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Preliminary communication

ENZYME CATALYSED OXIDATION OF FERROCENE COMPOUNDS

Roger Epton, Michael E. Hobson and George Marr*
Department of Physical Sciences, The Polytechnic, Wolverhampton, WV1 1LY (Great Britain)

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Summary

A facile transformation of ferrocene and a series of substituted ferrocenes to the corresponding ferricinium ions has been effected by hydrogen peroxide in the presence of the native or immobilized enzyme horseradish peroxidase.

Peroxidase, in the presence of hydrogen peroxide, is known to catalyse the oxidation of aromatic amines and phenols to give oxidation products depending primarily on the nature of the substituent[1].

We report the oxidation at room temperature of ferrocene and several substituted ferrocenes, in 50% methanol - phthalate buffer (pH 6.1) with hydrogen peroxide (5.0×10^{-2} mM) in the presence of horseradish peroxidase (HRP) (Sigma Type II, 0.6% in water) as the catalyst.

The addition of HRP and hydrogen peroxide to a yellow solution of ferrocene in aqueous methanol gave a blue solution[2,3]. The oxidation was allowed to proceed for 4h and on addition of a concentrated aqueous solution of ammonium diamminetetrathiocyanatochromate(III) (ammonium Reineckate) a precipitate of ferricinium diamminetetrathiocyanatochromate(III)

* To whom correspondence should be addressed.

TABLE 1. Rates of reaction of ferrocene and some ferrocene alcohols with H_2O_2 in the presence of HRP

Substrate	Substrate Concentration μ mol	Initial Rate ΔA/h/μg enzyme /μmol substrate[a]		Maximum Rate ΔA/h/μg enzyme /μmol substrate[a]	
		Native Enzyme	Immobilized Enzyme[b]	Native Enzyme	Immobilized Enzyme
FcH	5.4	0.026	0.0046	0.0099	0.0019
$FcCH_2OH$	7.2	0.012	0.0029	0.0050	0.0013
FcCHMeOH	6.2	0.012	0.0028	0.0056	0.0011
$FcCMe_2OH$	5.6	0.010	0.0028	0.0048	0.0011

[a] ΔA - change in absorbance

[b] 42.9 mg of HRP bound per gram of dry polymer

(yield 59%).(i.r. identical with that of an authentic sample[4]) was deposited. The oxidation was repeated with ferrocenemethanol and gave hydroxymethylferricinium diamminetetrathiocyanatochromate (III) (yield, 44%). Control experiements showed that both HRP and hydrogen peroxide were necessary to effect the oxidation in a short time (4h). The background oxidation of ferrocene by hydrogen peroxide, in the absence of HRP, was negligible over the 4h period but some oxidation did occur after 48h [5].

The rates of oxidation of ferrocene and the ferrocene-alcohols (equation 1; R=CH_2OH, CHMeOH, CMe_2OH) were determined

$$FcR + H_2O_2 \xrightarrow{HRP} FcR^+ \quad (1)$$

$$Fc = C_{10}H_9Fe$$

(Table 1) by following the change of absorbance at 619 nm for ferrocene and at 630 nm for the ferrocene-alcohols.

Oxidation of ferrocene to the ferricinium ion was effected with greater convenience by hydrogen peroxide in the presence of immobilized enzyme. HRP was attached to an activated poly(acryloylmorpholine) gel network[6], which contained acid hydrazide groups, via an acid azide coupling route. A suspension of the immobilized enzyme, ferrocene and hydrogen peroxide was stirred at 25 °, the solution was centrifuged and the supernatant was monitored at 619 nm to give the initial and maximum rates of reaction (Table 1). In the solvent system used the bound enzyme had 20% activity per unit weight of enzyme relative to that of the native enzyme.

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