

## Catalytic Oxidation of Aniline by Aqueous Hydrogen Peroxide in the Presence of Some Heteropolyoxometalates

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Anilina foi convertida em nitrosobenzeno e nitrobenzeno por oxidação com peróxido de hidrogênio aquoso 30%. A reação foi catalisada por vários heteropolioxometalatos, à temperatura ambiente, em diclorometano, em condições bifásicas. Descobriu-se que  $H_3PW_{12}O_{40}$  é o melhor catalisador na oxidação da anilina.  $Na_3PW_9Mo_3O_{40}$  e  $K_4SiW_9Mo_2O_{40}$  também exibiram alta atividade na oxigenação. Agentes de transferência de fase e temperatura também contribuíram para a eficiência da oxidação.

Aniline was selectively converted into the corresponding nitrosobenzene and nitrobenzene by oxidation with 30% aqueous hydrogen peroxide. The reaction was catalyzed by various heteropolyoxometalates, at room temperature, in dichloromethane under two-phase conditions. Findings show that  $H_3PW_{12}O_{40}$  is the best catalyst in the oxidation of aniline.  $Na_3PW_9Mo_3O_{40}$  and  $K_4SiW_9Mo_2O_{39}$  also displayed high reactivity in the oxygenation system. Phase transfer agents and temperature increase also contribute to the efficiency of the oxidation.

**Keywords:** oxidation, polyoxometalates, aniline

### Introduction

Oxidation of organic substrates by aqueous hydrogen peroxide is very attractive from the viewpoint of industrial technology and synthetic purposes.<sup>1</sup> Polyoxometalates have been widely studied as small compact oxide clusters.<sup>2-5</sup> Their redox properties and high electron density are ideal for their use as catalysts. It is well known that heteropolyoxometalates catalyze homogeneous oxidation of a wide range of organic compounds such as olefins,<sup>6,7,8</sup> thioethers,<sup>6</sup> and alcohols<sup>7</sup> with several terminal oxidants such as alkyl hydroperoxide,<sup>9</sup> molecular oxygen,<sup>10</sup> iodosyl benzene,<sup>8</sup> as well as hydrogen peroxide.<sup>11</sup>

Oxidation of amines to their corresponding oxygen-containing derivatives has attracted much attention during the past few decades.<sup>12</sup> Azobenzene,<sup>13,14</sup> azoxybenzene,<sup>15,16</sup> nitrobenzene<sup>17,18</sup> and nitrosobenzene,<sup>19-21</sup> have been formed in the oxidation of aniline by organic<sup>22</sup> and inorganic<sup>23</sup> oxidants. The product composition in the oxygenation of amines depends on the oxidant, catalyst, quaternary ammonium salts, and reaction conditions employed.<sup>16</sup>

Tungsten- and molybdenum-based heteropolyoxometalates have received attention as promising oxidation catalysts in the selective oxygenation of aromatic and aliphatic amines.<sup>24,25</sup> Recently, Ishii and colleagues have reported their results on the oxidation of amines by aqueous hydrogen peroxide under the influence of synthetic PCWP, peroxotungstophosphate, and CWP, tris(cetylpyridinium)12-tungstophosphate.<sup>26</sup> In this system,  $H_3PW_{12}O_{40}$  revealed little activity in  $CHCl_3$  and its efficacy varied with the reaction conditions.

We hereby present our results in the selective and fast oxidation of aniline by hydrogen peroxide in the presence of several simple heteropolyoxometalates at room temperature under simple reaction conditions.

### Results and Discussion

Table 1 introduces the results of aniline oxidation into nitrosobenzene as the major product and nitrobenzene as the minor product. The oxidant is 30%  $H_2O_2$  in the presence of some heteropolyoxometalates as catalysts under a two-phase reaction condition. Aniline is converted to nitrosobenzene by 2 equivalents of 30%  $H_2O_2$  with >86% selectivity at room temperature in dichloromethane. The reaction time is less than

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**Table 1.** Oxidation of Aniline with 30% $\text{H}_2\text{O}_2$  Catalyzed by Heteropolyoxometalates<sup>a</sup>

Catalyst	Conv.(%) <sup>b</sup>	Nitroso-Yield(%)	Nitro-Yield(%)	Selec.(%)	Time(min)
Without	0	0	0	0	240
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	55.5(92)	49.5(82.5)	6.2(9.8)	89(89.7)	15(50)
$\text{H}_3\text{PW}_{12}\text{O}_{40}$ <sup>c</sup>	91(90.2)	82.5(81.2)	8.4(9)	90.6(90)	15(30)
$\text{K}_5\text{Na}_2\text{PW}_{11}\text{O}_{39}$	43.5(86)	38.2(76.2)	5.3(9.8)	87.8(88.6)	20(60)
(TBA) <sub>7</sub> $\text{PW}_{11}\text{O}_{39}$	20(54)	17(46.5)	3(7)	85(86.1)	35(150)
(TBA) <sub>8</sub> $\text{SiW}_{11}\text{O}_{39}$	34(59.7)	28.8(52)	5.4(7.9)	84.7(87.1)	35(150)
$\text{K}_5\text{PW}_{11}\text{ZnO}_{39}$	2(5)	2(5)	0(0)	100(100)	40(180)
$\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	3.5(9.4)	3.5(8.7)	0(0.7)	100(92.5)	30(60)
$\text{H}_{14}\text{P}_5\text{W}_{30}\text{O}_{110}$	20	20	0	100	150
$\text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40}$	20(60)	18.4(56)	1.6(3.3)	92(93.3)	35(180)
$\text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$	41.5(82.7)	38.5(76.6)	3(6.1)	2.7(92.6)	35(130)
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	8.5(50)	8.5(48.5)	0(1.2)	100(97)	15(165)
(TBA) <sub>3</sub> $\text{PMo}_{12}\text{O}_{40}$	3.5(21)	3.5(20.5)	0(0.5)	100(97.6)	15(180)
$\text{Na}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$	3.4(8.1)	3.4(8)	0(0.1)	100(98.7)	60(150)
(TBA) <sub>3</sub> { $\text{PO}_4[\text{WO}(\text{O}_2)_2]_4$ }	17(40)	15.2(36)	2(3.8)	89.4(90)	40(120)
(TBA) <sub>3</sub> { $\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4$ }	5(16.5)	5(15.8)	0(0.6)	100(95.7)	60(180)

<sup>a</sup> Aniline(4 mmol) was allowed to react with 30% $\text{H}_2\text{O}_2$  (8 mmol) in the presence of catalyst (0.015 mmol), n equivalents of CPC(n= charge on polyanion) if present, in dichloromethane (7ml) under air at room temperature for the required time. <sup>b</sup> Determined by GLC. <sup>c</sup> under reflux.

3 hours. Nitrosobenzene monomer is formed as a clear green-colored solution in dichloromethane. It later converts into its dimeric form as yellowish solid. A typical  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  catalyzed oxidation of aniline to its corresponding products, has a 55.5% yield with 89% selectivity after only 15 minutes.  $\text{K}_5\text{Na}_2\text{PW}_{11}\text{O}_{39}$  is about as efficient catalyst as  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . It leads to 86% nitrosobenzene with 88.6% selectivity after 60 min. The catalytic activity of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  is much less than  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . It leads to 8.5% and 50% of product yield after 15 and 165 minutes, respectively, with 97-100% selectivity. The selectivity of oxidations with molybdenum analogs of heteropolyoxometalates is higher than those of tungstophosphates.

$\text{H}_3\text{PW}_{12}\text{O}_{40}$  shows comparable selectivity but higher conversion yield and requires a shorter reaction time at reflux.  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  resulted in 82.5% of nitrosobenzene with 90.6% selectivity after only 15 minutes under reflux. Elevation of reaction temperature has no effect on the selectivity of aniline oxidation with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as catalyst.

To study the effect of presence of phase transfer catalyst(CPC) on the oxidation of aniline, we compared the results obtained with  $\text{K}_5\text{Na}_2\text{PW}_{11}\text{O}_{39}$ +CPC and (TBA)<sub>7</sub> $\text{PW}_{11}\text{O}_{39}$ . The first system led to 86% conversion after 60 minutes, while 54% of conversion was obtained with the latter after 150 min. On the other hand,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  + CPC and (TBA)<sub>3</sub> $\text{PMo}_{12}\text{O}_{40}$  systems formed 50% and 21% of the products, respectively, at nearly the same times. According to the previous findings, efficiency of CPC and TBA in the formation of the peroxo-complex affects the efficacy of these oxygenations.<sup>27</sup>

The Si-substituted catalysts,  $\text{SiW}_{11}\text{O}_{39}$ <sup>-8</sup> and  $\text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$ , showed higher reactivity than  $\text{PW}_{11}\text{O}_{39}$ <sup>-7</sup> and  $\text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40}$ . The first two catalysts led to 34%

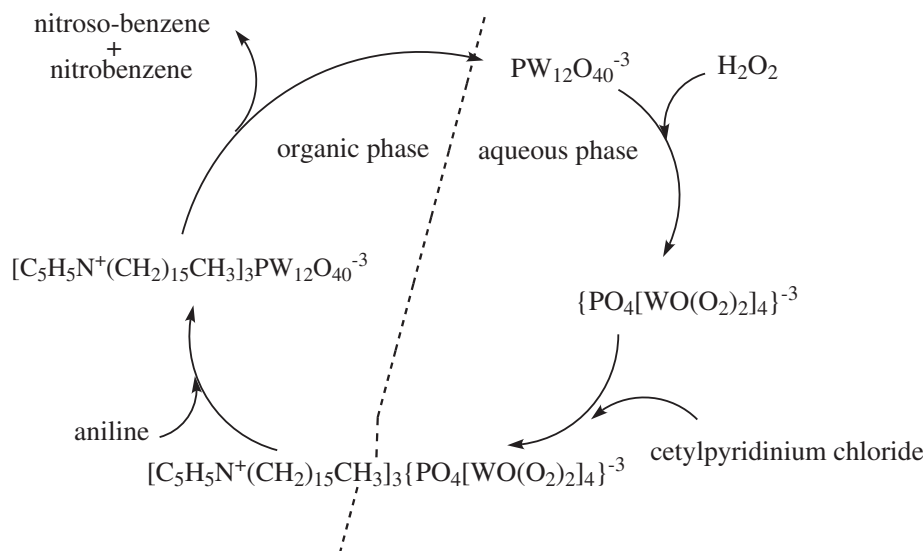
and 41.5% of conversions, respectively, after 35 min., but the latter two resulted in 20% and 22% conversions, respectively, at the same time. In contrast, the Zn(II)-substituted polytungstophosphate,  $\text{PZnW}_{11}\text{O}_{39}$ <sup>-5</sup>, had the lowest activity. Other Mo- and W- substituted polyoxometalates showed lower activity.

Venturello crystallographically characterized polyperoxometalate { $\text{PO}_4[\text{WO}(\text{O}_2)_2]_4$ }<sup>3-</sup> as the active oxygen transfer agent in the oxygenation of organic compounds by hydrogen peroxide catalyzed by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .<sup>28</sup> Accordingly, Scheme 1 represents the general formulation of the catalytic two-phase system in the oxygenation of aniline.

In summary, we have shown that the oxidation of aniline by 35% hydrogen peroxide, catalyzed by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  family (under two-phase conditions at room temperature or under reflux) provides a simple and general procedure for the preparation of nitrosoaniline, that is difficult to prepare selectively by conventional methods. The results clearly demonstrate that this oxidation system is more efficient than Ishii system in the selective oxidation of aniline with hydrogen peroxide.<sup>26</sup>

## Experimental

All starting materials were commercially available and were used without further purification. GLC analyses were performed with Shimadzu capillary column equipped with a flame ionization detector. The polyoxometalates  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,<sup>29</sup>  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,<sup>29</sup>  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ,<sup>30,31</sup>  $\text{K}_5\text{Na}_2\text{PW}_{11}\text{O}_{39}$ ,<sup>30,31</sup> and  $\text{K}_5\text{PW}_{11}\text{ZnO}_{39}$ ,<sup>32-35</sup> were prepared and characterized according to the literature procedures.



### General procedure for oxidation of aniline to nitrosobenzene

To a stirred solution of catalyst (0.015 mmol), *n* equivalents of CPC (*n*= charge on polyanion) if present, and 30% $\text{H}_2\text{O}_2$  (8 mmol) in  $\text{CH}_2\text{Cl}_2$  (7 mL) was added aniline (4 mmol), and the mixture was stirred at room temperature for the required time. Progress of the reaction was followed by the aliquots withdrawn directly and periodically from the reaction mixture, analyzed by gas chromatography. GLC analyses were performed on a Shimadzu 17A-GC with a flame ionization detector using a 25 m  $\times$  0.25 mm capillary column packed with CPB10 as stationary phase. After decomposition of unreacted hydrogen peroxide, the products were extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The products were purified by column chromatography on silica gel (1/5, ethyl acetate/hexane). The boiling point and spectral data of each product were compared with those of authentic samples and literature values.<sup>36</sup>

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