Reduction of Aromatic Nitro Compounds with 2-Mercaptoethanol and Oxidation of Thiophenol with Molecular Oxygen Mediated by Trinuclear Iron Acetate Complexes

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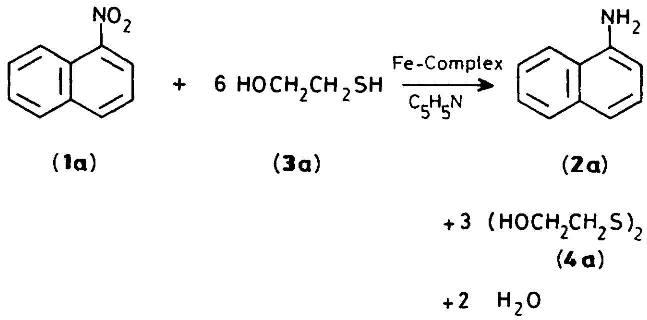
Aromatic nitro compounds (**1a–h**) were selectively reduced by 2-mercaptoethanol (**3a**) in the presence of trinuclear acetate complexes $[Fe^{III}_2M^{II}O(OAc)_6(py)_3]$[(**5a**; M = Fe), (**5b**; M = Mn), (**5c**; M = Co), and (**5d**; M = Ni)] to give the corresponding amines (**2a–h**). The reaction was found to follow pseudo-first-order kinetics. The activity order of these complexes for the reduction followed the sequence (**5b**) > (**5a**) > (**5d**) > (**5c**). These complexes also efficiently catalysed oxidation of thiophenol (**3b**) with molecular oxygen to produce diphenyl disulphide (**4b**) quantitatively. The activity order of the complexes for the oxidation was similar to that observed in the reduction of nitro compounds.

Oxo-centred tri-iron carboxylate complexes of the formula $[Fe_3O(OCOR)_6L_3]$ (L = neutral ligand) have recently attracted considerable attention, because they exhibit interesting physical properties[1–4] and act as unique catalysts for oxygenation of alkenes,[5] alkanes,[6] and amides,[7] these complexes being regarded as simple models for active sites of certain iron-containing proteins in biology.[8] Since it has been found that intramolecular electron transfer between the iron atoms in the complexes occurs very rapidly even at room temperature,[1d,4] the complexes may also be expected to function as catalysts for a reduction reaction which involves electron-transfer processes; we have found that trinuclear acetate complexes $[Fe^{III}_2M^{II}O(OAc)_6(py)_3]$ (M = Fe and Mn) can effectively mediate the reduction of aromatic nitro compounds with 2-mercaptoethanol to give the corresponding amines.[9]† In this publication, we report the details of the reduction reaction of the nitro compounds and the oxidation of thiophenol with molecular oxygen using these trinuclear complexes.

Results and Discussion

Reduction of Aromatic Nitro Compounds.—Treatment of 1-nitronaphthalene (**1a**) with 2-mercaptoethanol (**3a**) (8 equiv.) in pyridine in the presence of $[Fe_3O(OAc)_6(py)_3]$ (**5a**) (0.05 equiv.) with stirring at 25 °C under nitrogen for 18 h gave 1-naphthylamine (**2a**) (97%) together with 2-hydroxyethyl disulphide (**4a**) (95%) (Scheme 1 and Table 1). It was confirmed that the Fourier transform i.r. spectrum of the complex recovered (71%) by adding ether–hexane to the reaction mixture under conditions using a slight stoicheiometric excess of (**1a**) [(**1a**):(**3a**) = 1:5] was identical with the starting complex, suggesting that the complex (**5a**) keeps the trinuclear structure during the reaction. The related trinuclear iron complex (**6**) and the mixed complex (**5b**) could be successfully used in place of (**5a**). The other mixed complexes (**5c**) and (**5d**), μ-oxo-bis[*N*,*N*′-bis(salicylidene)ethylenediaminatoiron(III)] (**7**), mesotetraphenylporphyrinatoiron(III) complexes (**8a–c**), and simple iron salts (**9**) and (**10**) appeared to be less effective than (**5a**). A more polar solvent, either *N*,*N*-dimethylformamide (DMF) or *N*-methylpyrrolidone (NMP), was found to enhance



Scheme 1.

$[Fe_2MO(OAc)_6(py)_3]$ (**5**)
a; M = Fe, b; M = Mn, c; M = Co, d; M = Ni

$[Fe_3O(OAc)_6(py)_3]ClO_4$ (**6**)

$[Fe(salen)]_2O$ (**7**)

$[Fe(tpp)]_nX$ (**8**)
a; $n = 2$, X = O
b; $n = 1$, X = OAc
c; $n = 1$, X = Cl

$FeCl_2{\cdot}4H_2O$ (**9**)

$FeSO_4{\cdot}6H_2O$ (**10**)

Table 1. Reduction of 1-nitronaphthalene.[a]

Iron complex	Yield of (**2a**) (%)[b]	Recovery of (**1a**) (%)[b]
(**5a**)	97	
(**5b**)	99	
(**5c**)	38	57
(**5d**)	63	30
(**6**)	96	
(**7**)	54	45
(**8a**)	7	91
(**8b**)[c]	28	70
(**8c**)		96
(**9**)	11	88
(**10**)	12	87

[a] The reaction was performed in pyridine under nitrogen at 25 °C for 18 h. [(**1a**)]:[(**3a**)]:[Fe complex] 1:8:0.05. [b] Determined by g.l.c. analysis. [c] [(**8b**)] 0.15.

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† The related reduction systems Fe^{II}-dihydrolipoamide[10] and $[Fe_4S_4(SR)_4]^{2-}$-RSH[11] have been reported.

Table 2. Reduction of 1-nitronaphthalene in various solvents.[a]

Solvent (ratio)	Yield of (**2a**) (%)[b]	Recovery of (**1a**) (%)[b]
C_5H_5N	83	14
C_5H_5N–H_2O (9:1)	70	25
DMF	99	
DMF–H_2O (9:1)	99	
NMP	99	
MeCN	3	93
CH_2Cl_2		95

[a] The reaction was carried out under nitrogen at 25 °C for 5 h. [(**1a**)]:[(**3a**)]:[(**5a**)] 1:8:0.05. [b] Determined by g.l.c. analysis.

Table 3. Reduction of 2- or 4-substituted nitrobenzenes.[a]

Substrate	Yield of (**2**) (%)[b]	Recovery of (**1**) (%)[b]
(**1b**)	70	22
(**1c**)	54	46
(**1c**)[c]	99	
(**1d**)	99	
(**1e**)	27	60
(**1e**)[d]	97	
(**1f**)	99	
(**1g**)	90	7
(**1h**)	99	

[a] The reaction was undertaken in DMF under nitrogen at 25 °C for 18 h. [(**1**)]:[(**3a**)]:[(**5a**)] 1:8:0.05. [b] Determined by g.l.c. analysis. [c] The reaction at 50 °C. [d] The reaction for 60 h.

Table 4. Reduction of α-diketones, azobenzene, and azoxybenzene.[a]

Substrate	Iron complex	Product (%)[b]	Recovery (%)
(**11a**)	(**5a**)	(**12a**) (90)	5
(**11b**)	(**5b**)	(**12b**) (75)	12
(**11c**)	(**5b**)	(**12c**) (78)	
(**11a**)[c]	(**5a**)	(**12a**) (68)[e]	23[e]
(**11a**)[c]	(**5b**)	(**12a**) (69)[e]	26[e]
(**11a**)[c]	(**5c**)	(**12a**) (21)[e]	68[e]
(**11a**)[c]	(**5d**)	(**12a**) (48)[e]	45[e]
(**13**)	(**5a**)	(**15**) (85)	
(**13**)	(**5b**)	(**15**) (85)	2
(**14**)[d]	(**5a**)	(**15**) (45)	34
(**14**)[d]	(**5b**)	(**15**) (66) (**13**) (5)	18

[a] The reaction was carried out in DMF under nitrogen at 70 °C for 18 h. [Substrate]:[(**3a**)]:[(**5**)] 1:6:0.05. [b] Isolated yield. [c] Reaction at 30 °C. [d] Reaction for 40 h. [(**3a**)] 12. [e] Determined by ^1H n.m.r. analysis.

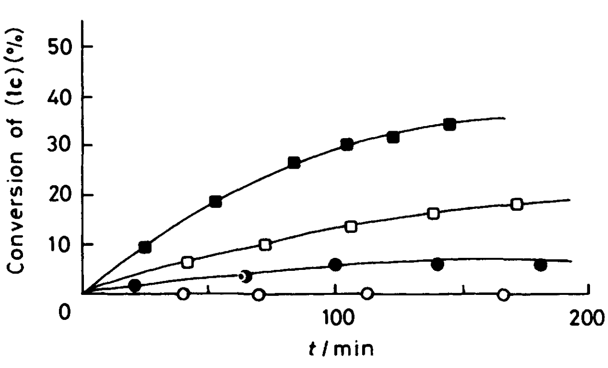
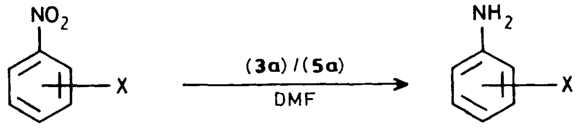


Figure 1. Reaction of 4-nitrotoluene (**1c**) with the thiols (**3a–d**) in pyridine at 40 °C in the presence of the iron complex (**5a**) under the conditions $[(\mathbf{1c})]_0$ 50 mmol dm^{-3}, $[(\mathbf{3})]_0$ 1.0 mmol dm^{-3}, and $[(\mathbf{5a})]_0$ 2.5 mmol dm^{-3}: (**3a**) (■), (**3b**) (●), (**3c**) (□), (**3d**) (○).

the rate of the reaction (Table 2). In contrast, the reaction did not proceed in acetonitrile or dichloromethane. When thiophenol (**3b**) or n-butanethiol (**3c**) could be used in place of (**3a**), the reaction rate was considerably decreased (Figure 1). 1,1-dimethylethanethiol (**3d**) was ineffective.

Table 3 shows the results for the reduction of 4- or 2-substituted nitrobenzenes (**1b–h**) with (**3a**) in the presence of (**5a**) in DMF (Scheme 2). Both aldehyde and ketone groups were not reduced and the corresponding amines (**2b–h**) were formed in high yield. Longer reaction time or higher temperature was needed to complete the reaction of the substrate having either an electron-donating group or an *ortho*-substituent. It is noteworthy that each amine produced was isolated in an almost pure state after being extracted with ether and washed with water.



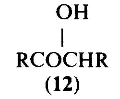
(**1**)
b; X = H
c; X = 4-Me
d; X = 4-Cl
e; X = 4-OMe
f; X = 4-COMe
g; X = 2-Cl
h; X = 2-CHO

(**2**)
b; X = H
c; X = 4-Me
d; X = 4-Cl
e; X = 4-OMe
f; X = 4-COMe
g; X = 2-Cl
h; X = 2-CHO

Scheme 2.

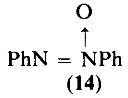
Reduction of Benzil, Azobenzene, and Azoxybenzene.—Benzil (**11a**) could also be reduced to benzoin (**12a**) with (**3a**) in the presence of the trinuclear acetate complexes (**5a–d**) in DMF (Table 4). The order of activity of these complexes for the reduction judged from the conversion of (**11a**) was found to follow the sequence (**5b**) ≃ (**5a**) > (**5d**) > (**5c**), a trend similar to that observed in the reduction of the nitro compound (**1a**). To obtain a higher yield, a somewhat higher reaction temperature was required. Azobenzene (**13**) and azoxybenzene (**14**) were also successfully reduced to hydrazobenzene (**15**).

RCOCOR
(**11**)
a; R = Ph
b; R = 3-$MeOC_6H_4$
c; R = 2-Furyl



$\mathrm{RCO\overset{OH}{\overset{|}{C}}HR}$
(**12**)
a; R = Ph
b; R = 3-$MeOC_6H_4$
c; R = 2-Furyl

PhN = NPh
(**13**)



$\mathrm{Ph\overset{\overset{O}{\uparrow}}{N}=NPh}$
(**14**)

PhNHNHPh
(**15**)

Kinetics for Reduction of 4-*Nitrotoluene* (**1c**).—The reduction reaction of 4-nitrotoluene (**1c**) with (**3a**) in the presence of (**5a**) was conducted at 40 °C in DMF by following the disappearance of (**1c**) periodically with g.l.c. No peak other than those for (**1c**), (**2c**), and (**4a**) was observed in each chromatogram. Under the experimental conditions, $[(\mathbf{1c})]_0$ 50 mmol dm^{-3}, $[(\mathbf{3a})]_0$ 1.0 mol dm^{-3}, and $[(\mathbf{5a})]_0$ 1.3–4.0 mmol dm^{-3}, the decrease in [(**1c**)] followed pseudo-first-order kinetics (Figure 2). Plots of the pseudo-first-order rate constants (k_{obs}) *versus* the initial concentration of the iron complex (**5a**) were linear. Change of the concentration of (**3a**) in the range of 0.50 to 2.0 mol dm^{-3} did not affect the rate constant (Figure 3). The rate constant *k* in equation (1) estimated from the slope

$$-d[ArNO_2]/dt = k[Fe_3O(OAc)_6(py)_3]_0[ArNO_2] \quad (1)$$

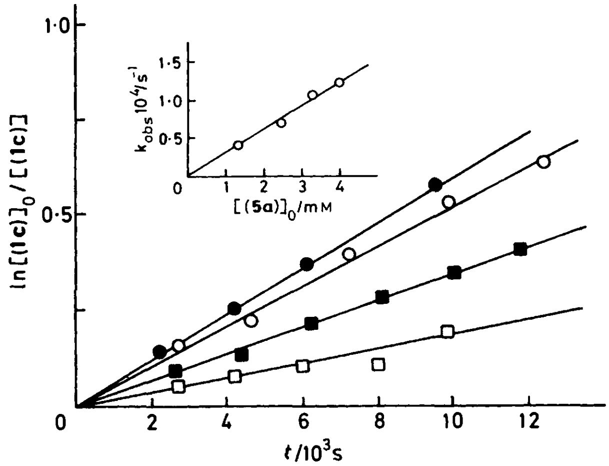


Figure 2. Plots for the reaction of 4-nitrotoluene (**1c**) with (**3a**) in the presence of (**5a**) in DMF at 40 °C: $[(\mathbf{1c})]_0$ 50 mmol dm^{-3}, $[(\mathbf{3a})]_0$ 1.0 mol dm^{-3}, and $[(\mathbf{5a})]_0$ 1.3 mmol dm^{-3} (□), 2.5 mmol dm^{-3} (■), 3.3 mmol dm^{-3} (○), and 4.0 mmol dm^{-3} (●).

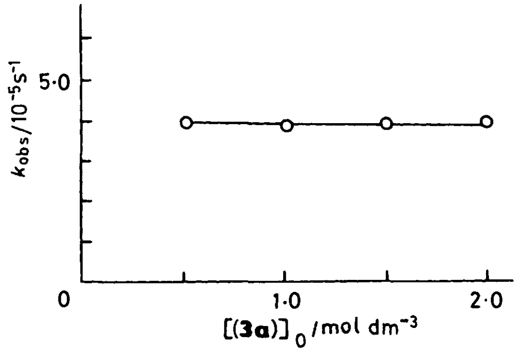


Figure 3. Effect of the concentration of the thiol (**3a**) on the reduction rate of 4-nitrotoluene (**1c**) in DMF at 40 °C. Initial concentrations of (**1c**) and (**5a**) were 50 and 1.3 mmol dm^{-3}, respectively.

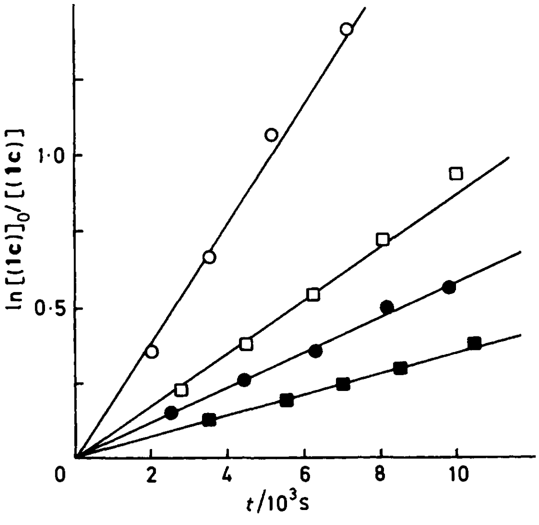


Figure 4. Plots for the reduction of 4-nitrotoluene (**1c**) with (**3a**) in the presence of the complexes (**5a–d**) in DMF at 40 °C. Initial concentrations of (**1c**), (**3a**), and (**5**) were 50, 1.0, and 2.5 mmol dm^{-3}, respectively: (**5a**) (□), (**5b**) (○), (**5c**) (■), (**5d**) (●).

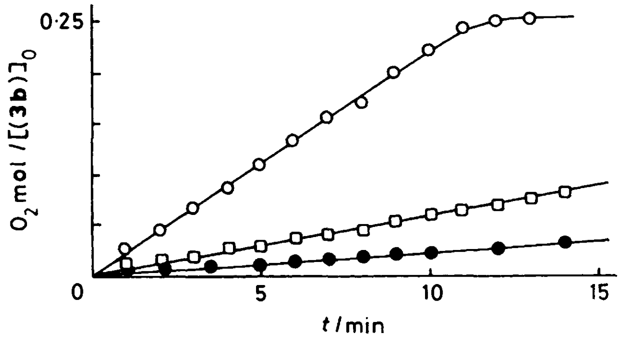


Figure 5. Oxygen uptake in the oxidation of thiophenol (**3b**) in pyridine at 15 °C: $[(\mathbf{3b})]$ 300 mmol dm^{-3}, $[(\mathbf{5a})]$ 1 mmol dm^{-3} (○), $[(\mathbf{8b})]$ 3 mmol dm^{-3} (□), $[(\mathbf{16})]$ 3 mmol dm^{-3} (●).

Table 5. The relative rate of oxygen uptake in the oxidation of (**3b**).[a]

Iron complex	Relative rate
(**5a**)	1.00
(**5b**)	1.02
(**5c**)	0.87
(**5d**)	0.93
(**7**)	0.88
(**8b**)	0.31
(**16**)	0.11

[a] Oxygen uptake was measured for the reaction of (**3b**) (0.3 mol dm^{-3}) in pyridine at 15 °C. Concentration of the total metal atoms was 3 mmol dm^{-3}.

in Figure 2 was 3.2×10^{-2} dm^{-3} mol^{-1} s^{-1}. The reaction of (**1c**) with (**3a**) using the complexes (**5b–d**) also followed pseudo-first-order kinetics, as did the reaction using (**5a**) (Figure 4). The activity order of these complexes ($k_{obs} = k[(\mathbf{5})]_0 \times 10^5$ s^{-1}) followed the sequence (**5b**) (15.0) > (**5a**) (6.9) > (**5d**) (4.6) > (**5c**) (2.7), this being also consistent with the preliminary estimation of the order in the reductions of (**1a**) and (**11a**).

Oxidation of Thiophenol with Molecular Oxygen.—When the complex (**5a**) (3.3×10^{-3} equiv.) was added to a solution of thiophenol (**3b**) in pyridine and stirred at 15 °C under oxygen, diphenyl disulphide (**4b**) was formed quantitatively, no other products being detected (Scheme 3). The time course of oxygen uptake in the reaction is shown in Figure 5. The reaction was completed within a period of 12 min during which time a stoicheiometric amount of oxygen was consumed. Under the reaction conditions employed, the rate of oxygen uptake followed zero-order kinetics with respect to the thiol concentration, as has often been observed in thiol oxidation with molecular oxygen in the presence of other metal complexes including a Fe_4S_4 type cluster.[12,13] Relative rates of oxygen uptake using (**5a–d**), (**7**), (**8b**), and $FeCl_3$ (**16**) are summarised in Table 5. The order of catalytic activity of these iron species was also similar to that observed in the reduction of nitro compounds. When the thiol (**3a**) was used instead of (**3b**), oxygen was absorbed more rapidly (Figure 6). In the case of the thiol (**3c**), plots of oxygen uptake *versus* time were not linear; a bluish precipitate was formed during the reaction.

$$\underset{(\mathbf{3b})}{4\,PhSH} + O_2 \xrightarrow[C_5H_5N]{\text{Fe-Complex}} \underset{(\mathbf{4b})}{2\,PhSSPh} + 2\,H_2O$$

Scheme 3.

Reaction Scheme.—When the thiol (**3a**) (20 equiv.) was added to a solution of the complex (**5a**) in pyridine under nitrogen, a peak at $\lambda_{max.}$ 430 nm (ε 4.9×10^3) appeared in the visible spectrum, suggesting that co-ordination of the thiol (**3a**) to the complex (**5a**) possibly occurred by ligand exchange (Figure 7).*

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* However, the number of thiol molecules co-ordinated to the complex could not be determined because thiol in dilute solution is easily oxidised by adventitious air.

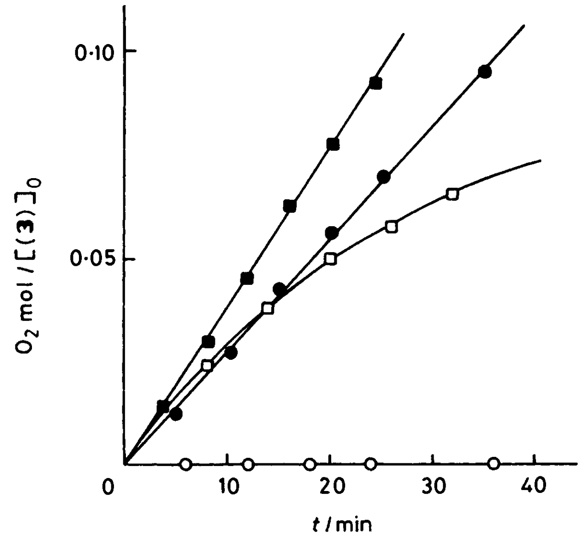

Figure 6. Oxygen uptake in the oxidation of thiols (**3a–d**) in pyridine under air at 0 °C. Initial concentrations of (**5a**) and (**3**) were 1 and 300 mmol dm^{-3}, respectively: (**3a**) (■), (**3b**) (●), (**3c**) (□), (**3d**) (○).

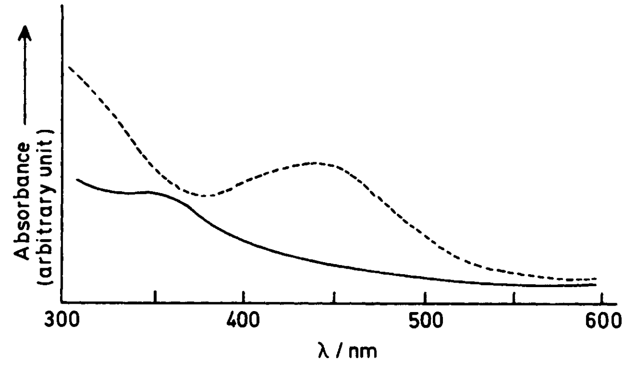

Figure 7. Visible spectrum of the iron complex (**5a**) in pyridine. The dashed curve is the same solution immediately after addition of the thiol (**3a**) (20 equiv.) under nitrogen

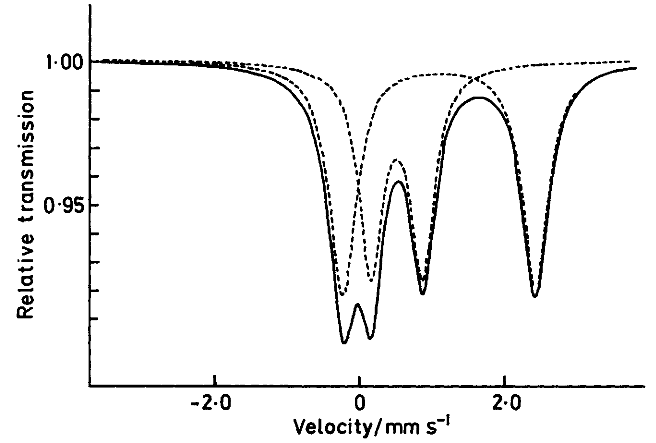

Figure 8. ^{57}Fe Mössbauer spectrum of the precipitate obtained from a mixture of the iron complex (**5a**) and the thiol (**3a**) (20 equiv.) at 77 K.

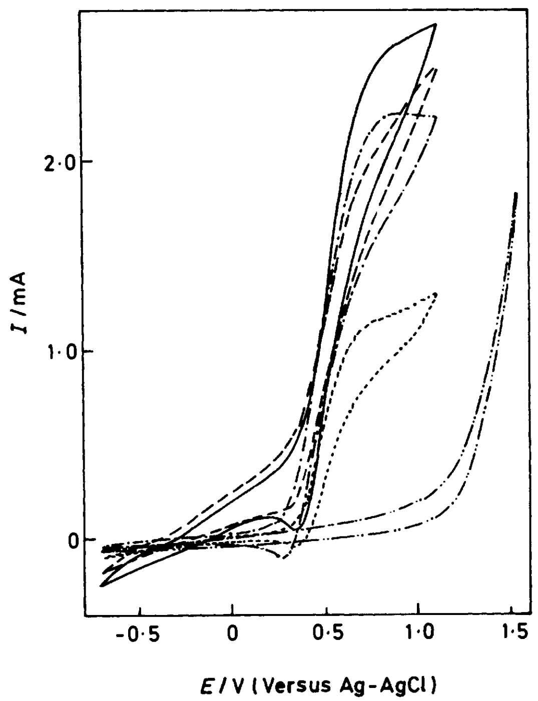

Figure 9. Cyclic voltammograms for the iron complex (**5a–d**) (5 mmol dm^{-3}) in the presence of the thiol (**3a**) (0.25 mol dm^{-3}) in DMF under nitrogen with lithium perchlorate (0.5 mol dm^{-3}) at a scan rate of 0.1 V s^{-1}: (**5a**) (——), (**5b**) (— — —), (**5c**) (- - - -), (**5d**) (— · —), in the absence of the complex (— · · —).

The spectrum of (**5a**) did not change on addition of the nitro compound (**1a**). Although the iron–thiol complex(es) formed *in situ* could not be isolated in pure state, the ^{57}Fe Mössbauer spectrum of the precipitate obtained by addition of ether–hexane to a mixture of the complex (**5a**) and the thiol (**3a**) (20 equiv.) in pyridine suggested formation of partially reduced species such as $Fe^{III}Fe^{II}_2$; the spectrum at 77 K showed four absorptions which can be assigned to two quadruply split doublets, one characteristic of high-spin Fe^{II} ($\delta = 1.107$ and $\Delta = 2.662$ mm s^{-1}) and the other high-spin Fe^{III} ($\delta = 0.526$ and $\Delta = 0.709$ mm s^{-1}) (Figure 8).[1d,4] The Fe^{II}/Fe^{III} ratio calculated from the peak areas was 56:44.* These results suggest that the active species which may transfer electrons to either a nitro compound or molecular oxygen would be the partially reduced species. Formation of the species by the reaction of (**5a**) with (**3a**) under the reaction conditions employed may be relatively fast compared with the successive electron-transfer process; the reduction rate of (**1c**) was not affected by the initial concentration of (**3a**) and the oxidation of (**3b**) with oxygen followed zero-order kinetics. It is, however, unclear how many electrons are transferred in each catalytic cycle. Figure 9 displays the cyclic voltammogram results for the complexes (**5a–d**) (5 mmol dm^{-3}) in the presence of an excess amount of the thiol (**3a**) (0.25 mol dm^{-3}) in DMF under nitrogen with lithium perchlorate (0.5 mol dm^{-3}) as the supporting electrolyte. While an apparent redox couple was not seen in each voltammogram, a fairly large oxidation current was observed at lower potential than that in the absence of the complexes. The current may be attributable to the anodic oxidation of (**3a**) mediated by the complexes, although the detail of change of the oxidation states of the iron and the other heteronuclear atoms in the complexes during the sweep is unclear. The potential at which the anodic current observed shifted was in the sequence (**5b**) $\simeq$ (**5a**) > (**5d**) > (**5c**), this trend being consistent with the activity order found in the reduction of (**1**) and the oxidation of (**3b**). Since the potentials at which the current appeared were significantly higher than those for the reduction of nitro compounds estimated by polarographic technique,[14] electron transfer from the active species to the nitro compounds may proceed by an inner-sphere process.

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* The precipitate was obtained as a fine powder and therefore did not show a clear-cut Mössbauer spectrum at room temperature.

Experimental

^1H N.m.r. spectra were obtained with a Nippon Denshi JMN-PS-100 spectrometer for $CDCl_3$ solutions. G.c.–m.s. spectra were obtained with a Hitachi RMU-6MG spectrometer, Fourier transform i.r. spectra with a Nippon Bunko FT/IR-3 spectrometer, and visible spectra with a Hitachi 124 spectrophotometer. G.l.c. analysis was carried out on a Shimadzu GC-8A gas chromatograph. ^{57}Fe Mössbauer spectra were measured using an Elron commercial set which consisted of an MFG-2 signal generator, an MVT-2 velocity transducer, and an MD-2 amplifier. The cyclic voltammetric experiment was carried out with a Hokuto Denko HA-301 potentiostat, HB-104 functional generator and Yokogawa Hokushin Electric model 3025 *X–Y* recorder. The potential was recorded *versus* an Ag–AgCl electrode and a glassy carbon electrode was used as the working electrode.

The trinuclear acetate complexes (**5a–d**)[1e] and (**6**),[2a] *N,N'*-bis(salicylidene)ethylenediaminatoiron(III) complex (**7**),[15] and mesotetraphenylporphyrinatoiron(III) complexes (**8a–c**)[16] were prepared by the methods reported previously. 3,3'-Dimethoxybenzil (**11b**) and furil (**11c**) were prepared by acyloin condensation of the corresponding aldehydes.[17] Other chemicals used were commercially available. The following experimental details given below may be regarded as typical in methodology and scale.

Reduction of 1-*Nitronaphthalene* (**1a**) *with* 2-*Mercaptoethanol* (**3a**) *in the Presence of the Iron Complex* (**5a**) *in DMF.*—A mixture of (**1a**) (1 mmol), (**3a**) (8 mmol), and (**5a**) (0.05 mmol) in DMF (10 cm^3) was stirred under nitrogen at 25 °C for 18 h. Formation of the amine (**2a**) (98%) and the disulphide (**4a**) (93%) was confirmed by g.c.–m.s. analysis. After extraction with ether and washing with water, the amine (**2a**) (92%) was also isolated by column chromatography on silica gel.

Oxidation of Thiophenol (**3b**) *with Molecular Oxygen in the Presence of the Iron Complex* (**5a**).—A solution of the iron complex (**5a**) (0.02 mmol) and pyridine (10 cm^3) was added to a flask equipped with a gas burette and a rubber cap. After the atmosphere of the flask and the gas buret was replaced with oxygen, the thiol (**3b**) (6 mmol) in pyridine (10 cm^3) was added *via* syringe to the flask and resulting mixture stirred at 15 °C for 30 min. Formation of diphenyl disulphide (**4b**) (98%) was confirmed by g.c.–m.s. analysis. The disulphide (**4b**) (85%) was also isolated by recrystallisation from ethanol.

Acknowledgements

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