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The pentacyanonitrosylferrate(2 –) ion

IV *. Reactions with the carbanions of pentane-2,4-dione and 3-methylpentane-2,4-dione **

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Abstract

The products from the reaction of pentane-2,4-dione (acac H) with the anion $[Fe(CN)_5(NO)]^{2-}$ in the presence of alkali are $[Fe(acac)_3]$, $[Fe(CN)_6]^{4-}$, NO, and the oxime $HON{=}C(COCH_3)_2$. A reaction mechanism is proposed involving formation of an adduct of $[Fe(CN)_5(NO)]^{2-}$ and the carbanion, metal-to-ligand charge transfer, loss of NO and ligand rearrangement. A similar reaction occurs with 3-methylpentane-2,4-dione.

Introduction

In the complex ion $[Fe(CN)_5(NO)]^{2-}$, the nitrosyl ligand is formally present as NO^+ [1], and there is ready addition of nucleophiles such as amines [2]. Carbanions also react with $[Fe(CN)_5(NO)]^{2-}$ and, in the case of ethyl cyanoethanoate, we were able to isolate the oxime $HON{=}C(CN)CO_2Et$ as the organic product of reaction [3]. Kinetics studies showed that the rate-determining step is reaction of the ethyl cyanoethanoate carbanion with $[Fe(CN)_5(NO)]^{2-}$ (eqs. 1 and 2) to form a coloured adduct (**1**). With dicyanomethane [4], a second ionization occurs and the rate-determining process is formation of **2**. In both these cases the intense colour of the adduct, **1** or **2**, fades fairly rapidly (ca. 5 min) to give a yellow solution consistent with formation of aquapentacyanoferrate(3 –) (**3**). Preliminary experiments with the carbon acids pentane-2,4-dione (acac H) and 3-methylpentane-2,4-dione (3-Meacac H) showed that their reactions are different. After initial formation of an

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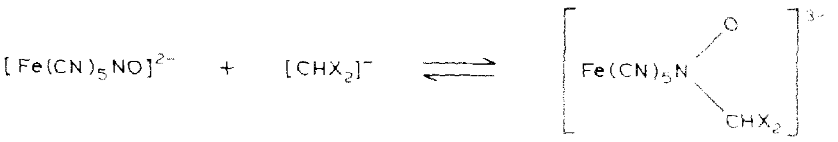
* For part 3, see ref. 3.

** Dedicated to Professor Colin Eaborn in recognition of his important contributions to mechanistic investigation in both organic and organometallic chemistry.

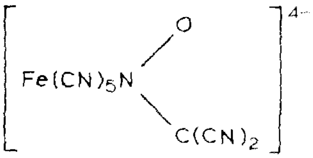


(1)

(1)

$$1 + H_2O \longrightarrow \underset{(3)}{[Fe(CN)_5(H_2O)]^{3-}} + \text{organic product} \qquad (2)$$

intensely coloured solution fading did not occur, but small quantities of tris(2,4-pentanedionato-*O,O*)iron(III), [Fe(acac)$_3$], or tris(3-methyl-2,4-pentanedionato-*O,O*)iron(III) [Fe(3-Meacac)$_3$] were precipitated from solution. In view of the



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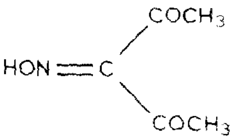

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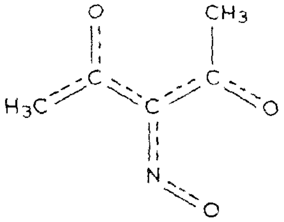

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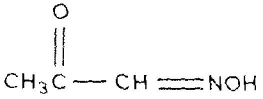
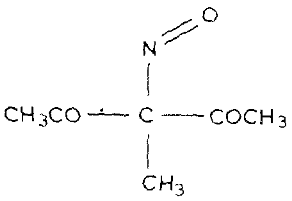


$CH_3C(=O)-CH=NOH$

(6)



$CH_3CO-C(N{=}O)(CH_3)-COCH_3$

(7)

unexpected ligand substitution and change in formal oxidation state of the iron, we decided to investigate the mechanism of these processes. We [5,6] have pointed out several times in print that, except under redox conditions, the reactions of $[Fe(CN)_5(NO)]^{2-}$ do not involve loss of the cyanide ligand, but here is a case where replacement of cyanide by another ligand appears to occur with great ease, and it might be supposed that free cyanide is liberated. This is significant in assessing the toxicity of $[Fe(CN)_5(NO)]^{2-}$ when used medically as a hypotensive agent [7].

Results and discussion

Addition of sodium hydroxide to a solution of pentane-2,4-dione and $Na_2[Fe(CN)_5(NO)]$ in water resulted in formation of an intense red solution and eventual precipitation of $[Fe(acac)_3]$; a similar reaction occurred with 3-methylpentane-2,4-dione. A series of experiments were conducted in which the ratio of reactants were varied and the yield of $[Fe(acac)_3]$ was determined, by extraction with dichloromethane, as a function of time. The yield increased over several hours but never exceeded 16% with respect to $[Fe(CN)_5(NO)]^{2-}$. The rate of production was higher from more concentrated solutions, but unaffected by the absence of dioxygen or light. Unfortunately, $[Fe(acac)_3]$ is not stable for long in alkaline solutions, and so the maximum yield could not be determined with accuracy.

The possible formation of free cyanide during reaction, not expected as the formation constants for all cyanoferrate complexes are very high e.g. (β_6 for hexacyanoferrate(II) is 10^{36}) was monitored by the use of a cyanide-sensitive electrode. This electrode functions only at a pH above 10, and enough sodium hydroxide was added to an aqueous mixture of pentane-2,4-dione and $Na_2[Fe(CN)_5(NO)]$ to attain a pH of 10.5. Over a period of 4 h, although $[Fe(acac)_3]$ came out of solution, the concentration of free cyanide remained below the limit of electrode detection (5×10^{-6} M) with an initial $[Fe(CN)_5(NO)]^{2-}$ concentration of 1.7×10^{-3} M. The same result was obtained for the reaction of 3-methylpentane-2,4-dione with $[Fe(CN)_5(NO)]^{2-}$. The amount of hydroxide present in the above was greater than that used in other experiments resulting in formation of $[Fe(acac)_3]$, and this may have influenced the result. Therefore a solution containing equimolar amounts of pentane-2,4-dione and hydroxide (0.012 M) and $[Fe(CN)_5(NO)]^{2-}$ (2.6×10^{-3} M) was allowed to stand for 1 h and then acidified (H_2SO_4). This would have converted any cyanide into volatile HCN. The solution was flushed with dinitrogen (300 ml min^{-1}) for 1 h and any HCN trapped in aqueous sodium hydroxide. The cyanide-sensitive electrode could detect no cyanide in this solution. Final confirmation of the absence of free cyanide in the reaction mixture came from the use of $[Fe(^{13}CN)_5(NO)]^{2-}$. The ^{13}C NMR spectrum of this reaction mixture had no signal at 120 ppm where it is known, from an independent measurement, that the resonance due to free cyanide occurs.

In view of the reproducibly low yield of $[Fe(acac)_3]$, which is quite easy to isolate quantitatively, it is clear that there must be other inorganic products of reaction. We attempted to identify them by the use of $[Fe(^{13}CN)_5(NO)]^{2-}$ and high field NMR spectroscopy. We [8] have examined the NMR spectra of a number of ^{13}C-labelled pentacyanoferrate complexes (i.e. $[Fe(CN)_5(NO)]^{2-}$, $[Fe(CN)_5(NO_2)]^{4-}$ and $[Fe(CN)_5(H_2O)]^{3-}$) and they all have characteristic chemical shifts for a doublet (equatorial cyano-ligands) and quintet (axial cyano-ligand). The spectrum of a reaction mixture containing $[Fe(^{13}CN)_5(NO)]^{2-}$ (2×10^{-2} *M*) and a four-fold excess of pentane-2,4-dione was examined immediately after mixing, with an accumulation time of 10 min. As well as those for $[Fe(CN)_5(NO)]^{2-}$, there were a number of signals in the region 176.7–178.3 ppm which were too weak to identify with certainty. Another spectrum, recorded after 3 h, showed only one signal, apart from those of residual $[Fe(CN)_5(NO)]^{2-}$: a singlet at 177.9 ppm which, from independent experiments [9], we identify as that due to the six equivalent cyano ligands in $[Fe(^{13}CN)_6]^{4-}$.

A solution of $Na_2[Fe(CN)_5(NO)]$ (0.75 *M*) and pentane-2,4-dione (1 *M*) and another of sodium hydroxide (2 *M*) were degassed separately on a vacuum line. The two solutions were mixed by means of evacuated connecting glassware and the resulting solution, protected from light, was left for 45 min. The gas over the solution was collected in an IR gas cell and the spectrum recorded immediately. Only the characteristic absorption of nitric oxide [10] at 1875 cm^{-1} was observed.

Reaction of $[Fe(CN)_5(NO)]^{2-}$ with alkaline ethyl cyanoethanoate results in formation [3] of the oxime $HON{=}C(CN)CO_2Et$. Other workers [11] have isolated oximes from the reaction of alkaline cyclic ketones with $[Fe(CN)_5(NO)]^{2-}$. It is possible that a parallel reaction occurs with pentane-2,4-dione. We examined this possibility by the use of natural abundance ^{13}C NMR spectroscopy. The nitrosation of pentane-2,4-dione in acid solution results in the formation of the oxime, 3-hydroxyiminopentane-2,4-dione (**4**) [12]. The spectrum of **4** in alkaline solution has signals at 25.3, 30.4, 156.4, 197.7 and 203.8 ppm, consistent with formation of the anion **5**. None of these peaks appeared in the spectrum of the reaction mixture $[Fe(CN)_5(NO)]^{2-}$/acac H/OH^-. So that, if **4** had been formed, it must have decomposed during the long accumulation time necessary to obtain the spectrum. Very early work by Cambi [13] is relevant. He claimed to have isolated the oxime **6** from the reaction of pentane-2,4-dione with alkaline $[Fe(CN)_5(NO)]^{2-}$ and this we confirmed (see later). The same oxime is obtained by the nitrosation of propanone. Cambi suggested that it is formed by the alkaline hydrolysis of **4** (eq. 3). The spectrum of the reaction mixture does contain signals corresponding to ethanoate

$$HON{=}C(COCH_3)_2 + [OH]^- \rightarrow HON{=}CHCOCH_3 + [CH_3CO_2]^- \qquad (3)$$

(23.7 and 187.4 ppm) but none corresponding to **6**. Equally we could not observe the spectrum of **6** in a reaction mixture propanone/OH^-/$[Fe(CN)_5(NO)]^{2-}$ where, from product isolation, it is known that **6** is formed. This suggests that, during the 15 h accumulation time necessary for the ^{13}C NMR spectrum, not only does **4** hydrolyze to **6** but **6** undergoes further decomposition to unidentified and spectrally undetected products, leaving ethanoate as the only proven organic product of reaction.

We attempted to overcome the long accumulation times necessary to obtain ^{13}C NMR spectra by the use of 3-methylpentane-2,4-dione labelled with ^{13}C in the 3-methyl group. The product of reaction here cannot, of course, be an oxime but the nitroso compound **7**, readily obtained by nitrosation in acid solution [14]. Low solubility in water made it necessary to use aqueous dimethylsulfoxide (dmso) as solvent to obtain the spectrum under alkaline conditions, with an accumulation time of less than 10 min. Even then, several peaks in the region 0.6–23.7 ppm were observed, indicating extensive decomposition. A similar number of peaks in that

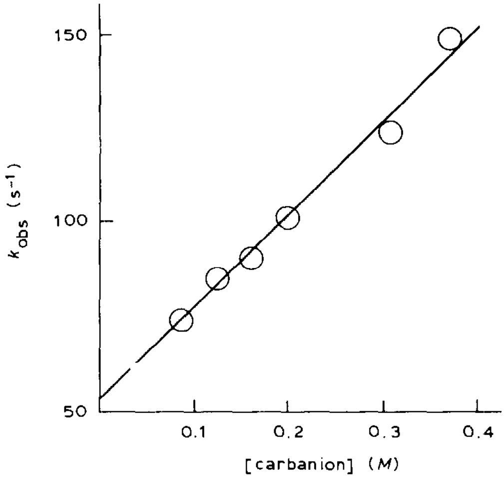


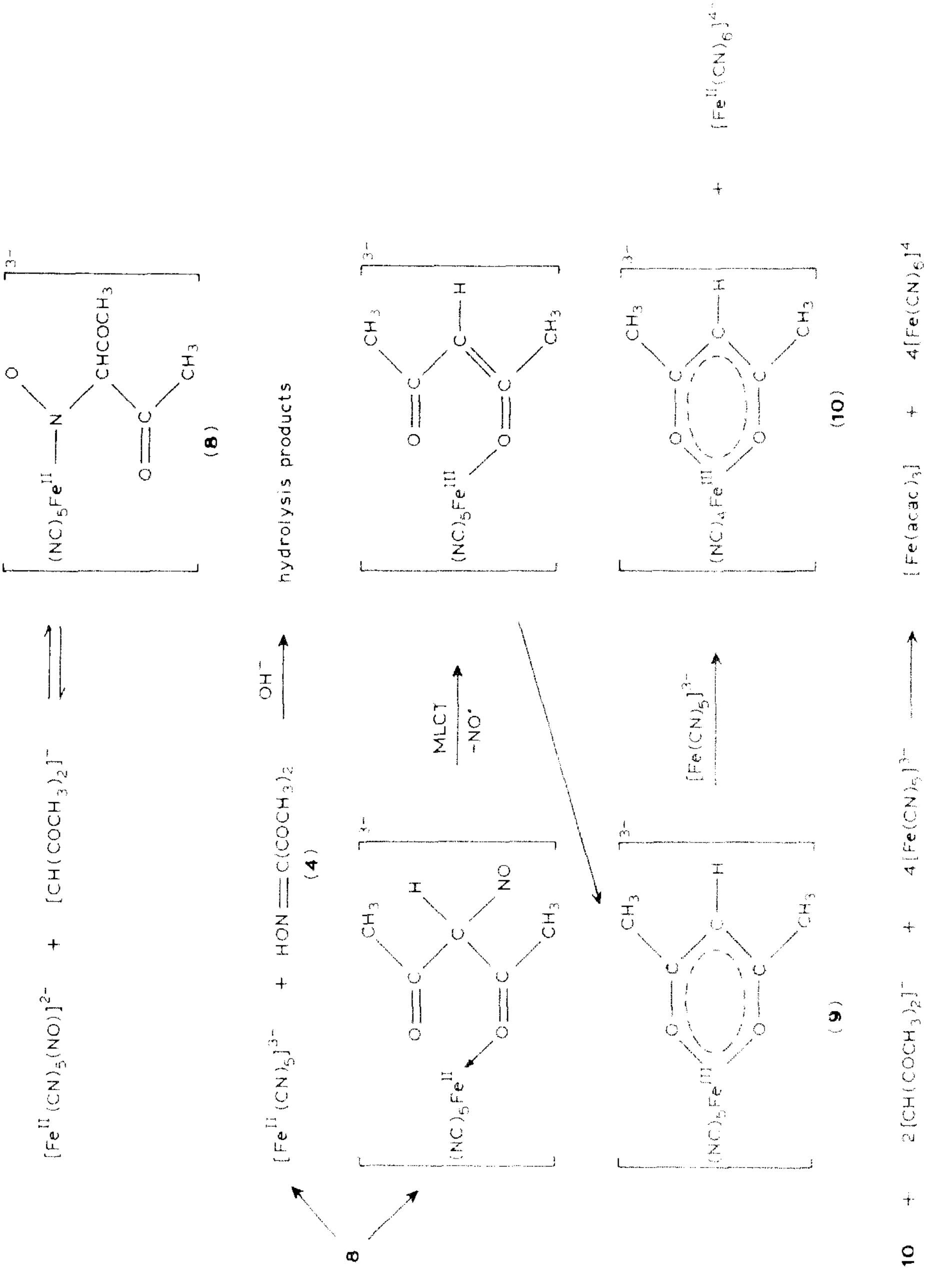
Fig. 1. Kinetic data for the reaction of $[Fe(CN)_5NO]^{2-}$ with $[acac]^-$ at 25 °C.

region was observed when an alkaline solution of labelled 3-Meacac H was treated with $[Fe(CN)_5(NO)]^{2-}$. There was no correspondence between peaks in the two spectra, but the solvent was different. Although no positive evidence that **7** is formed by the reaction with $[Fe(CN)_5(NO)]^{2-}$ was obtained, the spectral evidence was not inconsistent with that view.

We examined the changes in the visible spectrum of the reaction mixture acac $H/OH^-/[Fe(CN)_5(NO)]^{2-}$ as a function of time. They were found to be complicated and no full interpretation was possible. In essence, there was rapid formation of an absorption peak at 480 nm, as with other carbon acids, and during the course of an hour the maximum moved to 430 nm at a comparable intensity, unlike the behaviour of other carbon acids, for which fading is characteristic. For the change with pentane-2,4-dione, there was no tight isosbestic point. We suggest that this change is due to conversion of an adduct (**1**, $X = COCH_3$) to $[Fe(acac)_3]$ via a number of absorbing intermediates.

We were able to follow the formation of the initial species absorbing at 480 nm by stopped-flow spectrophotometry. From the known concentrations of pentane-2,4-dione and hydroxide and the pK_a [15], we calculated the concentration of the carbanion. There is a rectilinear relationship between k_{obs} and the carbanion concentration (Fig. 1), with a positive intercept indicating that the adduct is formed by rate-determining reaction of carbanion and $[Fe(CN)_5(NO)]^{2-}$ in an equilibrium, as is the case with diethyl propane-1,3-dioate [4]. Attempts to isolate the adduct (see Experimental section) resulted in a brown powder of inconsistent analysis, with UV-VIS and IR spectra consistent with a cyanoferrate(II) complex [16]. From an alkaline solution of this brown powder, we were able to isolate a small quantity of the oxime from propanone, (**6**).

The above is the evidence upon which we based a mechanism for the reaction of the pentane-2,4-dione carbanion with $[Fe(CN)_5(NO)]^{2-}$ to give $[Fe(acac)_3]$, $[Fe(CN)_6]^{4-}$, and the oxime **4**. The reaction involves a change of formal oxidation state of iron from II to III, substantial ligand rearrangement (but no liberation of



Scheme 1. Preferred mechanism for the reaction between $[Fe(CN)_5(NO)]^{2-}$ and $[acac]^-$.

cyanide), and formation of nitrogen oxide, NO. We suggest that the following four factors are responsible for this remarkable reaction.

(1) Both iron and NO have more than one formal oxidation state; in $[Fe(CN)_5(NO)]^{2-}$ they are present as iron(II) and NO^+, but iron(III) and NO or NO^- are also possible.

(2) The NO^+ ligand in $[Fe(CN)_5(NO)]^{2-}$ undergoes ready reaction with carbon-centred nucleophilic species.

(3) Although reaction of the pentane-2,4-dione carbanion in this instance occurs via attack at the carbon, the oxygen atoms of the carbonyl groups of the carbanion very readily coordinate with iron(III).

(4) Driving forces in the reaction include the aromatisation of the chelating ligand, the high formation constant of $[Fe(CN)_6]^{4-}$, and the irreversibility of NO loss.

The mechanism we propose is displayed in Scheme 1. The first step is addition of the carbanion to the nitrosyl ligand to form the adduct **8**; the transient ^{13}C NMR signals are consistent with this. Species **8** may decompose by two routes: dissociation to give the oxime and the pentacoordinated species $[Fe(CN)_5]^{3-}$ or, because of the special properties of **8**, metal-to-ligand charge transfer (MLCT) [17] permits coordination of the carbonyl oxygen atoms to iron(III) and aromatization of the ring, following loss of the nitrosyl group as NO. Compared with $[Fe(CN)_5(NO)]^{2-}$, there has been conversion of iron(II) to iron(III), and NO^+ to NO. The resultant species (**9**) is heptacoordinated but can transfer a cyano ligand to the pentacoordinated species formed in the other route to give two hexacoordinated species, **10** and $[Fe(CN)_6]^{4-}$. Then follows stepwise replacement of the cyano ligands in the substitution-labile **10** by the carbanion to give $[Fe(acac)_3]$ and $[Fe(CN)_6]^{4-}$. The low yield of $[Fe(acac)_3]$ (ca. 16%) is entirely consistent with this mechanism as five moles of $[Fe(CN)_5]^{3-}$ are required for every mole of $[Fe(acac)_3]$ produced. We do not claim that every step in this mechanism has been substantiated, but none of the evidence to hand is inconsistent with it.

In relation to the toxicity of $[Fe(CN)_5(NO)]^{2-}$ when used medically, this study does show that it is possible for $[Fe(CN)_5(NO)]^{2-}$ to lose its cyano ligands, but only because there is a species present ($[Fe(CN)_5]^{3-}$) ready to accept them; at no point was free cyanide present.

Experimental

Materials

Pentane-2,4-dione was redistilled before use, and solutions were used within a day. 3-Methylpentane-2,4-dione [18], 3-hydroxyiminopentane-2,4-dione [12], 3-methyl-3-nitropentane-2,4-dione [14], $Na_2[Fe(^{13}CN)_5(NO)]$ [8], 1-hydroxyiminopropane-2-one [19] and tris(3-methyl-2,4-pentanedionato-*O*,*O*)iron(III) [20] were made by literature methods. All other materials were reagent grade.

Product studies

In a typical experiment sodium hydroxide (0.03 mol) was added to a solution of pentane-2,4-dione (0.024 mol) and $Na_2[Fe(CN)_5(NO)]$ (0.005 mol) in water (50 ml). After standing in the dark for 3 h, red crystals of $[Fe(acac)_3]$ were removed by filtration {m.p. 175 °C, mixed m.p. 175 °C; mass spectrum m/z 353 (M^+)}.

With 3-methylpentane-2,4-dione red crystals of [Fe(3-Meacac)$_3$] were obtained {m.p. 145 °C, mixed m.p. 143 °C; mass spectrum m/z 395 (M^+)}.

Addition of ethanol, immediately after mixing, to a cold solution containing pentane-2,4-dione (0.25 M), sodium hydroxide (0.25 M) and $Na_2[Fe(CN)_5(NO)]$ (0.25 M) resulted in production of a red oil which, on trituration, formed a brown powder. This material was unstable, even when dry, and no consistent analyses could be obtained. However, the visible spectrum of an aqueous solution (maximum of 480 nm) was typical of a pentacyanonitrosylferratecarbanion adduct [4]. The IR spectrum of the powder contained a peak at 2040 cm^{-1}, characteristic of cyanide bound to iron(II) [16]. Addition of the red powder to aqueous sodium hydroxide (0.25 M) resulted in solution, and fading of the colour. The solution was extracted with dichloromethane, washed with water, dried ($MgSO_4$), and the solvent removed by evaporation to give crystals of 1-hydroxyiminopropane-2-one {m.p. 58 °C, mixed m.p. 58 °C; δ(H) ($CDCl_3$) 2.40 (s, 3H), 7.65 (s, 1H). δ(C) 27.5, 151.8, 203.0 ppm}.

Instrumentation

^{13}C NMR spectra were recorded either on a Varian CFT-20 spectrophotometer or on a Bruker WH-360 spectrophotometer at the SERC Regional NMR Service, University of Edinburgh. The cyanide sensitive electrode was obtained from Russell Electrodes, Auchtermuchty.

Kinetics

Rates of reaction were measured on a Hi-Tech stopped-flow spectrophotometer; data acquisition and processing were conducted on an Apple II microcomputer. One syringe contained a mixture of $Na_2[Fe(CN)_5(NO)]$ and pentane-2,4-dione, and the other sodium hydroxide. The ionic strength was maintained at 0.25 M by addition of KCl.

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