Catalytic Oxidation of Benzoin by 1,4-Benzoquinone in the Presence of 4Fe-Ferredoxin Model Complexes with Cysteine-containing Peptides

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The catalytic oxidation of benzoin by 1,4-benzoquinone in the presence of cysteine-containing peptides or bulky thiolate/Fe_4S_4 complexes using the 2−/1− redox couple is reported.

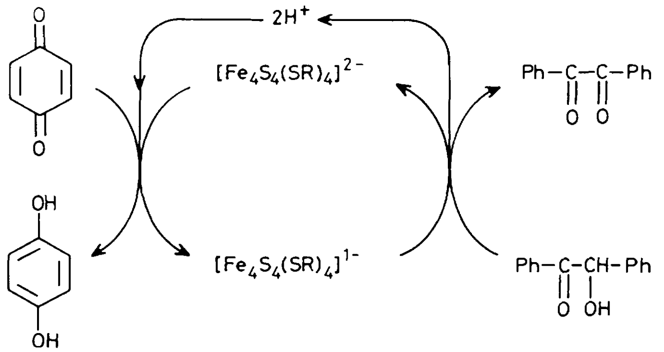
Studies on the catalytic or stoicheiometric reactions of various 4Fe-ferredoxin model complexes have been reported using the 3−/2− redox couple with a negative redox potential.[1—6] Recently, we have found a relatively stable 2−/1− redox couple for $[Fe_4S_4(\text{Z-Cys-Ile-Ala-OMe})_4]^{2-}$ (Z = benzyloxycarbonyl) (**1**) or $[Fe_4S_4(\text{tipbt})_4]^{2-}$ (tipbt = 2,4,6-tri-isopropylbenzenethiolato) (**2**) in *N*,*N*-dimethylformamide (DMF).[7] Both complexes are readily oxidised by 1,4-benzoquinone in organic solvents and, especially in a 5% Triton X-100 micellar solution, the 1− state is detectable by absorption and e.s.r. spectroscopy at 295 and 20 K, respectively.[8] Recently, the formation of the 1− state with one-electron oxidation of (**2**) has been independently reported by Millar *et al.*[9]

We examined the catalytic oxidation of benzoin by 1,4-benzoquinone in the presence of various Cys-containing peptide complexes or bulky thiolato complexes in DMF ([benzoin] : [1,4-benzoquinone] : [ferredoxin model complex] = 250 : 500 : 1). The [4Fe–4S] complexes of Cys-containing peptides were synthesized by the ligand exchange reactions of

Table 1. Catalytic oxidation of benzoin by 1,4-benzoquinone in the presence of $[Fe_4S_4(L)_4]^{2-}$ complexes.[a]

L	% Yield[b]
None	Trace
Z-Cys-Ile-Ala-OMe[c] [complex (**1**)]	16,800
Z-Cys-Pro-Leu-OMe	10,400
Z-Cys-Pro-Val-OMe	13,000
Z-Cys-Pro-Gly-OMe	2,400
tipbt[c] [complex (**2**)]	11,100
2,4,6-trimethylbenzenethiolato	9,600
S–Ph[d]	9,100
S–Bu^t [d]	8,100

[a] Reaction conditions: [benzoin], 2.5×10^{-1} M; [1,4-benzoquinone], 5×10^{-1} M; [complex], 1×10^{-3} M; 5 ml of DMF : tetrahydrofuran (1 : 1); 3 h; 25 °C. [b] Yield of benzil based on the $[Fe_4S_4(L)_4]^{2-}$ concentration. Determined by high performance liquid chromatography. [c] Z = benzyloxycarbonyl; tipbt = 2,4,6-tri-isopropylbenzenethiolato (see ref. 7 for preparation). [d] $[Fe_4S_4(S\text{–}Ph)_4]^{2-}$ and $[Fe_4S_4(S\text{–}Bu^t)_4]^{2-}$ were prepared by literature methods (ref. 11).



Scheme 1

$[Fe_4S_4(S\text{–}Bu^t)_4]^{2-}$ with the coresponding peptides.[10,11] Table 1 lists the yields of benzil from benzoin based on the ferredoxin model complex. The turnover number for the oxidation in the presence of (**1**) is 0.93 min^{-1} and the yield (16,800%) of benzil after 3 h is remarkable among known catalytic reactions using ferredoxin model complexes. The order for the catalytic activity of the Cys-containing peptide complexes was found to be (**1**) > $[Fe_4S_4(\text{Z-Cys-Pro-Val-OMe})_4]^{2-}$ > $[Fe_4S_4(\text{Z-Cys-Pro-Leu-OMe})_4]^{2-}$ > $[Fe_4S_4(\text{Z-Cys-Pro-Gly-OMe})_4]^{2-}$, whereas the order for the benzenethiolato complexes was (**2**) > $[Fe_4S_4(\text{2,4,6-trimethylbenzenethiolato})_4]^{2-}$ > $[Fe_4S_4(S\text{–}Ph)_4]^{2-}$. This trend is consistent with the stability of 2–/1– redox couples determined by cyclic voltammetry. Complexes (**1**) and (**2**) exhibit a quasi-reversible redox couple at +0.12 V *vs.* saturated calomel electrode (SCE) ($i_{p,c}/i_{p,a} \simeq 1.0$) and −0.03 V *vs.* SCE ($i_{p,c}/i_{p,a} \simeq 1.0$), respectively.[7] $[Fe_4S_4(\text{Z-Cys-Pro-Gly-OMe})_4]^{2-}$ has an irreversible redox couple ($E_{p,c}$ = −0.10 V *vs.* SCE). The instability of the 1– state of the ferredoxin model complex caused a gradual inactivation in the oxidation cycle.

No reaction of benzoin with 1,4-benzoquinone occurred in the absence of ferredoxin model complex. The 2– states of the above ferredoxin model complexes were inert to benzoin but readily reduced 1,4-benzoquinone at room temperature in DMF. Scheme 1 shows the catalytic oxidation of benzoin by 1,4-benzoquinone using the 2–/1– redox couple of the ferredoxin model complex in DMF.

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