Nitration of Aromatic Compounds Catalyzed by Divanadium-Substituted Molybdophosphoric Acid, H$_5$[PMo$_{10}$V$_2$O$_{40}$]

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Summary. The nitration of aromatic compounds was carried out in the presence of divanadium-substituted molybdophosphoric acid, H$_5$PMo$_{10}$V$_2$O$_{40}$, as catalyst and a mixture of nitric acid and acetic anhydride as nitrating agent. In the presence of this heteropolyacid the *ortho-* and *para*-nitro compounds were obtained in good to excellent yields under mild reaction conditions.

Keywords. Catalyst; Heteropolyacid; Aromatic substitution; Nitration; H$_5$PMo$_{10}$V$_2$O$_{40}$.

Introduction

The nitronium ion is usually the nitrating agent in electrophilic aromatic nitration. The nitronium ion is formed *in situ* from nitric acid, alkyl nitrate, acyl nitrates (XONO$_2$, X = H, RC(O)), in which it is bound to an oxygen atom [1].

On the other hand, nitration of aromatic substrates is a widely studied reaction of great industrial significance as many nitro-aromatics are extensively utilized and act as chemical feedstock for a wide range of useful material such as dyes, pharmaceuticals, perfumes, and plastics. Aromatic nitration is quite notorious for its unfriendly nature towards the environment. The use of large quantities of nitric and sulfuric acids, corrosiveness, and potential danger of explosion, low regioselectivity, and oxidative degra-dation of by-products are the disadvantages of this reaction [2].

Zeolite-based solid acid catalysts such as ZSM-5 [3], X [4], Y [3–5], and β [3, 5, 6] have been used for nitration of various activated as well as deactivated substrates [3, 4, 6–8].

A variety of other solid acids such as silica gel [9], clay supported metal nitrates [10–12], modified and sulfated zirconia [13], and vapor phase nitration of benzene by dilute nitric acid in the presence of heteropolyacid partially neutralized by Cs or Tl ions [14] have also been applied for nitration of aromatic compounds.

Heteropoly acids, *HPA*s, catalyze a wide variety of reactions in homogeneous or heterogeneous (liquid–solid, gas–solid, or liquid–liquid biphasic) systems, offering strong options for more efficient and cleaner processing compared to conventional mineral acids [15–18]. Catalysts based on heteropolyacids as *Brønsted* acids have many advantages over liquid acid catalysts. They are non-corrosive and environmentally benign, presenting fewer disposal problems. Solid heteropolyacids have attracted much attention in organic synthesis owing to easy work-up procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts [19]. Being stronger acids, heteropolyacids will have significantly higher catalytic activity than conventional catalysts such as mineral acids, mixed-

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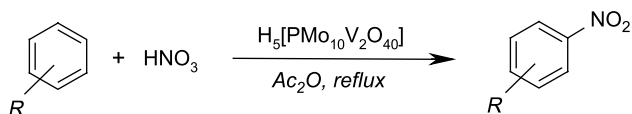
Scheme 1

oxides, zeolites, *etc.* In particular, in organic media the molar catalytic activity of heteropolyacid is often 100–1000 times higher than that of H_2SO_4 [17, 18]. This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or at a lower temperature. As stable, relatively nontoxic crystalline substances, heteropolyacids are also preferable regarding safety and ease of handling.

The *Keggin*-type *HPA*s typically represented by the formula of $[XM_{12}O_{40}]^{n-}$, when X is the heteroatom (most frequently P^{+5} or Si^{+4}), and M is the addenda atom (usually W^{+6} or Mo^{+6}), are the most important for catalysis [15–18]. They have been widely used as acid and oxidation catalysts for organic synthesis and found several industrial applications. Among the *Keggin HPA*s, transition metal-substituted $H_3[PMo_{12}O_{40}]$ compounds have been reported as effective catalysts in organic reactions [20–27]. Vanadium is the preferred element in heterogeneous and homogeneous catalysts for various reactions. The redox process of vanadium-substituted molybdophosphoric acid with *Keggin* structure is quite fast and facile.

In continuation of our work on the catalytic properties of heteropolyacids [28] we developed a convenient, efficient, and eco-friendly procedure for the nitration of aromatic compounds using a catalytic amount of $H_5PMo_{10}V_2O_{40}$ (Scheme 1).

Results and Discussion

A variety of different aromatic compounds, containing activating and deactivating groups were subjected to this reaction to investigate the generality of the methodology.

The catalyst was synthesized according to Ref. [29] and displays a *Keggin* structure [30]. At the first stage, because of complexity of behavior for this catalyst in a solvent, we studied nitration reactions in a solvent-free system. Transition metal cations have an important effect on the catalytic properties of these compounds when they substitute molybdenum cations in the *Keggin* units or when they are present as counter cations. The case of vanadium, which can occupy both anionic and cationic positions, is more complex. In fact, under catalytic conditions a rebuilding of the heteropolyanion generally occurs and vanadyl salts are formed.

However, initial attempts to carry out the reaction in a solvent-free system failed. Thus, among the tested solvents, acetic anhydride, Ac_2O, was applied as solvent of choice. Higher conversion with acetic acid is attributed to the *in situ* formation of acetyl nitrate as active nitrating agent in the presence of nitric acid [5, 6]. Acetic anhydride reacts with nitric acid to form acetyl nitrate intermediate species as follows:

$$(CH_3CO)_2O + HNO_3 \rightarrow CH_3COONO_2 + CH_3COOH$$

Ac_2O as solvent has been claimed to efficiently trap the water formed during the reaction. It acts as a dehydrating agent and consumes the water present in 65% HNO_3 to form acetic acid thus increasing the concentration of nitric acid and thereby enhancing the conversion of the substrate. $AcONO_2$ is only weakly dissociated in organic solvents and requires the presence of acids to exhibit sufficient reactivity in nitration [31]. Apparently, $H_5PMo_{10}V_2O_{40}$ can provide the required acidity for a facile dissociation of $AcONO_2$ to produce the nitronium ion for nitration. Without catalyst, in the blank experiments, the reactions are sluggish and considerable amounts of starting materials are recovered. The exact role of the divanadium-substituted molybdophosphoric acid, $H_5PMo_{10}V_2O_{40}$, in the nitration of phenol and its mechanism is not yet very clear and more study is needed to clarify this important point. The attempts to isolate intermediates or to analyze them failed so far in providing clear information. The catalytic performances of vanadium(V)-substituted heteropolymolybdates are the overall effects of all isomers. Positional isomers are always possible, and usually coexist, when two or more vanadium atoms are incorporated into the *Keggin* structure. For example, there are five positional isomers for the $H_5PMo_{10}V_2O_{40}$ [32] and the contribution of each isomer cannot be obtained separately. However, a literature survey has shown that VO_2^+ is formed in an isolated form or within heteropolyacids, Eq. (1) [33–38].

$$HPA - n \rightleftarrows VO_2^+ + HPA - (n-1) \qquad (1)$$

We believe that in addition of *Brønsted* acidity of $H_5PMo_{10}V_2O_{40}$ and an energy gap between the highest occupied molecular orbital and the lowest

Table 1. Heteropolyacid-catalyzed nitration of aromatic compounds

Entry	Substrate	Product	*Time*/h	Yield/%[a]
1	*Ph*OMe	4-NO$_2$*Ph*OMe	3	30
		2-NO$_2$*Ph*OMe		70
2	*Ph*OH	2-NO$_2$*Ph*OH	3	22
		4-NO$_2$*Ph*OH		44
3	4-Br*Ph*OH	4-Br-2,6-NO$_2$-*Ph*OH	5	100
4	*Ph*NH*Ac*	2-NO$_2$*Ph*NH*Ac*	9	60.3
		4-NO$_2$*Ph*NH*Ac*		1.3
5	*Ph*N*Me*$_2$	2-NO$_2$*Ph*N*Me*$_2$	0.7	17
6	Naphth	2-NO$_2$-Naphth	3	84
7	2-OH-Naphth	1,4-NO$_2$-2-OH-Naphth	1.5	63
8	*Ph*Br	2-NO$_2$*Ph*Br	1	62
9	*Ph*I	2-NO$_2$*Ph*I	7	22
10	3,5-*MePh*	2,6-*MePh*NO$_2$	0.25	79
11	*Ph*CO*Me*	3-NO$_2$*Ph*CO*Me*	9	41

[a] Yields analyzed by GC/MS

unoccupied orbital, VO$_2$$^+$ presents the key heteropolyacid structure responsible for our reaction.

Nitration of anisole in heterogeneous media was carried out affording 70% *o*-nitroanisole and 30% *p*-nitroanisole giving an *o/p* ratio of 2.3. A complete conversion of anisole to the corresponding nitro compounds is achieved under reflux condition. Upon increasing the temperature from room temperature to reflux *o*-nitroanisole was obtained with 70% selectivity. The nitration of phenol occurred similarly to that of anisole, yielding 2-nitro and 4-nitrophenol with 44% selectivity of the *p*-isomer. Table 1 shows examples of heterogeneous nitration of a variety of aromatic compounds.

For the nitration of *m*-xylene, 1,3-dimethyl-2-nitrobenzene was obtained in 79%. In this reaction no nitration of the side-chain was observed (entry 10). The nitration of alkanes with nitric acid by vanadium-substituted polyoxometalates has been reported by *Schinachi et al.* [39]. 2-Naphtol was nitrated under the same condition to give only 1,4-dinitro-2-naphtol in 63% yield. Interestingly, the nitration of acetamide under the same reaction condition gave 2-nitroacetanilide and 4-nitroacetanilide in 60.3 and 1.3% yields, respectively. It is noteworthy to mention that incomplete nitration of deactivated aromatic compounds such as naphthalene, iodobenzene, and bromobenzene was observed under these reaction conditions (Table 1).

The effect of temperature was studied by carrying out the reactions at different temperatures in the presence of this catalyst. It was observed that the yield is a function of temperature, thus the yield increased as the reaction temperature was raised. The results are summarized in Table 1.

In conclusion, this study demonstrates that H$_5$PMo$_{10}$V$_2$O$_{40}$ is an active and environmentally friendly catalyst for the nitration of aromatic compounds. This solid acid is superior in activity to the conventional acid catalysts such as H$_2$SO$_4$ or zeolites, which is in line with the stronger acidity of *HPA*. The catalyst can be reused after a simple work-up without any loss of catalytic activity.

Experimental

Melting points were measured using the capillary tube method with an electrothermal 9100 apparatus. IR spectra were recorded from KBr disks on the FT-IR Bruker Tensor 27. Yields are based on GC/mass analysis using Agilent 6890 GC system Hp-5 capillary 30 m × 530 μm × 1.5 μm nominal. All products are known and their physical and spectral data were compared with those of authentic samples. The heteropolyacid was synthesized according to Ref. [29].

Nitration of Aromatic Compounds: Typical Procedure
To a magnetically stirring mixture of 1 cm^3 acetic anhydride and nitric acid (65%, 1 mmol) 108.7 mg anisole (1 mmol) and H$_5$PMo$_{10}$V$_2$O$_{40}$ (0.02 g, 0.01 mmol) at room temperature, were added. The mixture was then refluxed for appropriate time. The progress of the reaction was monitored by TLC using petroleum ether: ethyl acetate as eluent. After completion of the reaction, the catalyst was filtered off. The mixture was then washed with 10 cm^3 satd. sodium hydrogen carbonate and the product extracted with 2 × 5 cm^3 dichloromethane. The combined organic extracts were washed with 10 cm^3 distilled

water, dried (MgSO$_4$), and the solvent was removed by evaporation to afford the nitrated product (Table 1).

Acknowledgements

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