Catalytic Function of the Fe_4S_4 Cluster in the Reduction of Aromatic Nitro Compounds with t-Butyl Thiol and Triethylamine

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The $Fe_4S_4(SPh)_4{}^{2-}$ cluster, in MeCN or MeCN–MeOH (1 : 1) containing t-butyl thiol and Et_3N, catalyses the reduction of nitrobenzene and *m*-dinitrobenzene to aniline and *m*-nitroaniline, respectively, with concomitant oxidation of the terminal ligand of the Fe_4S_4 cluster to t-butyl phenyl disulphide, and then di-t-butyl disulphide.

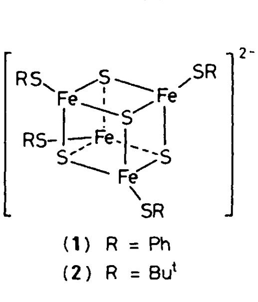
Recently we have reported that a synthetic Fe_4S_4 cluster acts as an electron-transfer agent in redox systems using carbanions such as phenyl-lithium and n-butyl-lithium[1] and as a hydride-transfer agent in the hydrogenation of unsaturated compounds.[2] We now report the novel function of $[Bu^n{}_4N]_2[Fe_4S_4(SPh)_4]$ (**1**) which catalyses the reduction of aromatic nitro compounds in the presence of t-butyl thiol in MeCN and MeCN—MeOH (1:1) containing Et_3N, accompanied by the conversion of (**1**) into $[Bu^n{}_4N]_2[Fe_4S_4(SBu^t)_4]$ (**2**) through the oxidation of terminal ligand of (**1**) [*e.g.* reactions (1) and (2)]. This function of (**1**) is of interest in connection with that of ferredoxin which reduces 2,4-dinitrophenol and *m*-dinitrobenzene to 2-amino-4-nitrophenol and *m*-nitroaniline respectively.[3]

$$6Bu^tSH + 3/4\,(\mathbf{1}) + ArNO_2 \xrightarrow{Et_3N} 3Bu^tSSPh + 3/4\,(\mathbf{2}) + ArNH_2 + 2H_2O \quad (1)$$

$$6Bu^tSH + ArNO_2 \xrightarrow[Et_3N]{(\mathbf{2})} 3Bu^tSSBu^t + ArNH_2 + 2H_2O \quad (2)$$

The reactions were carried out as follows. A degassed solution of t-butyl thiol, nitrobenzene or *m*-dinitrobenzene, and Et_3N in MeCN or MeCN–MeOH (1 : 1) was added under argon to (**1**) and the mixture was stirred at 50 °C for 20 h. The reaction was stopped by adding degassed dilute hydrochloric acid, the mixture was treated by the usual method, and the products were analysed by g.l.c. The results are summarized in Table 1.

In the absence of (**1**), nitrobenzene and *m*-dinitrobenzene were not reduced with the Bu^tSH–Et_3N system under the conditions shown in Table 1 and were recovered almost unchanged. The reaction of (**1**) with t-butyl thiol and Et_3N (molar ratio of 1 : 30 : 30) in MeCN did not give disulphides in detectable amounts. Furthermore, the visible spectrum of the Bu^tSH–Et_3N–(**1**) (30 : 5 : 1) system in MeCN–MeOH (1 : 1) exhibited an absorption at 433 nm (ε 1.63 × 10^4) [in the absence of Bu^tSH and Et_3N: 443 nm (ε 1.56 × 10^4)] and spectral changes were not observed. These facts indicate that (**1**) is not reduced with the Bu^tSH—Et_3N system, although there is an interaction between (**1**) and Bu^tS^- or Bu^tSH. The



(**1**) R = Ph
(**2**) R = Bu^t

Table 1. Catalytic reduction of nitrobenzene and *m*-dinitrobenzene using the Bu^{t}SH–Et$_3$N–(**1**) system.[a]

			mol of product relative to (**1**)			
ArNO$_2$	Molar ratio Bu^{t}SH : ArNO$_2$: Et$_3$N : (**1**)	Solvent	ArNH$_2$[b]	Bu^{t}SSPh	Bu^{t}SSBu^t	PhSSPh
PhNO$_2$	30 : 4 : 5 : 1	A–M	0.59	1.61	0.21	0.02
		A	0.25	0.58	0.12	0.03
	60 : 10 : 5 : 1	A–M	0.97	1.95	0.56	0.01
m-C$_6$H$_4$(NO$_2$)$_2$	30 : 4 : 5 : 1	A–M	2.08	3.93	1.53	0.02
		A	0.80	2.03	0.31	0.03
	60 : 10 : 5 : 1	A–M	3.41	3.97	5.46	0.01

[a] (**1**): 0.2 mmol in 20 ml of MeCN–MeOH (1 : 1) (A–M) or MeCN (A). Argon, 50 °C, 20 h. [b] ArNH$_2$ = PhNH$_2$ or *m*-C$_6$H$_4$(NH$_2$)(NO$_2$).

reaction of (**1**) with nitrobenzene and Et$_3$N (molar ratio 1 : 4 : 5) in MeCN–MeOH (1 : 1) gave little aniline and diphenyl disulphide. However, *m*-dinitrobenzene was converted into *m*-nitroaniline in amounts of 0.32 mol/(**1**)(MeCN) and 2.62 mol/(**1**) [MeCN–MeOH (1 : 1)] after 20 h under similar conditions [PhSSPh: 0.81 and 1.01 mol/(**1**) respectively] and the Fe$_4$S$_4$ core was destroyed.

In the reactions of nitrobenzene and *m*-dinitrobenzene with the Bu^{t}SH–Et$_3$N–(**1**) system, it was found that aniline and *m*-nitroaniline are produced together with t-butyl phenyl disulphide, di-t-butyl disulphide, and diphenyl disulphide, the sum of the amounts of which corresponds nearly to three times the amounts of the anilines produced, as Table 1 shows. The amounts of anilines produced increased with time. The behaviour of the cluster (**1**) which brings about the selective formation of *m*-nitroaniline was similar to that of ferredoxin,[3] but was different from that of a mononuclear complex consisting of an iron(II) salt and dihydrolipoamide [0.2 M carbonate buffer (pH 9.8)–EtOH (1 : 3); 50 °C].[4] t-Butyl phenyl disulphide was produced in the largest amount of the disulphides until it reached 4 mol/(**1**), thus indicating that the reaction proceeds *via* the oxidation of the terminal ligand. After the PhS$^-$ ligand of (**1**) had been oxidized entirely to Bu^{t}SSPh, the amount of di-t-butyl disulphide produced increased. When (**2**) was used instead of (**1**), nitrobenzene was reduced to aniline by the Bu^{t}SH–Et$_3$N system in a yield similar to that in the case of (**1**). Furthermore, in the reaction of *m*-dinitrobenzene with the Bu^{t}SH–Et$_3$N–(**1**) system [MeCN–MeOH (1 : 1) (10 ml); 20 h], when the reaction mixture, in which t-butyl phenyl disulphide had been produced to the extent of 4 mol/(**1**), was concentrated to one-half of the original volume and cooled to −20 °C, black crystals of (**2**) precipitated in 71% yield, thus indicating that the Fe$_4$S$_4$ core is not destroyed owing to the presence of t-butyl thiol. The use of methanol as a solvent and excess t-butyl thiol resulted in an acceleration of the reduction of nitrobenzene and *m*-dinitrobenzene to anilines (Table 1).

The above results provide evidence for the catalytic function of the Fe$_4$S$_4$ cluster in a redox system consisting of Bu^{t}SH, Et$_3$N, (**1**), and aromatic nitro compounds. Furthermore, this oxidative ligand substitution provides a novel method for preparing various Fe$_4$S$_4$ clusters.

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