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MULTIPLE REACTION PATHWAYS IN THE REACTIONS OF CARBONYLFERRATE ANIONS WITH CHALCOGENS, AND WITH CHALCOGEN-CONTAINING ANIONS

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Summary

The reactions of $[HFe(CO)_4]^-$ or $[HFe_3(CO)_{11}]^-$ with either sulphite or polysulphide, all yield a mixture of $Fe_2S_2(CO)_6$, $Fe_3S_2(CO)_9$, $Fe_3S(CO)_{10}$ and $Fe_3S(CO)_9(SO)$, together with $Fe_3(CO)_{12}$ in the reactions with sulphite. $Fe_2S_2(CO)_6$ readily undergoes cluster expansion with $[HFe(CO)_4]^-$ to yield $Fe_3S_2(CO)_9$, but further reaction to give $Fe_3S(CO)_{10}$, or reconversion to $Fe_2S_2(CO)_6$ is not posssible. In contrast, $[HFe(CO)_4]^-$ with selenite yields $Fe_3Se_2(CO)_9$ only, but $[HFe_3(CO)_{11}]^-$ yields not only $Fe_3Se_2(CO)_9$ but also $Fe_2Se_2(CO)_6$ and $Fe_3(CO)_{12}$. With high molar ratios of elemental sulphur or selenium, $[HFe(CO)_4]^-$ yields pure $Fe_2E_2(CO)_6$ ($E = S$ or Se) but with an equimolar amount sulphur a mixture of $Fe_3S_2(CO)_9$, $Fe_3(CO)_{12}$, $Fe_3S(CO)_{10}$ and $Fe_3S(CO)_9(SO)$, with no $Fe_2S_2(CO)_6$, is obtained: use of an equimolar amount of selenium yields both $Fe_2Se_2(CO)_6$ and $Fe_3Se_2(CO)_9$. The formation and interconversions of iron-chalcogen carbonyl clusters are discussed.

Introduction

Many years ago Hieber and Gruber reported [1] that the anion $[HFe(CO)_4]^-$, formed from $Fe(CO)_5$ in alkaline methanol, reacted with polysulphide, S_x^{2-}, and with sulphite, SO_3^{2-}, to yield $Fe_2S_2(CO)_6$ (**1**) and $Fe_3S_2(CO)_9$ (**2**) respectively. On a preparative scale, these complexes are conveniently isolated from the respective reaction mixtures by extraction with hot hexane, and purified by sublimation. Similar reactions of $[HFe(CO)_4]^-$ with SeO_3^{2-} and TeO_3^{2-} were reported to yield [1] the isostructural [2–5] $Fe_3Se_2(CO)_9$ and $Fe_3Te_2(CO)_9$, respectively, while mixtures of $[XO_3]^{2-}$ species ($X = S$, Se, Te) yield [6] the mixed products $Fe_3(CO)_9XY$ ($XY = S$, Se, Te; $X \neq Y$).

For the formation of $Fe_3X_2(CO)_9$ when $X = S$ or Se, the following stoichiometry has been reported [1,7], eq. 1:

$$3[HFe(CO)_4]^- + 2[XO_3]^{2-} + 7H^+ \rightarrow Fe_3X_2(CO)_9 + 2CO + CO_2 + 5H_2O \qquad (1)$$

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In contrast to this, the formation of $Fe_3Te_2(CO)_9$ is thought [8] to proceed via the successive intermediacy of both $Fe_2Te_2(CO)_6$ and $Fe_3Te_2(CO)_{10}$, in strictly linear form, eq. 2:

$$[HFe(CO)_4]^- \rightarrow Fe_2Te_2(CO)_6 \rightarrow Fe_3Te_2(CO)_{10} \rightarrow Fe_3Te_2(CO)_9 \qquad (2)$$

In the course of the preparation of several lots of $Fe_3S_2(CO)_9$, for use in nitrosylation studies [9], we observed that the reaction of $[HFe(CO)_4]^-$ with sulphite is much more complex than is implied by eq. 1, and that unlike the reaction of $[HFe(CO)_4]^-$ with tellurite [8,10], it does not proceed along a linear pathway, but rather along divergent pathways from a very early intermediate.

In the present paper we report the results of a product study of some reactions of $[HFe(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$ both with chalcogen containing anions, and with the elemental chalcogens.

Experimental

All solvents were dried and purified by conventional methods, and all reactions were performed under nitrogen at 0°C. Thin-layer chromatography was performed using silica (MN-Kieselgel-G) coated plates (ca. 0.25 mm thick), and dry-column chromatography using silica (Sorbsil M60) in 2.8 cm plastic dialysis tubing. Light petroleum had b.p. 40–60°C. Known compounds were identified by microanalysis, and by spectroscopic and chromatographic comparison with authentic samples. Typical procedures are described below for reactions in the iron-sulphur series: essentially identical procedures were adopted for iron-selenium and iron-tellurium compounds. Salts of the anion $[HFe_3(CO)_{11}]^-$ were prepared by the literature method [11].

Reaction of $[HFe(CO)_4]^-$ *with* SO_3^{2-}

A solution of $Fe(CO)_5$ (4.9 g, 25 mmol) in MeOH (50 cm^3) was added to 50% aqueous KOH (5 cm^3) and the whole run into a solution of $Na_2SO_3 \cdot 7H_2O$ (7.6 g, 30 mmol) in 100 cm^3 aqueous MeOH (v/v 1 : 1). CH_2Cl_2 (250 cm^3) was then added, and the whole mixture stirred vigorously for 30 min. The mixture was acidified with concentrated HCl, and the CH_2Cl_2 layer separated. The aqueous layer was extracted with CH_2Cl_2 (3×100 cm^3) and the combined CH_2Cl_2 fraction was washed with water (3×150 cm^3), dried over $MgSO_4$, and evaporated to dryness. Chromatography, using hexane as eluant, yielded, in order: $Fe_2S_2(CO)_6$ (135 mg, 3.1%), $Fe_3S_2(CO)_9$ (780 mg, 19.4%), $Fe_3(CO)_{12}$ (90 mg, 2.1%), $Fe_3S(CO)_{10}$ (305 mg, 7.6%), and $Fe_3S(SO)(CO)_9$ (165 mg, 3.9%).

Reaction of $[HFe(CO)_4]^-$ *with polysulphide*

A solution of $Fe(CO)_5$ (4.9 g, 25 mmol) in MeOH (50 cm^3) was added to 50% aqueous KOH (5 cm^3): this solution was added to a well-stirred mixture of $Na_2S \cdot 9H_2O$ (9.7 g, 40 mmol) and elemental sulphur (5.1 g, 160 mmol) in water (100 cm^3) and CH_2Cl_2 (300 cm^3). After 15 min, the aqueous layer was acidified with conc. HCl, and the CH_2Cl_2 layer separated. The aqueous layer was extracted with CH_2Cl_2 (5×100 cm^3) and the combined CH_2Cl_2 fraction was filtered through cotton wool, and then washed with water (5×100 cm^3), dried over $MgSO_4$, and evaporated. Chromatography, with hexane as eluant gave, in order: $Fe_2S_2(CO)_6$

(785 mg, 18.2%), $Fe_3S_2(CO)_9$ (230 mg, 5.7%), $Fe_3S(CO)_{10}$, (85 mg, 2.1%) and $Fe_3S(SO)(CO)_9$ (95 mg, 2.3%).

Conversion of $Fe_2S_2(CO)_6$ to $Fe_3S_2(CO)_9$

To a solution containing $Fe_2S_2(CO)_6$ (172 mg, 0.50 mmol) and $Fe(CO)_5$ (98 mg, 0.50 mmol) in MeOH (50 cm^3) was added 50% aqueous KOH (5 cm^3). After 15 min, the mixture was acidified with HCl, 50 cm^3 water was added, and then the whole extracted with CH_2Cl_2 (3 × 50 cm^3). The CH_2Cl_2 fraction was washed with water, dried over $MgSO_4$, and evaporated. Chromatography (hexane as eluant) yielded $Fe_3S_2(CO)_9$ (130 mg, 54%) together with traces of both $Fe_2S_2(CO)_6$ and $Fe_3S(CO)_{10}$.

Reaction of $Fe_3S_2(CO)_9$ with $HFe(CO)_4^-$

In a reaction similar to the foregoing, $Fe_3S_2(CO)_9$ (242 mg, 0.50 mmol) was reacted in strongly alkaline solution with $Fe(CO)_5$ (294 mg, 1.50 mmol). Chromatography gave $Fe_3S_2(CO)_9$ (165 mg, 68% recovery) accompanied by only traces of $Fe_3(CO)_{12}$, $Fe_3S(CO)_{10}$ and $Fe_3S(SO)(CO)_9$: $Fe_2S_2(CO)_6$ was absent.

Reactions of $[HFe(CO)_4]^-$ with selenium

A solution of $Fe(CO)_5$ (3.5 g, 18 mmol) in MeOH (25 cm^3) was added to 50% aqueous KOH (5 cm^3): to this solution was added selenium powder (14.4 g, 180 mmol) and the whole mixture stirred for 1 h. After addition of 75 cm^3 water, the mixture was acidified with HCl, and repeatedly extracted with light petroleum. The combined organic extracts were washed with water (3 × 100 cm^3), dried over $MgSO_4$, and evaporated at room temperature to yield $Fe_2Se_2(CO)_6$ (0.95 g, 24%), pure by TLC. In a reaction identical to the foregoing except that the quantity of selenium was 1.44 g, 18 mmol, the product was primarily $Fe_3Se_2(CO)_9$, accompanied by very little $Fe_2Se_2(CO)_6$.

Reaction of $[HFe(CO)_4]^-$ with a deficit of sulphur

In a reaction similar to the foregoing, employing $Fe(CO)_5$ (3.5 g, 18 mmol) and sulphur (0.58 g, 18 mmol), the reaction products identified by TLC were $Fe_3S_2(CO)_9$, $Fe_3(CO)_{12}$, $Fe_3S(CO)_{10}$, and $Fe_3S(CO)_9(SO)$: $Fe_2S_2(CO)_6$ was absent.

Results

Reactions of $[HFe(CO)_4]^-$ with chalcogen-containing anions

By conducting the reaction of $[HFe(CO)_4]^-$ and sulphite essentially as described by Hieber and Gruber [1], but maintaining the temperature throughout at 0°C, and using low-temperature solvent extraction into CH_2Cl_2 [8], and then submitting the crude reaction product to chromatography, at least six neutral reaction products can be detected whose identities are indicative of a divergent reaction scheme. In addition to both $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$, and $Fe_3(CO)_{12}$ (**3**), we have detected the known [12,13] tri-nuclear clusters $Fe_3S(CO)_{10}$ (**4**) and $Fe_3S(CO)_9(SO)$ (**5**), together with a very labile pale-yellow complex (**6**), whose lability has so far prevented its isolation and identification. Using dry-column chromatography on a silica gel column, and developing with hexane the order of mobilities of the several fractions is: **1** > **2** > **6** > **3** > **4** > **5**. In a typical reaction the yields, based upon total iron, were as follows: **1**, 3.1%; **2**, 19.4%; **3**, less than 1%; **4**, 7.6%; **5**, 5.2%: so that as usual, some 60% of the total iron appears in inorganic form, principally as metallic iron and iron sulphides. Under entirely similar conditions, the reaction of $[HFe(CO)_4]^-$ with excess of polysulphide yields **1** as the principal product, with lesser quantities of **2**, **4** and **5**: in the absence of the sulphite ion, acting as an oxidant, **3** was not detected.

In complete contrast to the reaction of $[HFe(CO)_4]^-$ with sulphite, reaction with selenite under identical conditions yielded $Fe_3Se_2(CO)_9$ as the sole carbonyl product: no $Fe_2Se_2(CO)_6$ could be detected, and hence this reaction of the selenium system differs from both the sulphur and the tellurium analogues.

Reactions of $[HFe_3(CO)_{11}]^-$ with chalcogen-containing anions

The reaction of $[HFe_3(CO)_{11}]^-$ with sulphite has been observed previously [13] to provide a mixture of **1**, **2**, **3**, **4**, and **5**: compound **4**, $Fe_3S(CO)_{10}$ was first identified by this procedure [13]. An almost identical mixture of compounds resulted from the reaction of $[HFe_3(CO)_{11}]^-$ with polysulphide, except that in the more reducing environment, $Fe_3(CO)_{12}$ was absent from the products.

When $[HFe_3(CO)_{11}]^-$ was allowed to react with selenite under conditions identical to those employed in the original preparation of $Fe_3S(CO)_{10}$ [13], which had also yielded $Fe_3S(CO)_9(SO)$, the product spectrum included not only $Fe_2Se_2(CO)_6$ and $Fe_3Se_2(CO)_9$, analogous to **1** and **2** respectively, and $Fe_3(CO)_{12}$ (**3**), but also two further, very labile compounds, one light brown and one dark brown, having chromatographic characteristics similar to **4** and **5**: these have not been adequately characterised, on account of their lability.

Reactions of $[HFe(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$ with elemental chalcogens

The anion $[HFe(CO)_4]^-$ has been shown to react with a large excess of elemental sulphur (molar ratio S/Fe of 10/1) to yield, after acidification, pure $Fe_2S_2(CO)_6$ in 52% yield uncontaminated by any other iron-sulphur carbonyl clusters [10]. We have confirmed this observation: this reaction is probably the most efficient route yet reported for the production of large quantities of $Fe_2S_2(CO)_6$. In an entirely similar way, $[HFe(CO)_4]^-$ reacted with a 10-fold molar excess of elemental selenium to yield pure $Fe_2Se_2(CO)_6$, albeit in only 24% yield, again unaccompanied by any other iron-selenium carbonyl species.

However, when the chalcogen/iron molar ratio was reduced from 10/1 to 1/1, the products were entirely different. The reaction of equimolar quantities of $[HFe(CO)_4]^-$ and sulphur yielded none of the di-iron complex $Fe_2S_2(CO)_6$, but rather a mixture of $Fe_3S_2(CO)_9$, $Fe_3(CO)_{12}$, $Fe_3S(CO)_{10}$ and $Fe_3S(CO)_9(SO)$. On the other hand, the reaction of equimolar $[HFe(CO)_4]^-$ and selenium yielded both di-iron and tri-iron species, mainly $Fe_3Se_2(CO)_9$ with some $Fe_2Se_2(CO)_6$.

In contrast to the very vigorous and exothermic reaction of $[HFe(CO)_4]^-$ with elemental sulphur, $[HFe_3(CO)_{11}]^-$ showed no reaction at 0°C.

Interconversions of iron-sulphur carbonyls

The treatment of a methanol solution, equimolar in $Fe(CO)_5$ and $Fe_2S_2(CO)_6$, with concentrated aqueous alkali, followed by acidification, gave a 54% yield, based upon total iron, of $Fe_3S_2(CO)_9$, accompanied by only traces of unreacted $Fe_2S_2(CO)_6$ and of $Fe_3S(CO)_{10}$. Further increase of the Fe/S ratio in the system (originally 1/1) from 3/2 to 3/1 in the similar reaction of $Fe_3S_2(CO)_9$ and a three-fold excess of

$Fe(CO)_5$, did not however yield more than a trace of $Fe_3S(CO)_{10}$: 68% of the $Fe_3S_2(CO)_9$ was recovered, along with traces of **3**, **4** and **5** but no $Fe_2S_2(CO)_6$. These observations are summarised formally in eq. 3:

$$Fe_2S_2(CO)_6 \xrightarrow{HFe(CO)_4^-} Fe_3S_2(CO)_9 \not\xrightarrow{3HFe(CO)_4^-} 2Fe_3S(CO)_{10} \qquad (3)$$

Although $Fe_2S_2(CO)_6$ can very readily be converted into $Fe_3S_2(CO)_9$, the reverse conversion did not occur when alkaline methanolic solutions of $Fe_3S_2(CO)_9$ were treated either with sulphite or with polysulphide. In each case, the majority of the $Fe_3S_2(CO)_9$ was recovered unchanged after acidification, accompanied by only traces of $Fe_2S_2(CO)_6$ and, in the case of sulphite only, of $Fe_3(CO)_{12}$.

The reactions of $Fe_3S_2(CO)_9$, in alkaline methanolic solutions, with $[HFe(CO)_{11}]^-$, sulphite, or polysulphide each yields a very similar range of products in similar yields. Control experiments in which pure samples of either $Fe_2S_2(CO)_6$ or $Fe_3S_2(CO)_9$ were held in alkaline methanol at 0°C for 15 min and then acidified showed a similar range of products: $Fe_2S_2(CO)_6$ gave small quantities of both $Fe_3S_2(CO)_9$, and $Fe_3S(CO)_{10}$; $Fe_3S_2(CO)_9$ gave similarly $Fe_2S_2(CO)_6$ and $Fe_3S(CO)_{10}$: neither control reaction gave any $Fe_3S(CO)_9(SO)$ or $Fe_3(CO)_{12}$.

When samples of $Fe_2S_2(CO)_6$ or $Fe_3S_2(CO)_9$ were extracted from the crude reaction mixtures by Sohxlet extraction using hexane, rather than by low temperature extraction at 0°C, subsequent chromatographic examination revealed that neither $Fe_3S(CO)_{10}$ nor $Fe_3S(CO)_9(SO)$ was present: however these complexes are not transformed to $Fe_3S_2(CO)_9/Fe_3(CO)_{12}$ mixtures upon heating, since control experiments using pure samples of $Fe_3S(CO)_{10}$ or $Fe_3S(CO)_9(SO)$ showed that upon reflux in hexane they rapidly decomposed depositing iron metal and iron sulphides; no other iron carbonyl species are formed during the decomposition. It is the thermal lability of these compounds, which are formed rather readily, which delayed for so long their isolation and characterisation [12,13].

Discussion

Contrary to the initial report of Hieber [1] the reactions of $[HFe(CO)_4]^-$ with sulphite or with polysulphide do not yield purely $Fe_3S_2(CO)_9$ or $Fe_2S_2(CO)_6$. A wide range of clusters are formed, although $Fe_3S_2(CO)_9$ and $Fe_2S_2(CO)_6$ are certainly the major products from sulphite and polysulphide respectively. $Fe_3(CO)_{12}$ is formed from $[HFe(CO)_4]^-$ only in the presence of the oxidant sulphite, but even when polysulphide is the sole source of sulphur, the thionyl complex $Fe_3S(CO)_9(SO)$, containing [12] the SO ligand, is formed. When this complex was first reported [12], from the reaction of $[HFe_3(CO)_{11}]^-$ with sulphite, the SO ligand was regarded as having been formed by only partial reduction of some of the sulphite by the weak reducing agent $[HFe_3(CO)_{11}]^-$, a weaker reductant than $[HFe(CO)_4]^-$. However this same thionyl complex is formed even in the reaction of $[HFe(CO)_4]^-$ with polysulphide: even in this very reducing mixture, some of the sulphur is oxidised to give the thionyl ligand. The only oxygen sources for formation of the SO ligand in this system are carbonyl ligands, and the methanol/water solvent: reduction of water with transfer of oxygen to form the thionyl ligand seems the most probable course of this reaction.

In its reactions with elemental sulphur, the behaviour of $[HFe(CO)_4]^-$ is dominated by the overall reaction stoichiometry, in particular the molar ratio S/Fe, providing pure $Fe_2S_2(CO)_6$ when this ratio is 10/1, but no $Fe_2S_2(CO)_6$ at all when it is 1/1.

Since control reactions of both $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ in alkaline methanol showed the formation of only traces of other iron-sulphur carbonyl species, it must be concluded that the observation of multiple products is not the result of spontaneous transformations effected upon a single iron-sulphur carbonyl species. Indeed, efficient interconversions of the iron-sulphur carbonyl clusters are rare under the reaction conditions used here: although $Fe_2S_2(CO)_6$ can be converted to $Fe_3S_2(CO)_9$ by addition using $[HFe(CO)_4]^-$, further addition of $[HFe(CO)_4]^-$ does not give $Fe_3S(CO)_{10}$, nor can $Fe_3S_2(CO)_9$ be converted back to $Fe_2S_2(CO)_6$, either with sulphite or polysulphide.

All of the iron-sulphur carbonyl clusters can be formed from the mono-iron precursor $[HFe(CO)_4]^-$, in spontaneous self-assembly reactions. As with ferredoxin type iron-sulphur clusters, the products of these self-assembly reactions are more influenced by the reaction stoichiometry than by thermodynamic stability: once formed, the carbonyl clusters can only be converted to other species, if at all, under forcing conditions, indicative of deep traps on the potential energy surface.

The courses of the reactions of $[HFe(CO)_4]^-$ (and of $[HFe_3(CO)_{11}]^-$), even with simple substrates such as sulphide or elemental sulphur, are at present undetermined. All of the intermediates appear to be anionic, since no clusters can be extracted into organic solvents until the aqueous reaction phase has been acidified. A simple precedent for the formation of a neutral, hydrogen-free, polynuclear carbonyl by protonation of an anion is found in the formation of $Fe_3(CO)_{12}$ by protonation, in aqueous solution, of $[HFe_3(CO)_{11}]^-$ [14]. The nature of the intermediates in both the iron-sulphur and the iron-selenium carbonyl systems are under active investigation.

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