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REDUCTION OF IMINES BY CLUSTER $[Fe_4S_4(SR)_4]^{3-}$

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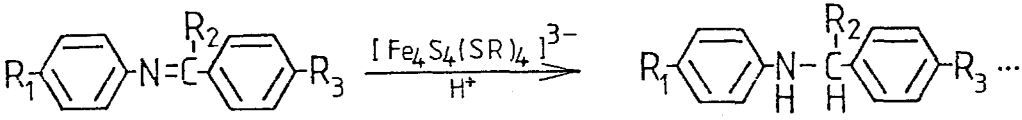
Abstract: The clusters $[Fe_4S_4(SR)_4]^{n-}$(n=3) generated electrochemically reduced imines to amines in a CH_3CN/CH_3OH solution. The correlations between the redox potentials of imines and the yields of the reductions were examined.

Iron-sulfur proteins[1)] have many important functions such as electron transfer in N_2 fixation, CO_2 fixation and steroid hydroxylation. The clusters $[Fe_4S_4(SR)_4]^{2-}$ reported by Holm,[2)] are considered to be models of iron-sulfur proteins. By Mossbauer, ESR, UV, and NMR spectra, Holm has shown in detail the similarities between the clusters and non-hem iron-sulfur proteins.[2)] However there have been few studies on chemical reactivities of the clusters including electron transfer,[3)] though various reactivities of the clusters may be predictable from their four redox states $[Fe_4S_4(SR)_4]^{n-}$;
n=1···3Fe(3+),Fe(2+); n=2···2Fe(3+),2Fe(2+); n=3···Fe(3+),3Fe(2+);
n=4···4Fe(2+). In previous papers, we reported that $[Fe_4S_4(SR)_4]^{2-}$ catalyzes two reactions, that is, the oxidation of thiol to disulfide by oxygen[4)] and the reduction of diphenylacetylene to cis-stilbene in the presence of $NaBH_4$.[5)]

In this paper, we report that imines are reduced to amines[6)] by the clusters $[Fe_4S_4(SR)_4]^{3-}$ (eq. 1). The clusters $[Fe_4S_4(SR)_4]^{3-}$ were prepared electrolytically, respectively, from the clusters $[Fe_4S_4(SR)_4]^{2-}$ with the constant potential vs the saturated calomel electrode (S.C.E.) (Yanagimoto Controlled Potential Electrolyser, Model VE-8). In a typical experiment, tetra-n-butyl ammonium bromide (0.1 M) as a supporting electrolyte was dissolved in a CH_3CN/CH_3OH (5/1) solution (120 ml) under Ar atmosphere in an

H-type cell in which cathodic and anodic chambers were separated from each other by a sintered glass disk. The substrate $C_6H_5N{=}CHC_6H_5$ (0.2 mmol) and the cluster $[Fe_4S_4(SR)_4]^{2-}$ (0.2 mmol) were added to the anodic chamber. Each electrode was a plate of Pt (50 cm^2). The reduction was carried out for 4 hr at a constant potential ($R{=}C_6H_5$, $p{-}C_6H_4Cl$, -1.2 V vs S.C.E.; $R{=}CH_2C_6H_5$ -1.4 V vs S.C.E.) to produce the amine $C_6H_5NH{-}CH_2C_6H_5$. The yield of amine was determined by HPLC (Table I). Imines having lower halfwave potentials than -1.8 V were not reduced to amines and the recoveries of imines were above 90% (Table I run 4, 5, 6).

The halfwave potentials of clusters $(Et_4N)_2[Fe_4S_4(SR)_4]$ ($R{=}C_6H_5$, $p{-}ClC_6H_4$ and $CH_2C_6H_5$) were -0.93 V, -0.89 V and -1.06 V, respectively, in a $CH_3CN/CH_3OH{=}5/1$ solution ($[Fe_4S_4(SR)_4]^{n-}$ n=2/n=3 $E_{1/2}$ vs S.C.E.). When the reaction potential in the reduction of these imines was -0.9 V, which was a value higher than the halfwave potential (-0.93 V) of the cluster $(Et_4N)_2[Fe_4S_4(SC_6H_5)_4]$, no amines were produced (Fig. 1). Amines were first produced when the reaction potentials were lower (-1.0 V, -1.05 V, -1.1 V)



···(1)

Table I The Yields of Amines by Clusters $[Fe_4S_4(SR)_4]^{3-}$ and the Halfwave Potentials of Imines

	Imines				Clusters		
Run	R_1	R_2	R_3	$E_{1/2}$*	$R{=}C_6H_5$	$R{=}p{-}C_6H_4Cl$	$R{=}CH_2C_6H_5$
1	H	H	H	-1.62V	51.2%	60.1%	60.5%
2	CH_3O	H	H	-1.65V	40.1%	40.0%	51.0%
3	Cl	CH_3	Cl	-1.74V	37.2%	41.3%	59.1%
4	CH_3O	H	CH_3O	-1.82V	0.0%	--	--
5	H	CH_3	H	-1.93V	0.0%	0.0%	4.8%
6	H	CH_3	CH_3O	-1.94V	0.0%	0.0%	<1%

reaction potentials $R{=}C_6H_5$, $p{-}C_6H_4Cl$ -1.20V vs S.C.E.
$R{=}CH_2C_6H_5$ -1.40V vs S.C.E.
reaction solvent $CH_3CN/CH_3OH{=}5/1$, reaction temp. 20°C
reaction time 4hr
*measured in the $CH_3CN/CH_3OH{=}5/1$

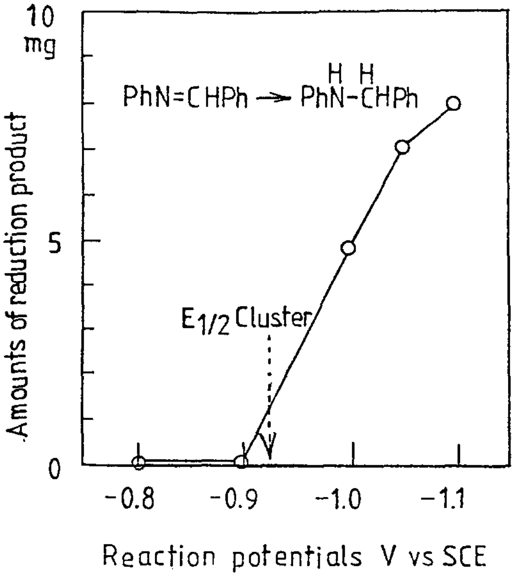


Fig. 1

The correlations between amounts of reduction product and reaction potentials.

Reaction conditions

Imine: PhN=CHPh 124 mg

Cluster:

$(nBu_4N)_2[Fe_4S_4(SC_6H_5)_4]$ 200 mg

Supporting electrolyte: 0.1M nBu_4NBr

Reaction time: 0.25 hr

Reaction temp.: 20°C

than the redox potential of the cluster. That is, the cluster (n=2) was reduced to the cluster (n=3) electrochemically and then the cluster (n=3) presumably reduced imines to amines. In the absence of the cluster, traces of imine were reduced even if the reaction potential vs S.C.E. was -1.3 V (Table II run 3). In the presence of $FeCl_3$, or $FeCl_3$ and C_6H_5SH instead of the cluster (n=2), the imine $C_6H_5N{=}CHC_6H_5$ was reduced in low yields (yield:3.9-7.7%) (Table II run 4, 5). The imine was not reduced at all, even if there was the cluster (n=2) in the reaction mixture, when the cluster (n=2) was not reduced to the cluster (n=3) electrolytically (Table II run 2). In addition, in CH_3CN only (in the absence of protic solvents such as CH_3OH) trace amounts of amine were found (2.6%). $C_6H_5ND{-}C(H)DC_6H_5$ was produced in the solvents of CH_3CN and CH_3OD. Thus in this reaction one

Table II Control Experiments

run	Components	Reaction Potential(V)	Yields(%)
1	$(Et_4N)_2[Fe_4S_4(SC_6H_5)_4]$	-1.20	51.2
2	$(Et_4N)_2[Fe_4S_4(SC_6H_5)_4]$	----	0.0
3	None	-1.30	1.6
4	$FeCl_3$	-1.30	3.9
5	$FeCl_3$, PhSH	-1.30	7.7

electron was presumed to transfer from the electrolytically reduced cluster (n=3) to the imine. A direct electron transfer to the imine through electrolysis did not occur without the cluster under the above reaction conditions.

Further studies on stereospecific reductions of imines by an optical active cluster are in progress.

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