

Participation of self-generated polyaniline support in copper(II) catalysed oxidative reaction of phenyl aldimines

Jyotirekha G. Handique, Lukumoni Borah, Rupam Jyoti Sarma, Jubaraj B. Baruah*

Department of Chemistry, Indian Institute of Technology, Guwahati 781 039, Assam, India

Received 9 January 2002; accepted 13 March 2002

Abstract

Aromatic aldimines, aldoximes and aldehydes can be converted to the corresponding carboxylic acid on reaction with catalytic amount of *cis*-bisglycinato copper(II) monohydrate in the presence of copper(II) catalyst. The reactions are facilitated by addition of polyaniline as support. In the case of aldimines, evidences on participation of self-generated polyaniline is observed. The mechanistic aspect involving an oxy radical attached to copper(II) is presented with ESR evidence.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation of aldoximes; Supported copper(II) catalysis; Self-generated support

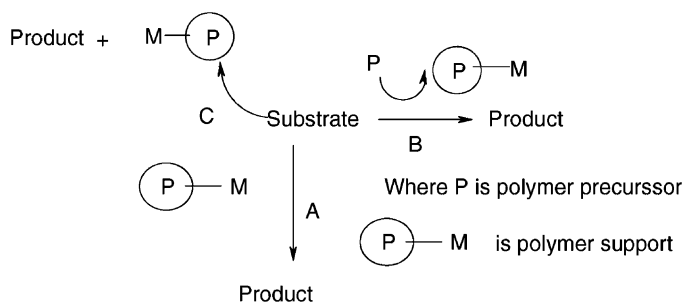
1. Introduction

Imine functional group constitutes backbone of inorganic schiff base ligands [1]. They act as protecting group of carbonyl functional group [2–4] and play an important role in key stereoselective transformations [5–7]. Another facet of imines is the ability of them to form N-oxide radical [8]. The N-oxide radicals are widely used as radical trap and have also found utilities in organic oxidation reactions [9]. The reduction of C=N bonds also has utility in the synthesis of optically active amino acids [10,11]. Biological reactions such as biosynthesis of amino acids take place via transformation on C=N functional group [12]. Thus, the study of oxidative reactions of C=N under biologically favourable condition would throw light on their capability to withstand the biochemical oxidative processes and their utilities in organic

synthesis. The protective and deprotective transformations of a C=N bond are conventional reactions and constantly efforts are made for selective and mild reagent development for such reactions [13]. The supported reagent in carbonyl functional group generation from oximes and imines is an important reaction and in such reactions continuous processing and selectivity can be achieved [14]. In general, there can be three approaches for such metal supported catalytic processes (Scheme 1) [14–18]. In process A, polymer can be bound to a metal centre or can be made to bind to a metal by adding it from an external source. In process B, a precursor for polymer can be added as a co-catalyst and it polymerises during the reaction to act as a support [14]. In the third process C, a polymer generated in situ from the substrate itself participate in the reaction. However, this approach is not conventional, we have studied such possibilities in oxidative reactions of few simple aromatic imines while they are transformed to corresponding acids.

* Corresponding author.

E-mail address: juba@iitg.ernet.in (J.B. Baruah).



Scheme 1.

2. Experimental

The *cis*-bisglycinato copper(II) monohydrate [19], adimines [20] and oximes [20], polyaniline [21] were prepared by standard procedure available in the literature. The products formation in the reactions were monitored by analysing the reaction mixtures by gas chromatography using Hewlett Packard Gas Chromatograph 6890 attached with SE-30 capillary column with an FID detector.

In all these reactions, the major product was found to be carboxylic acid. The formation of the carboxylic acid was also monitored by titration with standard sodium hydroxide with phenolphthalein as the indicator. The typical procedure for such study is as follows.

2.1. Oxidation of *N*-benzylideneaniline by *cis*-bisglycinato copper(II) monohydrate in the presence of H_2O_2

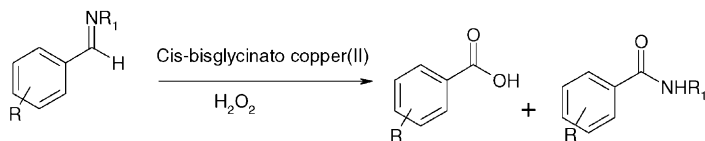
N-benzylideneaniline (109 mg, 0.6 mmol) and *cis*-bisglycinato copper(II) monohydrate (13.5 mg, 0.06 mmol) were dissolved in methanol (10 ml) in a round bottom flask. A solution of H_2O_2 (1 ml of 30%

an oil bath where the oil bath temperature was maintained at 60 °C. After each hour interval of time from the starting of the reaction, 1 ml of the reaction mixture was taken out to a conical flask. This solution taken in separate conical flask was diluted with water to 25 ml and was titrated against standard NaOH [0.086 N in this case] solution using phenolphthalein as an indicator.

The products formed after completion of the reactions were extracted with chloroform after removing the inorganic material by washing with water. Upon removal of chloroform by distillation a residue was obtained. The residue was purified by column chromatography. The identities of the purified products were confirmed by recording their IR, 1H and ^{13}C NMR and mass spectra as well as elemental analysis.

3. Results and discussions

The imines of aromatic aldehydes can be converted to corresponding acid on reaction with catalytic amount of *cis*-bisglycinato copper(II) monohydrate with hydrogen peroxide (Eq. (1)).



R = H, *p*-Me, *p*-OMe, *m*-NO₂,

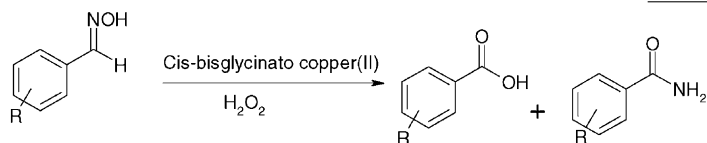
R₁ = C₆H₅, *p*-C₆H₅, *o*-C₆H₅

(1)

H_2O_2 in 5 ml of methanol) was added dropwise to the above solution. The reaction mixture was placed in

During the course of the reaction, the aldehydes and amides are formed as intermediate and side product,

respectively. The similar catalytic reaction of aromatic aldoxime leads to aromatic carboxylic acid and in this reaction amide is formed as side product (Eq. (2)).



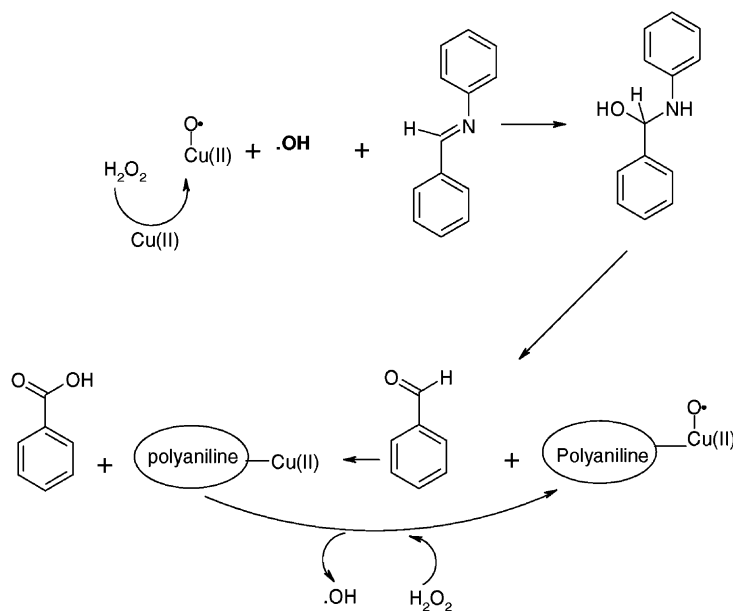
R = H, *p*-Me, *p*-OMe, *m*-NO₂.

(2)

As an illustrative example, imine prepared from condensation of aniline with *p*-methylbenzaldehyde reacted with catalytic amount of *cis*-bisglycinato copper(II) catalyst in the presence of hydrogen peroxide (30%, 100 vol.%) at 60 °C; after 6 h *p*-methylbenzoic acid (86%) and minor product *p*-methylbenzamide (8%) are formed. The formation of amide in these reactions suggests that the reaction can either pass through rearrangement or through attack of a hydroxy/oxy radical. If the reaction passes through Beckmann type of rearrangement, the final product acid has to be formed from hydrolytic reaction of the amide. Independent reaction of amide under identical condition led to less than 10% conversion of

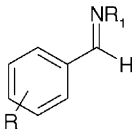
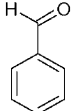
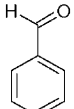
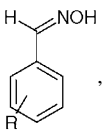
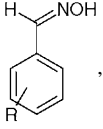
aldehyde (Scheme 2) to corresponding acid. For verification of this aspect, the corresponding aldehydes were reacted independently with hydrogenperoxide in the presence of catalytic amount of *cis*-bisglycinato copper(II). The yields and the reaction conditions for conversion of aldehydes to acids are listed in Table 1.

In order to establish the effect of participation of supported catalysis, various control experiments were performed, by varying the concentrations of the substrates and also with different substrates. The oxidation of benzaldehyde was greatly influenced by the catalytic reactions of *cis*-bisglycinato copper(II) in the presence of hydrogenperoxide and polyaniline as support (e–g in Fig. 1). The reaction of imine with



Scheme 2.

Table 1
Results on oxidative reaction of aldimine and aldoximes^a

Substrate	Reaction conditions	Yield of acid (%)	Yield of amide (%)
			
R = H, R ₁ = C ₆ H ₅	6 h, 60 °C	78	6
R = H, R ₁ = <i>p</i> -CH ₃ -C ₆ H ₄	6 h, 60 °C	82	Trace
R = H, R ₁ = <i>p</i> -CH ₃ O-C ₆ H ₄	6 h, 60 °C	76	Trace
R = <i>p</i> -CH ₃ , R ₁ = C ₆ H ₅	6 h, 60 °C	86	8
R = <i>p</i> -CH ₃ , R ₁ = <i>p</i> -CH ₃ -C ₆ H ₄	6 h, 60 °C	84	8
R = <i>p</i> -CH ₃ , R ₁ = <i>p</i> -CH ₃ O-C ₆ H ₄	6 h, 60 °C	82	Trace
R = H, R ₁ = C ₆ H ₅	2 h, 60 °C	78 ^b	Trace
R = <i>p</i> -CH ₃ , R ₁ = C ₆ H ₅	2 h, 60 °C	82 ^b	
	4 h, 60 °C	100	–
	2 h, 60 °C	100 ^b	–
 , R = H	6 h, 60 °C	72	9
 , R = <i>p</i> -CH ₃	6 h, 60 °C	84	Nil

^a The reactions were carried out with substrate (1 mmol), *cis*-bisglycinato copper(II) (0.1 mmol) in acetonitrile (5 ml) with hydrogen peroxide (1 ml, 30%, 100 vol.%).

^b Same as in footnote a, but polyaniline (100 mg) added.

hydrogen peroxide does not take place in absence of copper(II) catalyst and significant rate enhancement takes place in the presence of copper catalyst as well as aniline (a, c and d in Fig. 1). The role of aniline in the case of such reaction is to self polymerise to form polyaniline and act as a support.

It is observed that the imines derived from aromatic amine reacts more easily with *cis*-bisglycinato copper(II) monohydrate and hydrogen peroxide. The effect may be attributed to the formation of polyaniline (as demonstrated in path C of Scheme 1) that in turn anchor the metal to give supported catalytic reaction. In order to reason out this, we have taken help of two

control experiments. In the first case, we have added polyaniline prepared by oxidation by catalytic amount of *cis*-bisglycinato copper(II) and hydrogen peroxide [20] for oxidation of benzaldehyde. In this case, we have seen considerable improvement in the reaction both in terms of rate as well as yields from the simple copper catalysed reaction. In the second case, we have carried out the reaction of benzaldehyde with hydrogen peroxide in the presence of *cis*-bisglycinato copper(II) monohydrate and aniline. The reactions in each of these cases proceeded under milder conditions, but the latter reaction is found to be faster among the two (approximately 1.2 times by gas chromatography).

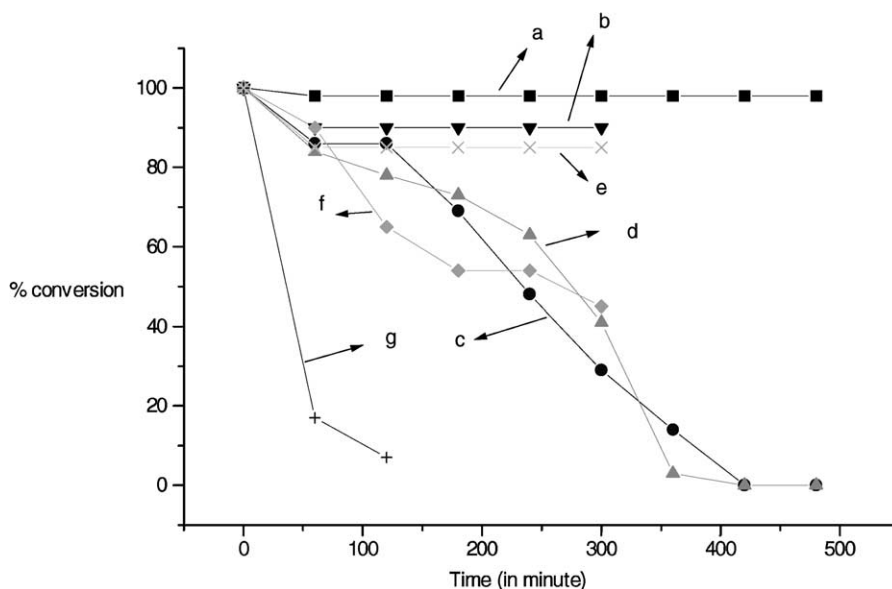


Fig. 1. The formation of carboxylic acid from oxidative reactions of— a: *N*-benzylideneaniline (3 mmol) with hydrogenperoxide (8.8 mmol); b: benzaldehyde (3 mmol) with polyaniline (10 mg) and hydrogenperoxide (8.8 mmol); c: *N*-benzylideneaniline (3 mmol) with *cis*-bisglycinato copper(II) (0.03 mmol) and hydrogenperoxide (8.8 mmol); d: *N*-benzylideneaniline (3 mmol) with *cis*-bisglycinato copper(II) (0.03 mmol), aniline (0.03 mmol) and hydrogenperoxide (8.8 mmol); e: benzaldehyde (3 mmol) and hydrogenperoxide (8.8 mmol); f: benzaldehyde (3 mmol) with *cis*-bisglycinato copper(II) (0.03 mmol) and hydrogenperoxide (8.8 mmol); g: benzaldehyde (3 mmol) with *cis*-bisglycinato copper(II) (0.03 mmol), polyaniline (10 mg) and hydrogenperoxide (8.8 mmol). In all the cases, methanol was added to the reaction mixture so as to maintain a constant volume (15 ml) and reactions were carried out at 60 °C.

In our earlier studies, we had observed that *cis*-bisglycinato copper(II) catalysed reactions leads to polyanilines that arises from the C–N bond formation at *ortho* as well as at *para*-position. The identity of the backbone is established on the basis of the ^{13}C NMR spectroscopy as shown in Fig. 2. The presence of the *ortho*-substituted polyaniline makes it a good ligating system for supported catalysis. The Scheme 2 may be put forward to explain the reaction mechanism. The role of the oxy radical is proved by recording the ESR of the crude mixture of the polyaniline (Fig. 3) prepared by catalytic reaction of *cis*-bisglycinato copper(II) as well as the byproduct of the imine oxidation reaction. It has two strong ESR absorptions, one due to a copper(II) centre (at 3165 G) and the other due to an oxy radical (at 3180 G). The presence of the oxy radical facilitates the oxidative reaction of the aldehyde. The polyaniline stabilises such radical and enhances the rate of the reaction by giving support to the catalyst system. In the case of an oxidative reaction of imine, the self-generated polyaniline participates by

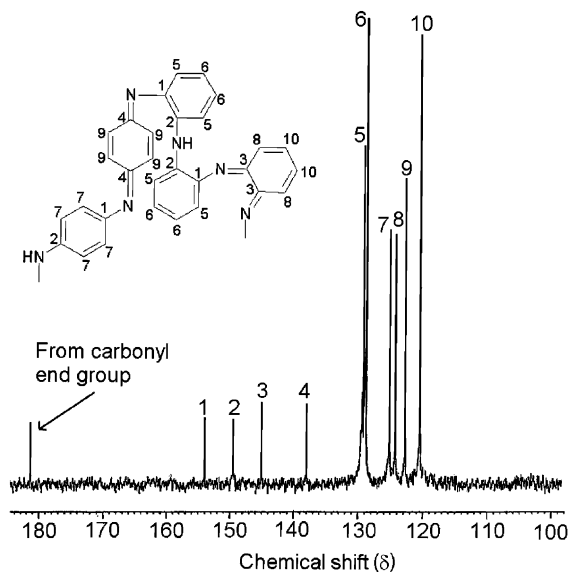


Fig. 2. The ^{13}C NMR spectra of polyaniline prepared by catalytic amount of *cis*-bisglycinato copper(II) in the presence of hydrogenperoxide.

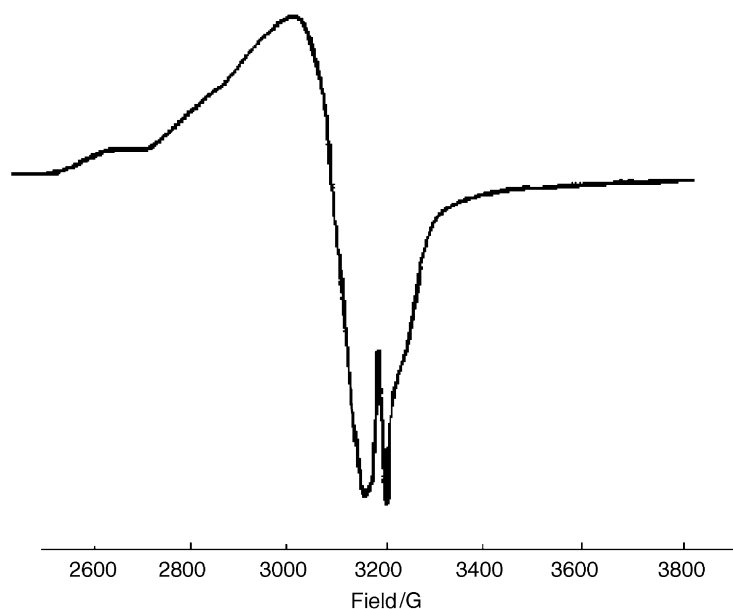


Fig. 3. ESR spectra of polyaniline prepared by catalytic reaction of *cis*-bisglycinato copper(II) in the presence of hydrogen peroxide (at 30 °C, central field 3200 G with 1500 G sweep width).

anchoring the catalytic radical species to make the reaction to proceed under a mild condition. However, the oxidation of the imine only with H_2O_2 without copper(II) catalysts is sluggish (a in Fig. 1) and the rate enhancement due to externally added *cis*-bisglycinato copper(II) complex provide evidence of the involvement of copper(II)-oxy radical. This is further proved from the ESR spectra of the support prepared by the reaction of polyaniline and *cis*-bisglycinato copper(II) complex with hydrogen peroxide. The role of self-generated polyaniline is also apparent from the comparison of aldimine of benzaldehyde with aniline and butylamine. In the latter case, the benzoic acid is formed in (23%) after 6 h at 60 °C of reaction where complete conversion of imine in the former case takes place under identical condition.

In conclusion, this study delineates a new possibility of self-generated polymer supported catalytic reaction.

Acknowledgements

Authors thank Department of Science and Technology, New Delhi, India, for financial assistance and

Sophisticated Instrumentation facility, Indian Institute of Science, Bangalore, for NMR facility.

References

- [1] M. Calliganin, L. Radaccio, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), *Comprehensive Co-ordination Chemistry*, Vol. 2, Pergamon Press, Oxford, 1987, pp. 715–738.
- [2] G.M. Robertson, in: G. Pattenden (Ed.), *Comprehensive Functional Group Transformations*, Vol. 3, Pergamon Press, Oxford, 1995, pp. 425–441.
- [3] T.W. Greene, P.G.M. Wuts, *Protective Groups in Organic Synthesis*, 3rd Edition, Wiley, New York, 1999.
- [4] S.R. Sandler, W. Karo, *Organic Functional Group Preparations*, Academic press, London, 1989, p. 430.
- [5] R. Bloch, *Chem. Rev.* 98 (1998) 1407.
- [6] S. Kobayashi, H. Ishitani, *JCS Chem. Commun.* (1995) 1397.
- [7] K.D. Sugi, T. Nagata, T. Yamada, T. Mukaiyama, *Chem. Lett.* (1997) 493.
- [8] Y. Katke, E.G. Jansen, *J. Am. Chem. Soc.* 111 (1989) 7319.
- [9] Y.V. Geletii, A.I. Shilov, in: W. Ando, Y. Moro-oka (Eds.), *The Role of Oxygen in Chemistry and Biochemistry*, Elsevier, Amsterdam, 1989, p. 289.
- [10] D.J. Drinkwater, P.W.G. Smith, *J. Chem. Soc. (C)* (1971) 1305.
- [11] M. Hudlicky, *Reductions in Organic Chemistry*, Ellis Horwood, Chichester, UK, 1986, p. 105.

- [12] A. L. Lehninger, D.L. Nelson, M.M. Cox, Principle of Biochemistry, CBS Publishers, Delhi, 1993 (Chapter 21).
- [13] B.A. Nathier, K.J. Eash, R.S. Mohan, Synthesis (2001) 1010.
- [14] J.H. Clark, Catalysis of Organic Reactions by Supported Inorganic Reagents, VCH, New York, 1994.
- [15] A.L. Augustine, Heterogeneous Catalysis for the Synthetic Chemist, Marcel Dekker, New York, 1996, pp. 153–177 (Chapter 9).
- [16] T. Castro, Y.Z. Li, R. Reitenbager, E. Choi, S.B. Park, R.P. Andres, in: R. Terry, K. Baker, L.L. Murrell (Eds.), Novel Materials in Heterogeneous Catalysis, American Chemical Society Symposium Series, Washington, 1990, pp. 329–341 (Chapter 30).
- [17] F.R. Hartley, Supported Metal Complexes, Reidel, Dordrecht, 1985.
- [18] J.G. Handique, J.B. Baruah, J. Mol. Catal. A 172 (2001) 19.
- [19] X.-Q. Xin, L.-M. Zheng, J. Phys. Chem. Solid 58 (1997) 951.
- [20] Vogel's Text Book of Practical Organic Chemistry Revised by B. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, Longman, Harlow, Essex, 1989.
- [21] A. Puzari, J.B. Baruah, J. Org. Chem. 65 (2000) 2344.