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Novel Catalytic Acetylation of Alcohols with Preyssler's Anion, $[NaP_5Wa_{30}O_{110}]^{14-}$ [1]

M. H. Alizadeh, H. Razavi***, F. Farrash Bamoharram*,**
M. K. Hassanzadeh, R. Khoshnavazi*, and F. Mohammadi Zonoz***
** Department of Chemistry, Ferdowsi University of Mashhad, Iran*
*** Department of Pharmaceutical Chemistry, School of Pharmacy, Mashhad University of Medical Sciences. Mashhad, Iran*
**** Department of Chemistry, Georgetown University, USA*
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Abstract—Sodium 30-tungstopentaphosphate, the so-called Preyssler's anion with a formula of $[NaP_5W_{30}O_{110}]^{14-}$ (**I**) catalyzes the acetylation of alcohols ($C_nH_{2n+1}OH$, $n = 2, 3, 4, 5$) with acetic acid. High yield is obtained with **I** as pure acid or supported on silica. Both homogeneous and heterogeneous catalysts are discussed and compared. $H_{14}[NaP_5W_{30}O_{110}]$, abbreviated as H_{14}-P_5, under homogeneous conditions, as well as supported on silica (heterogeneous conditions) is found to be an excellent catalyst. Our data indicate that, when the ammonium salt of **I** is employed as the catalyst, the yield increases as the alcohol carbon-chain is increased. This behavior is found to be quite general. The catalysts can be easily recovered and recycled with retention of their initial structure and activity.

1. INTRODUCTION

Esters are commercially important. Sulfuric, hydrochloric, and hydrofluoric acids are the most commonly used homogeneous catalysts in the esterification of carboxylic acids. However, these catalysts are toxic and corrosive.

Recently, they have been replaced by other acid catalysts such as sulfonic and heteropoly acids [1, 2]. In homogeneous catalysis, p-toluene sulfonic acid is well known. There are many heterogeneous catalysts: SO_3H resins, Nafion-H, the zirconium oxide–sulfate ion, the titanium oxide–sulfate ion, silica–alumina, zeolite HY, cation exchange resins, niobic acid, titanium alkoxide, alumina, and zirconium alkoxide supported on silica [3–6].

The synthesis of some of these catalysts is difficult, and there is the fear of unfavorable side reactions such as dehydration. Heteropoly compounds, on the other hand, provide a framework of mixed-oxide catalysts of high efficiency and favorable practical characteristics. The catalytic capability of heteropoly compounds has attracted much attention in the last two decades. They are used in solution as well as in the solid state [7–9]. Many important industrial reactions are facilitated by the use of these compounds [10–14].

Most catalytic research is focused on the Keggin and Dawson structures of heteropolyanions such as $[PW_{12}O_{40}]^{3-}$, $[PMo_{12}O_{40}]^{3-}$, $[P_2W_{18}O_{62}]^{6-}$, $[P_2Mo_{18}O_{62}]^{6-}$, etc. [14, 15–21]. Although Keggin and Dawson type polyoxoanions have widely been studied as catalysts, the application of Preyssler's anion has been very limited, with only a few demonstrations of catalytic activity [22]. In some cases there have been reports of no catalytic capability [23]. One of the more recent reports of reactions involving Preyssler's anion is its use for radioactive waste treatment [24].

The interesting feature of this heteropolyanion (of high surface area) is its hydrolytic stability, which is very important in catalytic processes [25]. In continuation of our research on the synthesis and application of heteropoly anions in organic syntheses [26], we hereby report the applicability of a novel and recyclable catalyst (sodium30-tungstopentaphosphate) for efficient esterification of acetic acid.

We have studied the pure and supported acid and salts of Preyssler's anion. They exhibit high selectivity and good yield in the esterification reaction. Some important features of this heteropolyanion are:

(1) Its stability in the pH range from 0 to 12, thus encompassing a wide range of acid and/or alcohol concentrations [25].

(2) The anion is not sensitive to water and the esterification does not require water-free conditions [27].

(3) The anion is thermally stable, rendering high-temperature reactions practical [27].

(4) Both pure and supported catalysts can be easily recovered and recycled without degradation and loss of activity.

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[1] This article was submitted by the authors in English.

2. RESULTS AND DISCUSSION

2.1. Acetylation of Alcohols by $(NH_4)_{14}[NaP_5W_{30}O_{110}]$, NH_4-P_5

In order to achieve heterogeneous catalysis and avoid strong acid strength on the surface, the esterification was carried out by NH_4-P_5. The anion has an approximate D_{5h} symmetry and consists of a cyclic assembly of five PW_6O_{22} units, each derived from the Keggin anion, $[PW_{12}O_{40}]^{3-}$, by the removal of two sets of three corner-shared WO_6 octahedra. A sodium ion is located within the polyanion on the fivefold axis and 1.25 Å above the pseudomirror plane that contains the five-phosphorus atoms (Fig. 1) [25].

In esterification of acetic acid by ethanol, propanol, butanol, and pentanol, a molar ratio of (acetic acid/catalyst) 467 was used. The yields of esters are shown in Table 1. The results show that the reactivities of alcohols were increased as the carbon chain of the alcohol grew longer. The yield of esters increased in this order: ethylacetate < propylacetate < butylacetate < pentylacetate.

In other words, NH_4-P_5 is a better catalyst for esterification of acetic acid by pentanol, whereas in the esterification by ethanol, shows a relatively poor activity. This trend may be general with any catalyst. However, what is of interest to us is the fact that Preyssler's anion is an effective catalyst for each esterification reaction studied.

Another effective way to generate a larger external surface area is generating supported heteropoly acids [28]. We examined H_{14}-P_5 in conjunction with NH_4-P_5 and p-toluene sulfonic acid, P-tolu (an inorganic and organic catalyst). H_{14}-P_5 and P-tolu were placed in the reaction system on an NH_4–P_5 support as the heterogeneous catalyst. The results are shown in Table 2.

In order to compare several catalytic systems, we selected $(NH_4)_3[PW_{12}O_{40}]$, NH_4-P, $(NH_4)_4[SiW_{12}O_{40}]$, NH_4-Si, and NH_4-P_5. The reaction results are summarized in Table 3. They show that the catalyst has a dramatic effect on the esterification yield. As expected, a series of control experiments with different concentrations of alcohols indicated that the yield of the esters produced is decreased with decreasing alcohol concentration.

Table 1. Esterification in the liquid phase by NH_4-P_5

Entry	Alcohol	% Yield
1*	Ethanol	7
2	Propanol	25
3	Butanol	63
4	Pentanol	68

Note: Reaction conditions: Catalyst: 3.75×10^{-5} mol, acetic acid: 1.75×10^{-2} mol, alcohol (29 ml), reflux for 4–6 h.
* Toluene (20 ml) was added, alcohol (7 ml).

Table 2. Esterification in the liquid phase by H_{14}-P_5/NH_4-P_5 and P-tolu/NH_4-P_5

Entry	Alcohol	% Product yield	
		H_{14}-P_5/NH_4-P_5	P-tolu/NH_4-P_5
1*	Ethanol	47	70
2	Propanol	52	81
3	Butanol	71	86
4	Pentanol	92	90

Note: Reaction conditions: Catalyst: H_{14}-P_5/NH_4-P_5: 3.75×10^{-5} mol and P-tolu/NH_4-P_5: 3.75×10^{-5} mol, acetic acid: 1.75×10^{-2} mol, alcohol (29 ml), reflux for 4–6 h.
* Toluene (20 ml) was added, alcohol (7 ml).

Table 3. Comparison between NH_4-P_5, NH_4-PW_{12}, and NH_4-SiW_{12} (liquid phase)

Entry	Alcohol	NH_4–P_5	% Product yield	
			NH_4-PW_{12}	NH_4-PW_{12}
1*	Ethanol	7	Trace	Trace
2	Propanol	25	4	3
3	Butanol	63	22	18
4	Pentanol	68	36	44

Note: Reaction conditions: Catalyst: 3.75×10^{-5} mol, acetic acid: 1.75×10^{-2} mol, alcohol (29 ml), reflux for 4–6 h.
* Toluene (20 ml) was added, alcohol (7 ml).

2.2. Acetylation of Alcohols by H_{14}-P_5

In esterification reactions, there is a strong demand for new solid acids with favorable characteristics to replace conventional liquid and solid catalysts such as sulfuric acid, hydrochloric acid, and ion-exchange resins [14]. Sulfuric acid poses serious environmental and operational problems. Acidic ion-exchange resins such as Amberlyst-15 are widely employed. They are useful only at temperatures below 100°C due to their low thermal stability. It should be noted that, in the reactions where water may be present (as a product or otherwise), there are only a few solid acid catalysts that meet the criteria for activity and stability. To avoid these problems, we selected pure H_{14}-P_5. To enhance the acid strength, solid H_{14}-P_5 catalyst was dehydrated under vacuum at 150–300°C for 1–2 h [16].

The results of the liquid-phase esterification of acetic acid with ethanol, propanol, butanol, and pentanol in the presence of H_{14}-P_5 are listed in Table 4. The molar ratio of acetic acid to heteropolyanion was 467.

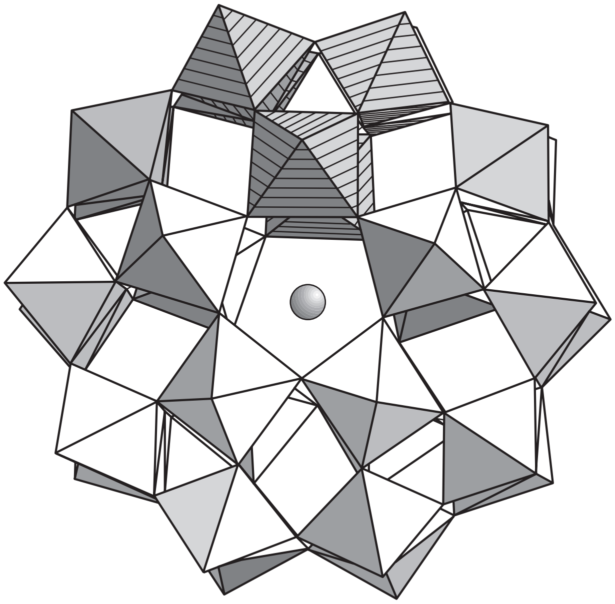

Fig. 1. Structure of Preyssler's anion.

The results show that H_{14}-P_5 produces a higher ester yield than does its ammonium salt. It seems clear that the acid strength of the protons on H_{14}-P_5 is sufficient to catalyze the esterification reaction and potentially all protons are active sites. In other words, the acid strength of the solid H_{14}-P_5 is comparable to that of liquid H_2SO_4.

2.3. Supported Heteropoly Acids versus Homogeneous Conditions

The reactivities of H_{14}-P_5/NH_4-P_5 and H_{14}-P_5/SiO_2 (supported acid on H_{14}-P_5 and SiO_2) have been studied. In all cases, the supported polyacid is less active than the unsupported one (Table 5). One plausible interpretation of this observation is that, in H_{14}-P_5/SiO_2, there are polyanion-support interactions of an acid–base nature. Some protons of the polyacid and some basic sites of the support (for example hydroxyl groups) can interact. This would lead to a diminished availability due to this extra ionic interaction [29].

The results of the comparison between H_{14}-P_5, H_{14}-P_5/NH_4-P_5, and H_{14}-P_5/SiO_2 are shown in Fig. 2. Although H_{14}-P_5/SiO_2 and H_{14}-P_5/NH_4-P_5 are less active than the homogeneous H_{14}-P_5, they can be easily separated from the reaction mixture and reused (by filtering).

2.4. Recycling of the Catalyst

One of the most desirable properties for a catalyst is the ease of its recovery. We have found that Preyssler's anion can be reused several times without any appreciable loss of activity. In this study, at the termination of each reaction, the catalyst was recovered. In the heterogeneous case, the catalyst was simply filtered and dried. In the homogeneous catalysis, the reaction mixture was distilled and dried. IR spectra of the resulting solids are shown in Fig. 3. They indicate that the catalyst can be recovered without structural degradation. The recovered solids were reused as catalyst for new reactions. The recovery had only slightly decreased their catalytic activity, pointing to the stability and retention capability of this useful polyanion.

3. CONCLUSIONS

Efficient acetylation of ethanol, propanol, butanol, and pentanol have been studied for the first time by an inexpensive, recyclable, and easily prepared Preyssler's anion with high selectivity. Important features of this catalyst are high thermal and hydrolytic stability throughout a wide pH range. Thus, a wide range of catalytic reactions can be effected without loss of structure and activity.

Among the different forms of Preyssler's anions (H_{14}-P_5, NH_4-P_5, H_{14}-P_5/SiO_2, and H_{14}-P_5/NH_4-P_5) that were studied, H_{14}-P_5 was found to produce the highest yield of esters. Comparison between H_{14}-P_5, H_{14}-P_5/SiO_2, and H_{14}-P_5/NH_4-P_5 (unsupported and supported polyacid) indicated that the activity was always higher with the unsupported catalyst.

Table 4. Esterification in the liquid phase by H_{14}-P_5

Entry	Alcohol	% Yield
1*	Ethanol	78
2	Propanol	83
3	Butanol	96
4	Pentanol	99

Note: Catalyst: 3.75×10^{-5} mol, acetic acid: 1.75×10^{-2} mol, alcohol (29 ml), reflux for 4–6 h.
* Toluene (20 ml) was added, alcohol (7 ml).

Table 5. Esterification in the liquid phase by H_{14}-P_5/SiO_2

Entry	Alcohol	% Yield
1*	Ethanol	66
2	Propanol	80
3	Butanol	86
4	Pentanol	90

Note: Catalyst: 3.75×10^{-5} mol, acetic acid: 1.75×10^{-2} mol, alcohol (29 ml), reflux for 4–6 h.
* Toluene (20 ml) was added, alcohol (7 ml).

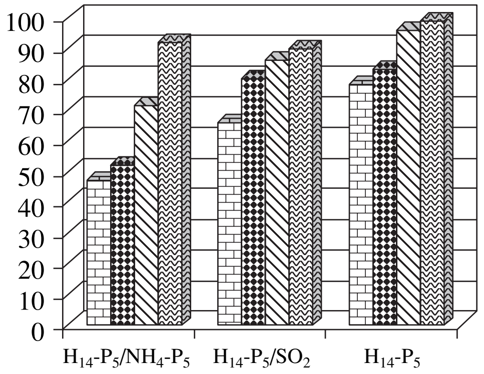

Fig. 2. Comparison between H_{14}-P_5/NH_4-P_5, H_{14}-P_5/SiO_2, and H_{14}-P_5 as catalyst in esterification reactions. ▤ Ethanol; ▦ propanol; ▧ butanol; ▨ pentanol.

The catalyst in both homogeneous and heterogeneous conditions can be recovered and reused without loss of structure and activity. The reactivities of alcohols were increased as the carbon chain of the alcohols grew longer.

By using the ammonium salt of Preyssler's anion, the yield of esters increased in this order: ethylacetate < propylacetate < butylacetate < pentylacetate. Comparison of NH_4-P_5, NH_4-PW_{12}, and NH_4-SiW_{12} showed that the activity was always higher for NH_4-P_5.

The highly efficient esterification of acetic acid, accomplished via a simple experimental setup and procedure, makes this method a useful addition to the present methodologies. Furthermore, this method demonstrates the applicability of Preyssler's anion for some reactions that require solid catalysts with strong acidic strength, highly thermal stability and functionality over a wide range of pH.

4. EXPERIMENTAL SECTION

Materials. Acetic acid, alcohols, and solvents were commercially available, and their purity was monitored by gas chromatography. The reaction products were characterized by comparing their spectroscopic properties and retention times with those of authentic samples. All yields were determined by calibration curves (External Standard Procedure).

Instruments. ^{1}H-NMR spectra were recorded on a FT-NMR Bruker 100 MHz Aspect 3000 spectrometer (with tetramethylsilane as an internal standard). IR spectra were obtained with a Buck 500 scientific spectrometer (KBr pellets). GLC analysis was performed on a Sigma 300 Perkin-Elmer gas chromatograph. Nitrogen was used as the carrier gas with FID detector; the GC column used for analysis was OV-1.

Catalysts preparation. The ammonium and potassium salts of Preyssler's anion were prepared according to the literature [25]. The free acid was prepared by passage of a solution of the potassium salt in water through a column (50 × 1 cm) of Dowex 50W × 8 in the H^+ form and evaporation of the elute to dryness under vacuum [25].

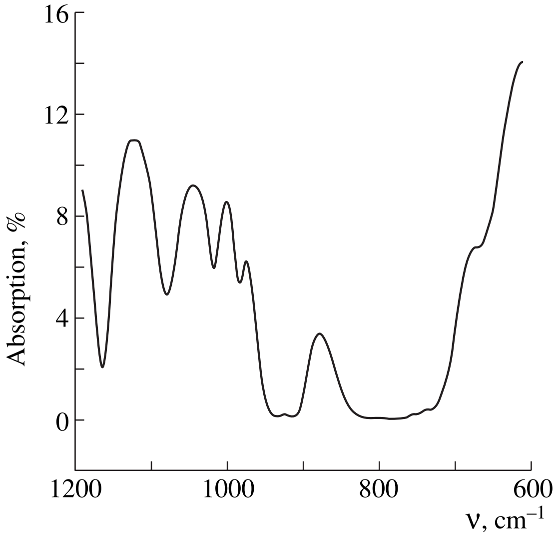

Fig. 3. IR spectrum of catalyst (Preyssler's anion) at the end of reaction.

Supported heteropoly acid catalysts were prepared by impregnating a support in the form of powder (SiO_2) with an aqueous solution of the heteropoly acid. After stirring the heterogeneous solution–support mixture, the solvent was evaporated. Samples were dried at 120–140°C, and the catalysts were calcined at 300°C in a furnace prior to use.

The Keggin-type heteropoly acids were of commercially available purity. Their ammonium salts were prepared by adding ammonium chloride powder to an aqueous solution of the heteropoly acid. The white precipitate was filtered and dried under vacuum.

In a typical reaction, a catalyst (3.75×10^{-5} mol) was added to a solution of 1-pentanol (29 ml) in acetic acid (1.75×10^{-2} mol). The reaction mixture was stirred and refluxed for 4–6 h. After filtering the catalyst, the products were analyzed by gas chromatography and the yields were determined by the External Standard Method (calibration curves were drawn with 5, 10, 15, 20, and 30 mmol of pure esters).

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