same as that identified [6] as an intermediate in the thermal decomposition of the adduct $Fe(NO_3)_3,N_2O_4$, and is therefore a significant member of this family of compounds. The main bands in the infrared spectrum are as follows: 1610w, sh, 1580s, 1560vs, sh, 1550vs, 1500vs, sh, (all ν_4 for $-ONO_2$), 1270vs, b. (ν_1) 1010s (ν_2), 800m (ν_6), and 765m (ν_3 or ν_5). These indicate the presence of a covalent nitrate, which may be unidentate or bidentate, and the absence of nitrate ions, nitrite groups, or nitrosyl groups; the compound is therefore formulated as $(Fe^{III}NO_3)O$. The molar susceptibility χ_M is 4980×10^{-6} at $23°$, $\mu_{eff.} = 3.50$ BM. This is low for an iron(III) high-spin compound, especially since in the related compound $Fe(NO_3)_3,N_2O_4$ the Fe ions have five unpaired


FIGURE 2. The thermal decomposition of $(FeNO_3)O$. (Heating rate $2°$ per minute. The vertical axis expresses weight loss in terms of 1 g. mol. of original compound.)
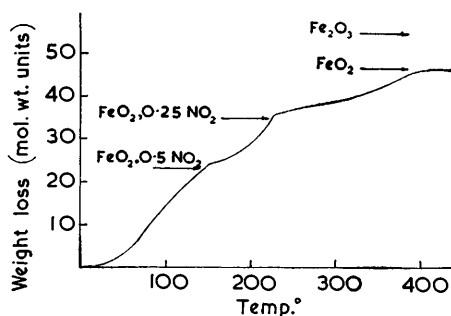
electrons, with $\mu_{eff.} = 5.83$. However, $(FeNO_3)O$ may be no longer magnetically dilute, and there may be ferro-magnetic effects. The low susceptibility is attributed to these causes, rather than to a metal atom which is in other than the Fe^{III} oxidation state.

When the compound $(FeNO_3)O$ is added to liquid dinitrogen tetroxide, there is an immediate vigorous reaction, and complete conversion into $Fe(NO_3)_3,N_2O_4$ occurs. This dismisses the possibility that the compound might be a $1:1$ mixture $Fe_2O_3 + Fe(NO_3)_3$, since the oxide Fe_2O_3 does not react with dinitrogen tetroxide under these conditions.

Thermal decomposition. Over the temperature range up to $400°$, the thermal decomposition is represented by the equation

$$(FeNO_3)O \longrightarrow FeO_2 + NO_2$$
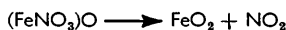
Evolution of nitrogen dioxide becomes apparent at $40°$, and the course of the decomposition is shown as a thermogravimetric analysis curve in Figure 2. Breaks in the curve occur at positions corresponding to the loss of half, and three-quarters, of the available nitrogen dioxide, but the most interesting feature is the plateau which is reached at $400°$ corresponding to the composition FeO_2; no nitrogen remains in the product at this stage. As with the parent compound $(FeNO_3)O$, it is no doubt misleading to relate the molar susceptibility directly with the number of unpaired electrons in the iron atom, but it should be recorded that χ_M for FeO_2 is 1.00×10^{-2} at $23°$; $\mu_{eff.} = 4.91$ B.M. which is close to the spin-only value for the Fe^{4+} ion.

Solution properties. The compound $(FeNO_3)O$ is insoluble in all common organic solvents; it is almost insoluble in water but readily soluble in dilute acids to give a clear yellow solution. Aqueous solutions were made (*a*) by solution of the compound in dilute hydrochloric acid, (*b*) by treatment of the solid compound with an ammonium hydroxide-

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

ammonium chloride solution, followed by filtration, (c) by solution of the compound in molten sodium hydroxide, and extraction with water. The only characteristic feature in the ultraviolet spectra of these solutions was the nitrate band at 302·5 mμ; this confirmed that nitrite is neither present in, nor produced from, the compound.

Mechanism of formation. The limited evidence at present available indicates that simple (anhydrous) metal nitrites are only stable if (as with the alkali and alkaline earth metals) a higher valency state of the metal is not readily available. Otherwise, the reaction

$$M^nNO_2 \longrightarrow M^{n+1}O + NO$$

occurs to achieve the higher valency state. Since nickel(II) is the stable valency state for nickel, a smoke of stable $Ni(NO_2)_2$ is produced in a reaction identical with that described above.[4] Cobalt(III) is not readily achieved in simple cobalt compounds, so that $Co(NO_2)_2$ does not decompose further when produced in the dicobalt octacarbonyl–nitrogen dioxide reaction. Using cobalt nitrosyl carbonyl,[5] the initial product $(NO)Co^{II}(NO_2)_2$ decomposes to a sufficient extent, *i.e.*, to $Co_2(NO)_2(NO_2)_2O_3$, to achieve the cobalt(III) oxidation state, which is presumably more readily accessible in this complex. By analogy with the above, it is reasonable to assume that the initial product in the iron carbonyl–nitrogen dioxide reaction is $Fe^{II}(NO_2)_2$. In this case, the higher oxidation state, Fe^{III}, is much more readily achieved than with nickel or cobalt, and, even when produced in aqueous solution, this compound is known to decompose immediately, evolving nitric oxide. When produced in a vapour-phase reaction, the initial stage in the decomposition

$$Fe(NO_2)_2 \longrightarrow FeO(NO_2) + NO \longrightarrow FeO_2 + 2NO$$
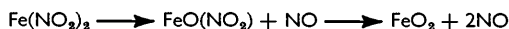
appears to be followed immediately by the second reaction. The oxide FeO_2 has been mentioned above, and it is relevant that thermogravimetric analysis (Figure 2) shows no evidence whatsoever for the transitory existence of $FeO(NO_2)$. The species FeO_2 may be regarded as a free radical containing Fe^{III} or as an oxide of Fe^{IV}; in either case it might be expected to display high chemical reactivity, especially in the finely divided state in which it is produced in the smoke. The fact that the oxide will combine with nitrogen dioxide

$$FeO_2 + NO_2 \longrightarrow (FeNO_3)O$$
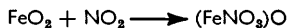
but not with nitric oxide is a useful example of the relative stability of transition-metal nitrates and nitrites, since it is not complicated by the presence of other ligands or solvents.

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