

NOTE**Environmentally Benign Oxidation of Aniline with 30 % H₂O₂ Catalyzed by Some Heteropolyoxometalates**

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Oxidation of aniline with 30 % hydrogen peroxide catalyzed by different heteropolyoxometalates of tungsten and molybdenum under air at room temperature is studied. Findings showed that aniline was converted into nitroso-benzene in water, as well as in CH₂Cl₂, with good yields and high selectivities.

Key Words: Oxidation, Heteropolyoxometalate, Aniline, Hydrogen peroxide, Water.

The oxidation of organic substrates with aqueous hydrogen peroxide is very attractive from the viewpoint of industrial technology and synthetic purposes. The reason being its ready availability, low cost and the environmentally friendly by-products produced (water and molecular oxygen)¹⁻⁵. In view of environmental mandates, there is a global effort to replace conventional catalysts by eco-friendly catalysts. The replacement of current chemical processing with more environmentally benign alternatives is an increasingly attractive subject⁶.

Heteropolyacids (HPAs) catalyze a wide variety of reactions in homogeneous liquid phase, offering strong options for more efficient and cleaner processing compared to conventional mineral acids⁷⁻¹¹. The selected examples reviewed show the broad scope of potentially promising applications of HPAs as acid and redox catalysts in low-temperature liquid-phase organic reactions. Due to their unique physicochemical properties, HPAs can be profitably used in homogeneous, biphasic, or heterogeneous systems, providing a broad operational choice¹². The high effectiveness of HPAs as acid catalysts is primarily due to their strong Bronsted acidity, greatly exceeding that of ordinary mineral acids and solid acid catalysts. Such important HPA properties as the ability of polyanions to stabilize organic intermediates and lack of side reactions like sulfonation, *etc.*, also contribute to enhancing the catalytic activity and reaction selectivity. In liquid-phase oxidation, polyoxometalates can be applied as catalysts in conjunction with environmentally friendly oxidants such as H₂O₂¹³.

Oxidation of amines to their corresponding oxygen-containing derivatives has attracted the interest of several research during the past few decades. Azobenzene, azoxybenzene, nitrobenzene¹⁴ and nitrosobenzene¹⁵, have been formed in the oxidation of aniline with organic and inorganic oxidants¹⁶. The product composition in these reactions depends on the oxidant, catalyst and reaction condition employed.

In present studies, the results of the selective and fast oxidation of aniline with hydrogen peroxide in water and in CH_2Cl_2 in the presence of some heteropolyoxometalates as catalyst were introduced.

All starting materials were commercially available and were used without further purification. GLC analyses were performed by gas chromatography (Shimadzu 17A) using a $25 \text{ m} \times 0.25 \text{ mm}$ CPB 10 capillary column equipped with a flame ionization detector. The polyoxometalates were prepared and characterized according to the literature procedures^{16,17}.

General procedure for oxidation of aniline to nitrosobenzene: To a stirred solution of catalyst (0.015 mmol), *n* equivalents of $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$, in two phase system, (*n* = charge of polyanion) and 30 % H_2O_2 (8 mmol) in H_2O (5 mL) or in CH_2Cl_2 (7 mL), aniline (4 mmol) was added. The mixture was stirred under air at room temperature for the required time. Progress of the reaction was followed by the aliquots withdrawn from the reaction mixture. After completion of the reaction, the products were extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. Then, the products were purified by column chromatography on silica gel (1/5, ethyl acetate/hexane).

Table-1, introduces the results of oxidation of aniline into nitrosobenzene as the major product and nitrobenzene as the minor product with 30 % H_2O_2 catalyzed by some heteropolyoxometalates under two-phase ($\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$) or single phase (H_2O) reaction conditions. Aniline was converted into nitrosobenzene with 2 equiv. of 30 % H_2O_2 with > 90 % selectivity, the ratio of nitrosobenzene %/conversion %, at room temperature at < 3 h. A typical $\text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$ catalyzed oxidation of aniline into its corresponding products in 81 % yield with 94 % selectivity in water after 60 min. Whereas, 83 % of nitrosobenzene with 93 % selectivity was obtained in dichloromethane after 130 min. Oxidation of aniline in the presence of $\text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40}$, led

TABLE-1
OXIDATION OF ANILINE WITH 30 % H_2O_2 CATALYZED BY
HETEROPOLYOXOMETALATES IN WATER AND IN CH_2Cl_2 ^a

Catalyst	Conv.% ^b	Nitroso-Yield%	Selec.% ^c	Time (min)	in CH_2Cl_2 as solvent			
					Conv.% ^b	Nitroso-Yield%	Selec.% ^c	Time (min)
Without	0	0.0	0	240	0.0	0.0	0	240
$\text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$	81	76.0	94	60	83.0	77.0	93	130
$\text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40}$	64	60.0	94	180	30.0	27.0	90	60
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	67	59.0	88	30	92.0	82.0	89	60
$\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	24	23.0	96	30	9.5	8.7	91	60
$\text{Na}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$	19	18.5	97	60	3.0	3.0	100	150
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	5	24.0	96	60	50.0	48.0	96	165
$\text{H}_{14}\text{P}_5\text{W}_{30}\text{O}_{110}$	5	5.0	100	150	20.0	20.0	100	150

^aAniline (4 mmol) was allowed to react with 30 % H_2O_2 (8 mmol) in the presence of catalyst (0.015 mmol), in H_2O (5 mL) or in CH_2Cl_2 (7 mL); *n* equivalents of CPC in the case of CH_2Cl_2 (*n* = charge on polyanion), under air at room temperature for the required time.

^bDetermined by GLC. ^cSelectivity % refers to the ratio of nitrosobenzene % / conversion %.

to 64 and 30 % of products with greater than 90 % selectivity in water and in CH₂Cl₂ after 130 and 60 min, respectively. Therefore, Na₃PW₉Mo₃O₄₀ catalytic system is much more reactive in water than in dichloromethane. With H₃PW₁₂O₄₀ as catalyst, the oxidation system resulted in 67 % of conversions in water after 0.5 h. Whereas, 92 % of nitrobenzene was obtained in dichloromethane after 1 h. Different catalytic activity of the examined catalysts introduced in Table-1, should be explained considering easy formation and higher stability of the catalytically active species in the catalytic oxidation system^{18,19}. For example, K₆P₂W₁₈O₆₂ and Na₆P₂Mo₁₈O₆₂ are nearly 2.5-6.0 times more reactive in water than in CH₂Cl₂.

In summary, it is showed that the oxidation of aniline with 30 % hydrogen peroxide catalyzed by H₃PW₁₂O₄₀ family under mono- and bi-phasic systems provides a clean, fast and cheap general procedure for environmentally benign oxidation of aniline into nitrosobenzene at room temperature.

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