

Available online at www.sciencedirect.com



CHINESE CHEMICAL LETTERS

Chinese Chemical Letters 21 (2010) 43-46

www.elsevier.com/locate/cclet

# Selective oxidation of primary substituted aromatic amines to azoxy products using lacunary catalyses

A. Nezhadali<sup>a,\*</sup>, M. Akbarpour<sup>a,b</sup>

<sup>a</sup> Department of Chemistry, Payame Noor University (PNU), Mashhad, Iran <sup>b</sup> Department of Chemistry, Payame Noor University (PNU), Bojnourd, Iran

Received 18 May 2009

#### Abstract

Some of the substituted anilines were selectively converted in to the corresponding azoxy and azobenzenes by oxidation with 30% aqueous hydrogen peroxide. The reactions were catalyzed by various heteropolyoxometalates, at boiling point of the used solvents. An improvement in the product yield and selectivity towards azoxybenzens was also observed. Azobenzenes was obtained as by-product. In the all similar cases, the highest yield of azoxy compounds was observed using  $K_5PW_{11}ZnO_{39}$  as catalyst in *N*,*N*-dimethylformamide solvent.

© 2009 A. Nezhadali. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Heteropolyoxometalates; Catalyst; Azobenzene; Azoxybenzene

The heteropolyoxometalates as catalysts has been paid considerable attention by researchers [1-5]. Also, polyoxometalates have been widely studied as small compact oxide clusters [6-10] and used in hydration of olefins, esterification and its related reactions, condensation, polymerization of tetrahydrofuran, paraffin alkylation, Friedel-Crafts and oxidation [11]. The polyoxometalates with several preparation including molecular compositions, size, shape, charge density, redox potentials, acidity, and solubility made them to use in various reactions [12].

Lacunary species generally react readily with any potential addenda or with a wide variety of octahedral coordinating metal ions to refill the vacant sites [13]. The product compositions in the oxidation of aniline, azobenzene azoxybenzene, nitrobenzene and nitrosobenzene, depends on the oxidants, catalysts, and reaction conditions employed [14–17]. In this context, it is interesting to study the catalytic activity of heteropolyoxometalate compounds. These species are attractive as oxidation catalysts because they may be considered as reactive complexes containing both low valent transition metal centers and inorganic ligands that have high electron affinity. The most common types of heteropolyoxometalates used in catalytic applications are based on Keggin and Wells-Dawson structure. However, other heteropolyoxometalates with sandwich structure have been lately studied for the biphasic oxidation of alcohols, alkenes and amines [18–23].

In this article, the results obtained for selective oxidation of some primary aromatic amines like as 4-bromoaniline, 4-chloroaniline, 4-methylaniline, to azoxybenzene derivatives in the presence of hydrogen peroxide, employing heteropolyoxometalates as catalyst at different conditions.

\* Corresponding author.

E-mail address: aziz\_nezhadali@yahoo.com (A. Nezhadali).

<sup>1001-8417/\$-</sup>see front matter © 2009 A. Nezhadali. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved. doi:10.1016/j.cclet.2009.07.017

## 1. Experimental

The standard quality compounds, sodium tungstate dehydrate, 4-bromoaniline, 4-chloroaniline, 4-methylaniline, nickel (II) nitrate hexahydrate, zinc (II) nitrate 6-hidrate and potassium chloride were purchased from Merck. ethanol (EtOH), *N*,*N*-dimethylformamide (DMF), acetonitrile (AN), acetic acid, phosphoric acid, hydrogen peroxide and silica gel with the highest grade were purchased from Merck. Helium gas was 99.999% pure and obtained from Sabalan Co. (Iran).

The amount 54.5 g Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O was dissolved in 90 mL water at 40–45 °C. Then 15 mL H<sub>3</sub>PO<sub>4</sub> and 26.4 mL CH<sub>3</sub>COOH were added to the solution and refluxed for 1 h. Then 20 g KCl was gently added to the solution. This solution was stirred for 30 min. The precipitate was isolated as the product Keggin.

The amount 0.5 g of nickel (II) nitrate or zinc (II) nitrate was dissolved at pH 5 (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa). Then gradually, added 5 g of Keggin powder to obtained solution. After 15 min, 5 g KCl was added to the solution. The precipitate powder stirred for 30 min. After filtration of the salt the remained solution left for 1 night at 5  $^{\circ}$ C till the crystals of the lacunary was formed.

To a stirred solution of catalyst  $(1 \times 10^{-3} \text{ mmol})$  in the appropriate solvent was added the aromatic amine (with mole ratio of 1:6 for catalyst to the aromatic amine). Then hydrogen peroxide was added to the stirred solution and refluxed the solution for 4 h. The solvent was evaporated to found the salt. The product was purified by column chromatography using silica gel. The melting points and spectral data of each product were compared with those of authentic samples and the literature values. Azoxy and azo compounds were isolated and determined for those percent by GC-Mass. Also, FT-IR spectrometer was used for further identifications.

The GC/MS analysis was carried out on a Shimadzu GC/MS model QP5050. The capillary column was BD-5 (30 mm  $\times$  0.2 mm, film thickness 0.32  $\mu$ m). The relative percentage of the azoxy and azo compounds were calculated from GC peak areas. IR spectra's were run on a Shimadzu 8300 FT-IR spectrophotometer.

#### 2. Results and discussion

IR spectra of the transition metal substituted phosphotungstate complexes show the absorption bands characteristic of Keggin structure, viz. peaks at 1061 cm<sup>-1</sup>, 960 cm<sup>-1</sup>, 891 cm<sup>-1</sup> and 812 cm<sup>-1</sup> respectively due to  $\nu$  [P–O–(W<sub>a</sub>)],  $\nu$  (W–O<sub>b</sub>), and the two  $\nu$  (W–O<sub>c</sub>–W) where a: central P–O bond, b: terminal double bond between tungsten and oxygen, c: the two types of bridging bonds between metal–oxygen–metal. This behavior is reported in the literature [24].

The effect of solvent, catalyst type temperature and time of reaction on the efficiency of oxidation of 4-bromo, 4chloro and 4-methyl aniline in the presence of 30% hydrogen peroxide as the oxidant and lacunary catalyst were studied in our work. The substrates and products structure are shown in Scheme 1. The result of present work shows, in all cases, the azoxy and azo compounds are major and minor products, respectively (Tables 1 and 2).

It has been shown [25] that, the efficiency of the azoxy product depends to the solvent nature. In the first stage, many oxidation reactions in various solvents with low boiling points such as ethanol, acetonitrile and dimethylformamide were performed. The results are summarized in Table 1. As an example, Fig. 1 shows the effect of solvent on oxidation of  $S_1$ ,  $S_2$  and  $S_3$  to the azoxy products in the presence of  $PW_{11}$ -Zn catalyst (runs 1–9 of Table 1). Dimethylformamide was found to be the appropriate solvent for the oxidation of 4-bromo, 4-chloro and 4-methyl aniline.



Table 1 The results of oxidation of some primary aromatic amines with  $H_2O_2$  catalyzed by lacunary catalyst in solvent of choice at 4 h reflux conditions.

Run	Substrate	Catalyst	Solvent	% Azoxy	% Azo
1	$S_1^{a}$	PW <sub>11</sub> -Zn	DMF	90.10	8.00
2	S <sub>1</sub>	PW <sub>11</sub> -Zn	EtOH	55.53	23.01
3	<b>S</b> <sub>1</sub>	PW <sub>11</sub> -Zn	AN	34.60	7.93
4	$S_2^{b}$	PW <sub>11</sub> -Zn	DMF	93.35	5.30
5	$\overline{S_2}$	PW <sub>11</sub> -Zn	EtOH	58.52	26.19
6	$S_2$	PW <sub>11</sub> -Zn	AN	71.45	28.55
7	$S_3^c$	PW <sub>11</sub> -Zn	DMF	79.45	19.52
8	<b>S</b> <sub>3</sub>	PW <sub>11</sub> -Zn	EtOH	_	_
9	S <sub>3</sub>	PW <sub>11</sub> -Zn	AN	27.59	9.92
10	<b>S</b> <sub>1</sub>	PW <sub>11</sub> -Ni	DMF	82.70	11.50
11	S <sub>1</sub>	PW <sub>11</sub> -Ni	EtOH	79.79	12.95
12	<b>S</b> <sub>1</sub>	PW <sub>11</sub> -Ni	AN	_	_
13	$S_2$	PW <sub>11</sub> -Ni	DMF	91.68	7.93
14	$\overline{S_2}$	PW <sub>11</sub> -Ni	EtOH	60.45	39.55
15	$S_2$	PW <sub>11</sub> -Ni	AN	68.67	31.33
16	$\overline{S_3}$	PW <sub>11</sub> -Ni	DMF	71.71	26.65
17	S <sub>3</sub>	PW <sub>11</sub> -Ni	EtOH	_	_
18	$S_3$	PW <sub>11</sub> -Ni	AN	39.81	12.70

<sup>a</sup> S1, 4-bromoaniline.

<sup>b</sup> S2, 4-chloroaniline.

<sup>c</sup> S3, 4-methylaniline.

Table 2
---------

Dependence of azoxy yields with time of reaction in DMF solvent.

Run	Substrate	Catalyst	Time	% Azoxy	% Azo
1	$S_1^{a}$	PW <sub>11</sub> -Zn	1 h	98.11	1.89
2	$\mathbf{S}_1$	PW <sub>11</sub> -Zn	2 h	98.04	1.96
3	$S_1$	PW <sub>11</sub> -Zn	3 h	97.22	2.78
4	$\mathbf{S}_1$	PW <sub>11</sub> -Zn	4 h	90.10	8.00
5	$S_1$	PW <sub>11</sub> -Zn	5 h	97.66	2.34
6	$S_2^{b}$	PW <sub>11</sub> -Zn	1 h	95.37	2.71
7	$S_2$	PW <sub>11</sub> -Zn	2 h	96.89	2.66
8	$S_2$	PW <sub>11</sub> -Zn	3 h	97.59	2.41
9	$S_2$	PW <sub>11</sub> -Zn	4 h	93.35	5.30
10	$S_2$	PW <sub>11</sub> -Zn	5 h	97.64	2.36
11	$\mathbf{S}_1$	PW <sub>11</sub> -Ni	1 h	93.64	4.77
12	$S_1$	PW <sub>11</sub> -Ni	2 h	91.65	4.73
13	$\mathbf{S}_1$	PW <sub>11</sub> -Ni	3 h	96.70	2.69
14	$S_1$	PW <sub>11</sub> -Ni	4 h	82.70	11.50
15	$S_1$	PW <sub>11</sub> -Ni	5 h	97.40	1.32
16	$S_2$	PW <sub>11</sub> -Ni	1 h	91.14	8.86
17	$S_2$	PW <sub>11</sub> -Ni	2 h	92.83	7.17
18	$S_2$	PW <sub>11</sub> -Ni	3 h	95.77	4.23
19	$S_2$	PW <sub>11</sub> -Ni	4 h	91.68	7.93
20	$S_2$	PW <sub>11</sub> -Ni	5 h	96.17	3.83

<sup>a</sup> S1, 4-bromoaniline.

<sup>b</sup> S2, 4-chloroaniline.

In the present work we investigated the activity of various lacunary hetropolyanions forms as pure  $PW_{11}$ -Zn and  $PW_{11}$ -Ni. The obtained results of catalytic oxidation of some primary aromatic amines are shown in Table 1. The primary aromatic amines were oxidized to the azoxy compounds in satisfactory yields along with a small amount of azo compounds. The results indicate that the nature of the catalyst plays an important role on their catalytic activities for oxidation of the amines. As Table 1 shows, the highest yield of products has been achieved in the presence of  $PW_{11}$ -Zn as catalyst.



Fig. 1. The effect of solvent of reaction on the amount of azoxy product in the presence of PW<sub>11</sub>-Zn and reflux conditions.

In order to obtain the best reaction time, the effect of reaction time on the efficiency of major product, azoxy, was studied. The oxidation of  $S_1$  and  $S_2$  were investigated with various times in the presence of DMF and the catalysts. Table 2 shows, dependence of azo and azoxy product efficiency to the reaction time.

As it is shown in Table 2, there is no difference between 1 h and 5 h reaction time on the efficiency of the product in the presence of  $PW_{11}$ -Zn as catalyst. A minor difference in the azoxy efficiency was observed at 4 h reaction time in the presence of  $PW_{11}$ -Zn, that might be comes from the experimental errors. As it is shown in Table 2, the oxidation of both S<sub>1</sub> and S<sub>2</sub> to azoxy products in the presence of  $PW_{11}$ -Ni as catalyst dose not depends to the reaction time. It means there are no differences between the results of 1 h and 5 h reaction times.

All of the reactions, in various solvents of the primary aromatic oxidation in the presence of  $PW_{11}$ -Zn and  $PW_{11}$ -Ni catalysts were carried out at two temperatures including room temperature and reflux temperature. The highest yield of azoxy compounds was obtained at reflux temperature.

## References

- [1] T.J.R. Weakley, S.A. Malik, J. Inorg. Nucl. Chem. 29 (1967) 2935.
- [2] S.A. Malik, T.J.R. Weakley, J. Am. Chem. Soc. (1968) 2647.
- [3] W.H. Knoth, P.J. Domaille, D.C. Roe, Inorg. Chem. 22 (1983) 198.
- [4] W.H. Knoth, P.J. Domaille, Inorg. Chem. 22 (1983) 818.
- [5] S.T. Sakaue, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 3633.
- [6] M.H. Alizadeh, H. Razavi, F.M. Zonoz, et al. Polyhedron 22 (2003) 933.
- [7] F. Hussain, L.H. Bi, U. Rauwald, et al. Polyhedron 24 (2005) 847.
- [8] L.H. Bi, B. Li, Y.Y. Bo, et al. Inorg. Chim. Acta 362 (2009) 1600.
- [9] M. AngelesBallesteros, M. AngelesUlibarri, V. Rives, et al. J. Solid State Chem. 181 (2008) 3086.
- [10] M.H. Alizadeh, H. Eshtiagh Hosseini, R.J. Khoshnavazi, Mol. Struct. 688 (2004) 33.
- [11] I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311.
- [12] M.M. Heravi, R. Motamedi, N. Seifi, et al. J. Mol. Catal. 249 (2006) 1.
- [13] C. Louis, W. Baker, C. Diana Glick, J. Am. Chem. Soc. (1998) 3247.
- [14] E. Wenkert, E.C. Angell, Synth. Commun. 18 (1988) 1331.
- [15] G. Barak, Y. Sasson, J. Org. Chem. 54 (1989) 3484.
- [16] Z. Weng, J. Wang, X. Jian, Catal. Commun. 9 (2008) 1688.
- [17] M.G. Egusquiza, G.P. Romanelli, C.I. Cabello, et al. Catal. Commun. 9 (2008) 45.
- [18] W. Adam, A. Hermann, J. Lin, et al. J. Org. Chem. 59 (1994) 8281.
- [19] F. Minisci, A. Citterio, E. Visnara, et al. J. Org. Chem. (1989) 728.
- [20] A. Fischer, G. Henderson, Synthesis (1985) 641.
- [21] S. Yamazaki, Tetrahedron Lett. 42 (2001) 3355.
- [22] R. Neumann, A. Khenkin, D. Juwiler, et al. J. Mol. Catal. A: Chem. 117 (1997) 169.
- [23] L. Salles, C. Aubry, R. Thouvenot, et al. Inorg. Chem. 33 (1994) 871.
- [24] O.A. Kholdeeva, V.A. Grigoriev, G.M. Maskimov, et al. J. Mol. Catal. 114 (1996) 123.
- [25] F.F. Bamoharram, M.M. Heravi, M. Roshani, et al. J. Mol. Catal. 255 (2006) 193.