A Novel Synthetic Metal Catalytic System for Dehydrogenative Oxidation based on Redox of Polyaniline

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Polyaniline serves as a synthetic metal catalyst with reversible redox under oxygen to induce dehydrogenative and/or decarboxylative oxidation of benzylamines and 2-phenylglycine into the corresponding imines and, in combination with copper(II) chloride or iron(III) chloride, dehydrogenation of cinnamyl alcohol into cinnamaldehyde possibly due to complexation.

Catalytic systems for oxidation principally depend on the efficient reversible redox processes of a catalyst and transition metal complex catalysts are of potential importance in this respect. Various organic compounds such as quinones, flavins and viologens have also been invoked as redox mediators in organic and/or enzymic reactions.

Conducting polymers are especially interesting as many can exist in both oxidized and reduced forms *via* one-electron transfer, which has led to their utilization as versatile electrically conducting materials.[1] The application of their chemical and electrical properties in the construction of a redox cycle for catalytic reactions has not yet been investigated. We herein describe a novel synthetic metal catalytic system for dehydrogenative oxidation reactions based on polyaniline.

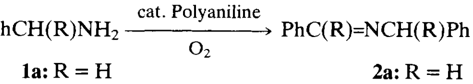
Treatment of benzylamine **1a** with a catalytic amount of polyaniline under oxygen resulted in oxidation to *N*-benzylidenebenzylamine **2a** [eqn. (1)],† the formation of which is explained by dehydrogenation to benzylideneamine and transamination with benzylamine. Selected results are listed in Table 1.

$$\mathrm{PhCH(R)NH_2} \xrightarrow[\mathrm{O_2}]{\text{cat. Polyaniline}} \mathrm{PhC(R){=}NCH(R)Ph} \qquad (1)$$

$$\begin{array}{ll} \mathbf{1a}: \mathrm{R = H} & \mathbf{2a}: \mathrm{R = H} \\ \mathbf{b}: \mathrm{R = Ph} & \mathbf{b}: \mathrm{R = Ph} \end{array}$$

The catalytic oxidation was performed with polyaniline under oxygen; only a small amount of the imine **2a** was produced under nitrogen. When the reaction was carried out in the dark, the distinct difference in yields of **2a** was not observed, which suggests that photoactivation is not necessarily involved. The oxidation reaction proceeded in *N,N*-dimethylformamide (DMF) or *N*-methyl-2-pyrrolidone although polyaniline employed here was slightly soluble. The reaction time was greater with polyaniline which was almost insoluble in acetonitrile or ethanol. The dimethylamino group of DMF was exchanged with benzylamine giving *N*-benzylformamide as a byproduct. α-Disubstituted amine **1b** was also oxidized to the imine **2b**.

The catalysis appears to depend on the reversible redox cycle of polyaniline under oxygen (Scheme 1). The blue heterogeneous system in DMF or *N*-methyl-2-pyrrolidone indicates the continuing involvement of the active oxidizing species under the conditions employed above. The redox process was monitored by UV–VIS spectra of the partially



Scheme 1

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† Polyaniline was prepared by chemical oxidation of aniline with copper(II) salt and HBF_4 and contains less than 2 ppm of copper species after washing. A representative experimental procedure is as follows. To the mixture of polyaniline (9.1 mg) in DMF (0.5 ml) was added **1a** (1.0 mmol). The blue heterogeneous mixture was stirred at 80 °C under ambient oxygen. Diethyl ether was added to the reaction mixture, which was filtered and concentrated. GLC analysis showed the formation of **2a**, which was assigned by comparison of the spectral data with those of the authentic sample.

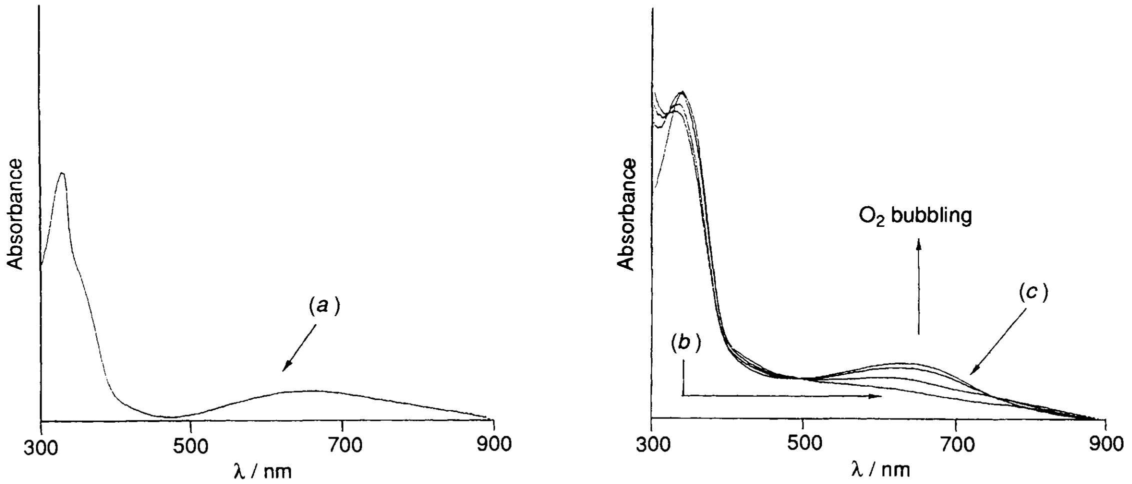

Fig. 1 UV–VIS spectra: (*a*) Polyaniline in *N*-methyl-2-pyrrolidone under nitrogen, (*b*) treatment with benzylamine at 80 °C for 2 h under nitrogen and (*c*) molecular oxygen was bubbled into the solution at room temp. for 20 min

Table 1 Oxidative transformation catalysed by polyaniline[a]

Substrate	Metal salt (equiv.)[b]		Atmosphere	Solvent	t/h[c]	Product	Yield (%)[d]
1a	—		O_2	*N*-Methyl-2-pyrrolidone	10	**2a**	77
1a	—		O_2	DMF	10	**2a**	74[e]
1a	—		N_2	DMF	10	**2a**	15[e]
1a	—		O_2	MeCN	40	**2a**	98
1a	—		O_2	EtOH	40	**2a**	53
1b	—		O_2	DMF	10	**2b**	66[g]
3	—		O_2	DMF	20	**2a**	62[e]
4	$CuCl_2$	0.1	O_2	DMF	10	**5**	40
4	$CuCl_2$	0.2[f]	O_2	DMF	10	**5**	68
4	$CuCl_2$	0.2[f]	N_2	DMF	10	**5**	9
4	$FeCl_3$	0.1	O_2	DMF	20	**5**	39

[a] Substrate, 1.0 mmol; polyaniline, 9.1 mg; solvent, 1.0 ml. [b] To **4**. [c] Temp. 80 °C. [d] Yields were determined by GLC. [e] *N*-Benzylformamide was produced as a byproduct. [f] Polyaniline, 18.2 mg. [g] Yield of benzophenone after hydrolysis.

soluble polyaniline as shown in Fig. 1. The broad 640 nm absorption assignable to the oxidized form of polyaniline was not observed after treatment with benzylamine at 80 °C under nitrogen. The absorption reappeared with isosbestic points and colouring to blue only by bubbling oxygen into the mixture for 20 min. The oxidative transformation of the *leuco*-emeraldine base has been reported to be accomplished by oxygen leading to the emeraldine form.[2] The similar one-electron oxidation based on the redox of polyaniline is considered to operate upon the polyaniline-catalysed dehydrogenation reaction of **1**.

Use of polyaniline as a synthetic metal catalyst is also realized in the oxidation of 2-phenylglycine **3** into the imine **2a** [eqn. (2)]. It should be noted that dehydrogenation of the amino group accompanies decarboxylation in this case. The similar decarboxylative dehydrogenation of **3** is attained by the $VO(OEt)Cl_2$-induced one-electon oxidation giving ethyl benzoate *via* oxidative esterification.[3]

$$\underset{\mathbf{3}}{PhCH(NH_2)CO_2H} \xrightarrow[O_2]{\text{cat. Polyaniline}} \mathbf{2a} \quad (2)$$

A complex system of synthetic metal catalysts is required for the oxidation of alcohol. A combination of polyaniline and copper(II) chloride constituted an efficient catalyst for dehydrogenation of cinnamyl alcohol **4** to cinnamaldehyde **5** in DMF [eqn. (3), Table 1]. A poor result was obtained with each individual component. Increase in the catalytic amount of both components raised the yield of **5**. Iron(III) chloride was similarly used instead of copper(II) chloride. The failure of oxidation in benzyl alcohol is considered to be due to the difference in the redox potentials.

$$\underset{\mathbf{4}}{PhCH{=}CHCH_2OH} \xrightarrow[O_2]{\text{cat. Polyaniline–}CuCl_2\ (FeCl_3)} \underset{\mathbf{5}}{PhCH{=}CHCHO} \quad (3)$$

The insoluble polyaniline recovered after the oxidation reaction of **4** in the presence of copper(II) chloride in DMF involved one copper species to two aniline units.‡ This finding suggests that the complexation of copper(II) chloride with polyaniline affords a catalyst to induce the dehydrogenative oxidation reaction although the redox mediation of iron(III) chloride is known to facilitate oxidation of reduced polyaniline.[2]

The above-mentioned results indicate that polyaniline serves as a versatile synthetic metal catalyst in dehydrogenative oxidation. Coordination of transition metal to the π-conjugated chain is considered to contribute an efficient system for electron transfer. To our knowledge, the present oxidative transformation is the first example for the catalytic redox reaction achieved by conducting polymers. Further investigations on synthetic metal catalysts including other conducting polymers are now in progress.

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‡ Satisfactory elemental analysis was obtained.