

Cobalt(II) diacetylmonoxime complex-catalysed oxidative coupling reactions of few aromatic compounds

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Received 5 March 1999; received in revised form 20 May 1999; accepted 11 August 1999

Abstract

Catalytic amount of a diacetylmonoxime cobalt(II) chloride complex [A] along with hydrogen peroxide reacts with toluene to give benzylalcohol, benzaldehyde and trace amount of *p*-cresol and *o*-cresol. Similar catalytic reaction of aniline gives C–N-bonded oligomer having M_n and M_w of 1256 and 1892, respectively. Mass spectra determined by MALDI suggests the polyaniline to have highest mass from 14 units of aniline with CoCl_2 unit attached at the end. The oligomer thus formed have semiconducting properties. Similar reaction of phenol with cobalt(II) diacetylmonoxime (Co–DAM) complex in the presence of hydrogen peroxide gives C–O-bonded polyphenol. The reaction of 2-aminophenol with [A] and hydrogen peroxide leads to aggregate that has property of irreversible thermoelectric sensor. ESR suggests this property to originate from free radical present in the aggregate. Substituted aniline such as 2,4-dimethoxyaniline can also form low molecular aggregate from similar reaction that has semiconducting property in the range of 35°C–180°C. © 2000 Elsevier Science B.V. All rights reserved.

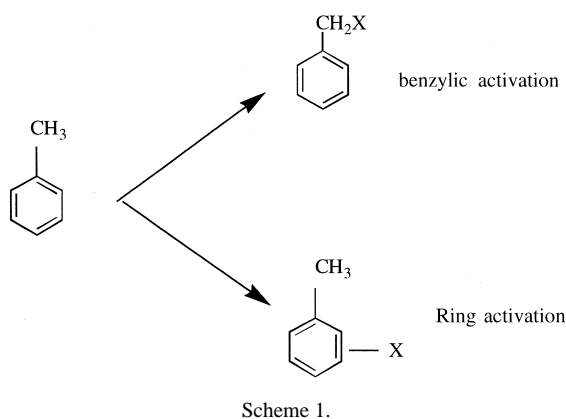
Keywords: Polyaniline; Oxidative coupling; Cobalt(II) diacetylmonoxime complex; Hydrogen peroxide

1. Introduction

Vitamin B₁₂ contains cobalt ion bound to its cofactor through nitrogen atoms [1]. This part of the cofactor of vitamin B₁₂ causes the C–C bond formation and several oxidation reactions [2]. Several of such reactions are mimicked by synthetic organic chemist. In this context, the cobalt(II) dimethylglyoxime complexes are of great value [3–5]. However, selectivity and mildness are two aspects of these reactions that require special attention. The reactions of cobalt(II) Schiff base complexes under oxida-

tive conditions have also been extended to high yield stereoselective synthesis [6–9]. We have demonstrated that recycling of liberated oxygen from hydrogen peroxide is possible in the cobalt(II)-catalysed oxidative C–H activation at the benzylic position [10,11]. The C–H bond activation by cobalt complexes also finds industrial application. Brichima process for hydroxylation of aromatic compounds is one of such industrial process [12,13]. In contrast, there are less report on the chemistry of cobalt(II) diacetylmonoxime primarily because of limitations in synthesis of these complexes in solution [14–16]. The C–H bond in an aromatic compound can be substituted through different paths. A ring hydrogen atom can be replaced to yield a

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C–X (X = incoming group) bond or a C–H bond at the aliphatic carbon of a functional group attached to the ring can be substituted (Scheme 1). Here we present result of such catalytic reaction by use of a cobalt(II) dionemoxime complex that leads to substrate dependent reactivity and also the electrical properties of materials prepared by oxidative oligomerisation process.

2. Experimental

The IR spectra were recorded on a Nicolet DSP-800 FT-IR, ESR were recorded on a EPR-E-112 and gas chromatograph were recorded on a Hewlett Packard Gas chromatograph 6890 using SE-30 capillary column and FID as detector. The resistance of the samples were measured of film made on mica plate by using a set up comprising of Hewlett Packard 34401 multi-meter, Kiethley 6512 programmable electrometer and Agronics 93-C DC power supply unit. MALDI mass were recorded on Kratos PC-Kompact instrument by dissolving the sample in THF with dithranol and AgTFA and spectra were recorded in positive ion mode.

2.1. Preparation of cobalt–diacetylmonoxime (Co–DAM) complex [A]

A mixture of cobalt(II) chloride hexahydrate (118 mg, 0.5 mmol) and DAM (303 mg, 3

mmol) were mixed together and ground to make a homogeneous mixture in a pestle and mortar. This mixture on keeping in oven at 110°C for 4 h resulted in a crystalline mass. The mass on washing with petroleum ether (20 ml) gave a black compound having composition $\text{Co}_2(\text{DAM})_7\text{Cl}_4$ (234 mg). Elemental analysis found: C 34.41, H 4.97, N 10.02, Cl 14.93; calculated for $\text{C}_{28}\text{H}_{49}\text{Cl}_4\text{N}_7\text{O}_{14}\text{Co}_2$: C 34.74, H 4.97, N 10.01, Cl 14.68. IR (KBr) 2916 (s), 2848 (s), 1574 (vs), 1402 (bs), 1227 (s), 1084 (s), 981 (w) cm^{-1} .

2.2. Reaction of toluene with [A] in the presence of hydrogen peroxide

A mixture of hydrogen peroxide (1 ml, 30%), Co–DAM (0.50 g, 0.679 mmol) and toluene (1 ml) was heated at 60°C for 6 h in a Schlenk tube under closed condition and to the resulting mixture 5 ml water was added and extracted with dichloromethane (2×25 ml). The dichloromethane extract was dried over anhydrous sodium sulphate. The products thus obtained were analysed by a GC HP 6890 with FID detector and N_2 as carrier gas and SE-30 as capillary column. The retention values were compared with benzaldehyde, benzylalcohol, toluene and cresols.

2.3. Reaction of aniline with [A] in the presence of hydrogen peroxide

To a well-stirred mixture of aniline (1 g, 11 mmol) and hydrogen peroxide (1 ml, 30%), Co–DAM (0.050 g, 0.679 mmol) was added. The reaction mixture was kept at 60°C for 2 h. The reaction mixture was then cooled and solvent was removed under reduced pressure. The residue thus obtained was washed with cold water (3 ml) followed by petroleum ether (2×25 ml) to obtain the black solid. Elemental analysis calculated $(-\text{C}_6\text{H}_6\text{N} 0.5\text{H}_2\text{O})_n$ calcd.: C 72.00, H 6.00, N 14.00, found: C 72.05, H 5.04, N 13.75, $^1\text{H}(\text{CDCl}_3)$ 8–6.6 (m).

$^{13}\text{C}\{^1\text{H}\}(\text{CDCl}_3)$ 131, 129.2, 129.0, 121.3, 112.4, 100.2. IR (KBr) 3300 (b), 2925 (w), 1670 (m), 1600 (s), 1500 (s), 1440 (m), 1310 (m), 750 (s), 690 (s).

Similar reaction was carried out with phenol, the residue on repeated washing gave brown solid. Yield (25%). Elemental analysis calculated for $(-\text{C}_6\text{H}_5\text{O}-)_n$: C 77.41, H 4.30, found: C 76.92, H 4.12, M_w 8400, M_n 3500; ^1H NMR ($\text{DMSO}-d_6$) 6.1–7.6 (broad multiplet) IR (KBr) 3400 (bw), 1610 (s), 1590 (s), 1490 (s), 1200 (s), 1100 (w), 830 (s), 750 (s), 690 (m). In addition to this, it gave low molecular weight oligomer soluble in dichloromethane whose mass spectra is discussed in the text.

2.4. Reaction of 2,4-dimethoxyaniline with hydrogen peroxide and Co–DAM catalyst

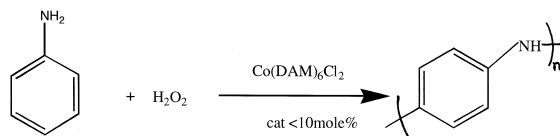
To a well-stirred mixture of 2,4-dimethoxyaniline (0.918 g, 6 mmol) and hydrogen peroxide (1 ml, 30%) in acetonitrile (1 ml) Co–DAM (0.050 g, 0.679 mmol) was added. The reaction mixture was kept at 60°C for 2 h. The reaction mixture was cooled and solvent was removed under reduced pressure and the residue was washed with cold water (3 ml) followed by petroleum ether (2×25 ml) to obtain the aggregate as black paste (0.5 g, 54%). Elemental analysis found: C 62.8, H 7.2, N 9.2, calculated for $(\text{C}_8\text{H}_{11}\text{NO}_2)_n$: C 63.1, H 6.5, N 9.2. ^1H NMR (CDCl_3) 6.5–6.8 (m) 3.8–3.9 (m), 8.1 (bs). IR (neat) 3359 (m, br), 2943 (w), 1600 (s), 1508 (s), 1282 (s), 1208 (s), 1034 (s), 829 (m). The GPC recorded in CHCl_3 has four sets of (M_n , M_w) at (2592, 2843); (1473, 1486); (1006, 1081); (611, 639).

Similar reaction of 2-aminophenol gives black solid as aggregate having M_n and M_w of 1800 and 1900, respectively. Elemental analysis calculated for $(\text{C}_6\text{H}_6\text{NO})_n$: C 66.67, H 5.56, N 12.96, found: C 65.10, H 5.00, N 12.31; IR (neat) 3382 (s), 3308 (s), 3052 (bs), 1575 (s), 1514 (s), 1474 (s), 1400 (s), 1273 (s), 897 (s), 749 (s).

2.5. Result and discussions

A solid state reaction of cobalt(II) chloride pentahydrate and diacetylmonoxime leads to a black mass, elemental analysis suggests this to have composition $(\text{DAM})_7\text{Co}_2\text{Cl}_4$ (abbreviated as Co–DAM). Catalytic amount of Co–DAM (10 mol%) reacts with toluene in the presence of hydrogen peroxide yielding benzylalcohol as the major product. In addition to these, benzaldehyde and traces of *p*-cresol and *o*-cresol are formed. Similar reaction of benzylalcohol with Co–DAM in the presence of H_2O_2 yields benzaldehyde, this shows that the oxidation of toluene to benzaldehyde passes through benzylalcohol. The overall conversion of the toluene in this reaction is 12%.

Analogous reaction of this catalyst with aniline in the presence of H_2O_2 (30%) at 60°C gives polyaniline as black solid. This is not unusual as polyanilines are prepared by oxidative coupling of aniline by different oxidising agent [17–19]. The M_n and M_w values for the polyaniline prepared by Co–DAM-catalysed reaction are 1256 and 1892, respectively. Polyaniline thus prepared (Scheme 2) has resemblance with reported IR of polyaniline prepared by nickel-catalysed dehalogenative coupling reactions [20]. However, elemental analysis deviates from the calculated elemental analysis of polyaniline; suggesting the presence of some amount of the catalyst in it. To ascertain this, MALDI mass spectra of the sample is recorded and the spectra is shown in Fig. 1. The highest *m/e* obtained at 1405 is due to a composition of $[\text{C}_6\text{H}_5(\text{NHC}_6\text{H}_4)_{13}\text{NH}_2\text{CoCl}_2]^{++}$ unit, few of the other mass fragments obtained are at 1310.6, 973.7, 757.6, 664.1, 558.8 are due to



Scheme 2.

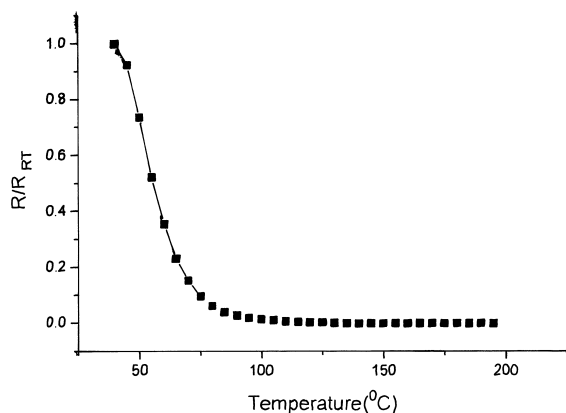


Fig. 2. Plot of the resistance (R) normalised to room temperature resistance (R_{RT}) vs. temperature of aggregate prepared from 2,4-dimethoxyaniline by Co-DAM.

of the polyaniline prepared by Co-DAM-catalysed reactions are measured by two probe method of film made on a mica plate. The polyaniline and the aggregate of 2,4-dimethoxyaniline prepared by cobalt(II)-catalysed reaction shows the change in resistivity profile similar to semiconductor (Fig. 2). However, in the case of the material obtained from Co-DAM-catalysed reaction of 2-aminophenol have limiting temperatures till which the resistance increases and then falls down showing the property of sensor (Fig. 3). However, measurement of resistance on reheating leads to the similar

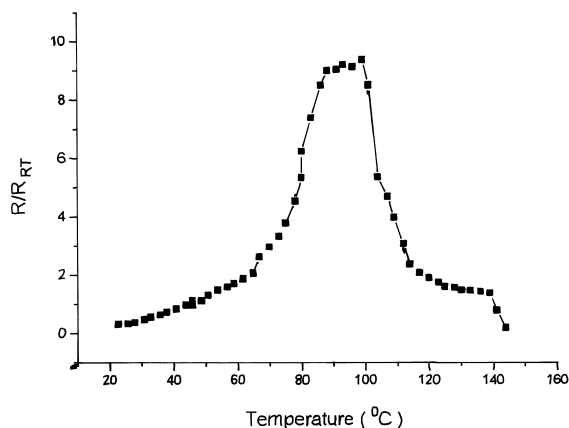


Fig. 3. Plot of the resistance (R) normalised to room temperature resistance (R_{RT}) vs. temperature of the aggregate prepared from 2-aminophenol.

profile but with a different hike in the resistance at the limiting temperature, suggesting the property to be irreversible. In the case of 2-aminophenol we have recorded the ESR spectra and found that there is a signal at 3260 G (Fig. 4) similar to a radical at room temperature. Aminophenol radical attached to cobalt(II) is a well-known phenomenon [23], but in the reported cases a weak signal around 1000 G was observed, which is not observed by us. The signal obtained at 3260 G remains intact in the system on heating to 180°C. Nevertheless, the system has interesting electrical property. Initially, in the aminophenol aggregate the resistance increases as the thermal energy cleaves H-O-H bonds and there is a competition between the radical conductivity with proton conductivity at lower temperature and the latter predominates. However, after significant amount of thermal energy being supplied to the system, the former predominates.

All the above discussed results suggests that the catalytic reaction of Co-DAM complex can lead to the homolytic cleavage of peroxide to

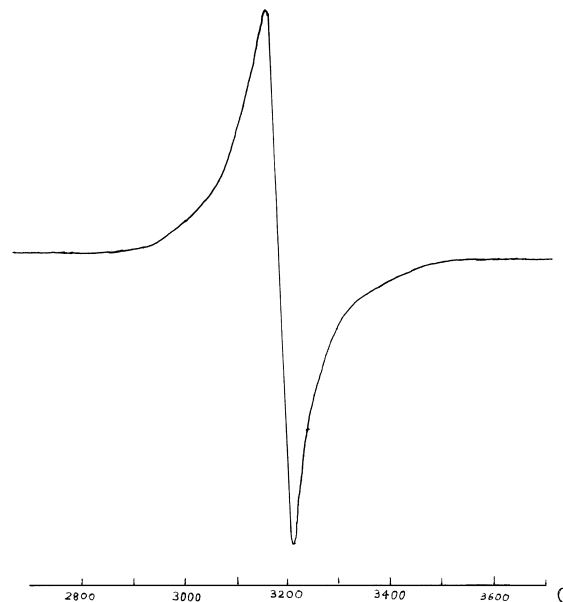


Fig. 4. ESR spectra of the aggregate prepared from 2-aminophenol by Co-DAM and hydrogen peroxide.

generate hydroxy radical, which can either cause hydroxylation at the benzylic position, or can initiate oligomerisation of activated aromatic compounds such as phenols and anilines.

In conclusion, this study demonstrates few aspects of substrate dependent reactions of activated aromatic with Co–DAM catalyst and also the possibility of obtaining properties of thermoelectric sensor from cobalt-doped aggregates of anilinic and phenolic compounds.

Acknowledgements

We are thankful to Prof. P. Balaram of Indian Institute of Science, Bangalore, for the MALDI spectra, Prof. K. Osakada of Tokyo Institute of Technology for the GPC, Dr. A. Srinivasan of Indian Institute of Technology, Guwahati for the resistivity measurement. The authors thank Council of Scientific and Industrial Research (India) for financial assistance.

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