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Friedel–Crafts Acylation and Related Reactions Catalyzed by Heteropoly Acids[1, 2]

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Abstract—The Friedel–Crafts acylation of anisole (AN) with acetic anhydride (AA) and the Fries rearrangement of phenyl acetate in the liquid phase catalyzed by bulk and silica-supported heteropoly acids (HPA), mainly $H_3PW_{12}O_{40}$ (PW), have been studied. In anisole acylation, PW exhibits very high activity, yielding up to 98% *para* and 2–4% *ortho* isomer of methoxyacetophenone (MOAP) at 90-110°C and an AN/AA molar ratio of 10–20. The reaction appears to be heterogeneously catalyzed; no contribution of homogeneous catalysis by HPA was observed. PW is almost 100 times more active than the zeolite H-Beta, which is in agreement with the higher acid strength of HPA. The PW catalyst is reusable, although gradual decline of activity was observed due to the coking of the catalyst. The acylation is inhibited by the product because of adsorption of MOAP on the catalyst surface. In contrast to anisole, the acylation of toluene with HPA is far less efficient than that with H-Beta. Evidence is provided that the activity of HPA in toluene acylation is inhibited by preferential adsorption of acetic anhydride on the catalyst. It is demonstrated that PW is a very efficient and reusable catalyst for the Fries rearrangement of phenyl acetate in homogeneous or heterogeneous liquid-phase systems at 100–150°C.

INTRODUCTION

The Friedel–Crafts aromatic acylation and related Fries rearrangement of aryl esters catalyzed by strong acids are the most important routes for the synthesis of aromatic ketones that are intermediates in manufacturing fine and speciality chemicals as well as pharmaceuticals [1, 2]. Present industrial practice requires a stoichiometric amount of soluble Lewis acids (e.g., $AlCl_3$) or strong mineral acids (e.g., HF or H_2SO_4) as catalysts, which results in a substantial amount of waste and corrosion problems [2]. The overuse of catalyst is caused by product inhibition—the formation of strong complexes between the aromatic ketone and the catalyst. In view of increasingly strict environmental legislation, the application of heterogeneous catalysis has become attractive. In the last couple of decades, considerable effort has been put into developing heterogeneously catalyzed Friedel–Crafts chemistry using solid acid catalysts such as zeolites, clays, Nafion-H, heteropoly acids, etc. [2], zeolites being the most studied catalysts ([2–6] and references therein).

Heteropoly acids (HPAs) are promising solid acid catalysts for aromatic acylation [7–15]. They are stronger than many conventional solid acids such as mixed oxides, zeolites, etc. The Keggin-type HPAs typically represented by the formula $H_{8-x}[XM_{12}O_{40}]$, where X is the heteroatom, x is its oxidation state, and M is the addenda atom (usually Mo^{6+} or W^{6+}), are the most important for catalysis [7–11]. They have been widely used as acid and oxidation catalysts for organic synthesis and have found several industrial applications [7–11]. However, only a few studies on the use of HPAs for Friedel–Crafts acylation [7, 12–15] and Fries rearrangement [16, 17] have been published.

The aim of the present work is to study the acylation of anisole (AN) and toluene with acetic anhydride (AA) and the Fries rearrangement of phenyl acetate (PhOAc) in the liquid phase catalyzed by bulk and silica-supported Keggin HPAs such as $H_3PW_{12}O_{40}$ (PW), $H_4SiW_{12}O_{40}$ (SiW), and $H_3PMo_{12}O_{40}$ (PMo). The acyla-

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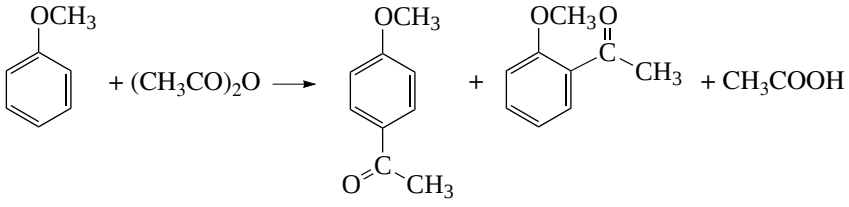
tion of anisole with the strongest acid PW to yield *para*-methoxyacetophenone (*p*-MOAP) and *ortho*-methoxyacetophenone (*o*-MOAP) (I) and the rearrangement of PhOAc (II) have been studied in more detail.



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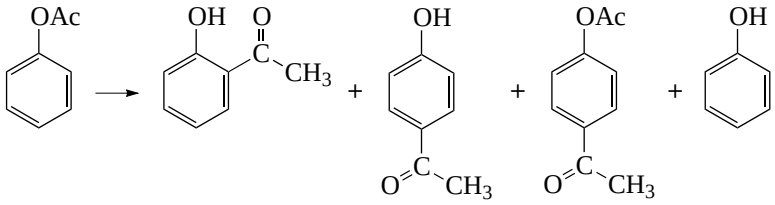

(II)

EXPERIMENTAL

Chemicals. $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ from Aldrich, $H_4SiW_{12}O_{40}$ from Fluka, and Aerosil 300 silica from Degussa were used. Anisole and toluene were obtained from Aldrich and distilled over calcium hydride prior to use. Acetic anhydride and phenyl acetate (also from Aldrich), >99% purity, were used without further purification. Other reagents and solvents were of analytical purity.

Catalysts. Supported HPA catalysts were prepared by impregnating Aerosil 300 silica (S_{BET}, 300 $m^2\ g^{-1}$) with an aqueous solution of HPA. The mixture was stirred for 6 h at room temperature followed by drying using a rotary evaporator, as described elsewhere [18]. The acidic salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) was prepared by the published method [19]. Prior to reaction, the catalysts were heated at 150°C/0.1–0.5 Torr for 1.5 h, unless stated otherwise.

Aromatic acylation. The acylations were carried out in the liquid phase in a 50-ml glass reactor equipped with a condenser and a magnetic stirrer. The reactor was charged with an aromatic substrate (100 mmol) and acetic anhydride, the substrate taken in excess over the acylating agent. No solvent was used. Decane was added as a GC internal standard. The system was purged with nitrogen to expel air and moisture and heated to a required reaction temperature (70–110°C). The preactivated catalyst was added to the reactor in an appropriate amount. To monitor the reaction, 0.1-ml samples of the reaction mixture were taken periodically, diluted to 1 ml with 1,2-dichloroethane, and analyzed by gas chromatography (Varian 3380 chromatograph with autosampler) using 30 m × 0.25 mm BP1 capillary column.

Fries rearrangement. The rearrangement of phenyl acetate was carried out in the liquid phase (7.0 g of PhOAc + solvent) at 100–160°C under a nitrogen atmosphere in a 25-ml glass reactor equipped with a condenser and a magnetic stirrer. The reaction was monitored by GS as described above.

Characterization techniques. ^{31}P MAS NMR spectra were recorded on a Bruker Avance DSX 400 NMR spectrometer. FTIR spectra were recorded with KBr pellets using a Nexus FTIR spectrometer. Surface area and porosity of HPA catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA 7 instrument under a nitrogen flow.

RESULTS AND DISCUSSION

Catalyst Characterization

Bulk and silica-supported HPA catalysts, mainly those based on PW, were characterized after a standard pretreatment (150°C/0.1–0.5 Torr, 1.5 h) by ^{31}P MAS NMR, FTIR, and TGA, as well as by surface and porosity measurement. PW supported (10 to 50 wt %) on silica showed a well-known ^{31}P NMR spectrum (a singlet line at about –15 ppm referenced to 85% H_3PO_4) characteristic of the Keggin structure [8–11]. The spectrum did not change after use of the catalysts in anisole acylation or phenyl acetate rearrangement, indicating that the PW structure remained unchanged. FTIR of the bulk and supported PW contained well-known Keggin bands (1081, 985, 892, and 596 cm^{-1} for bulk PW, the bands at 1081 and 596 cm^{-1} being obscured in supported PW catalysts by absorption of silica) [8]. The BET surface area and porosity of some HPA catalysts are given in Table 1. Bulk HPAs possess very low surface areas, typically 1–10 m^2g^{-1}, as well as very low porosities [8–11]. Supporting HPA on silica increases the surface area of HPA. It should be noted that the total surface area decreases with HPA loading (cf. 20 and 50% PW on silica).

Acylation of Anisole

Catalyst pretreatment. Control of water content in HPA catalysts proved essential for their efficient performance in aromatic acylation. This can be achieved by thermal pretreatment of the catalysts, which is typically done at 130–200°C [10, 11]. Figure 1 shows the effect of catalyst pretreatment on the yield of *p*-MOAP and on the initial rate of anisole acylation with bulk PW and 50% PW/SiO_2. It can be seen that both curves pass a maximum at an optimum pretreatment temperature of 150°C. This justifies our choice of this pretreatment temperature throughout this work. From TGA, the amount of water remaining in the bulk PW after pretreatment at 150°C is about three to four H_2O molecules per Keggin unit. Apparently, these water molecules are hydrogen-bonded to the acidic protons. The effect of water may be attributed to the HPA acid strength and the number of proton sites, as well as to catalyst deactivation [10, 11]. The amount of acetic anhydride that may be consumed reacting with this water is negligible (ca. 1% of AA). Excess water causes a decrease in the HPA acid strength and thus a decrease in its catalytic activity. Dehydration of the catalyst increases the acid strength but decreases the number of acid sites, which will reduce the catalytic activity unless the reaction is highly demanding for the catalyst acid strength. In addition, too strong acid sites thus created tend to deactivate (coke) faster.

Product yield and selectivity. Table 2 illustrates the performance of various bulk and supported HPAs at 70–110°C and anisole to acetic anhydride molar ratio AN/AA = 10–20. The *para* acylation by far dominates, only a few percent of the *ortho*-acylation product being formed, which is typical of this reaction. The selectivity towards monoacylation is practically 100%; no other aromatic products were found. The strongest acid, PW, is the most efficient catalyst, as expected, closely followed by SiW, which is a slightly weaker acid than PW [10, 11]. With PW, the yield of *p*-MOAP is up to 98%, only 2–4% *o*-MOAP being formed. In contrast, PMo shows a very poor performance. This is probably due to reduction of this HPA by the reaction medium [10, 11]. The acylation of anisole appears to be a truly heterogeneously catalyzed reaction. No contribution of homogeneous catalysis by HPA was observed when the catalyst (40% PW/SiO_2) was filtered off at the reaction temperature.

Table 3 compares our results for PW/SiO_2 with those for H-Beta zeolite [3] under similar reaction conditions. Both systems give comparable yields, but the HPA is much more active. Catalyst turnover numbers (TON) were calculated as the number of moles of *p*-MOAP obtained per mole of protons in the catalyst. For 10% PW/SiO_2, it was assumed three active H^+ per Keggin unit, and for H-Beta the number of active protons was taken to be equivalent to the Al content (Si/Al = 12.5). For the HPA, TON is found to be 14 times greater than that for H-Beta. The turnover frequency (TOF) for

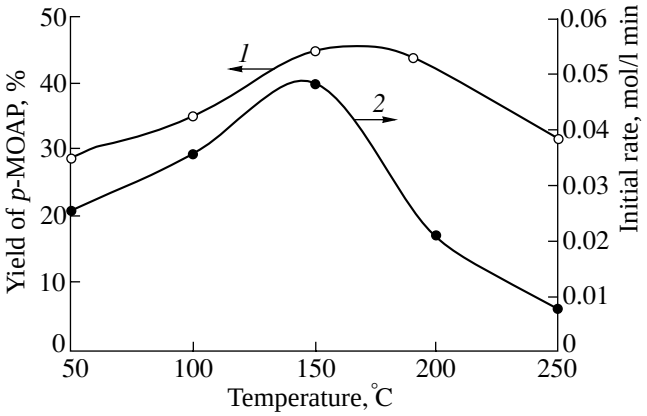

Fig. 1. Effect of catalyst pretreatment (specified temperature/0.1 Torr, 1.5 h) in the acylation of anisole: (a) yield of *p*-MOAP (50% PW/SiO_2 (0.83 wt %), AN/AA = 10 mol/mol, 50°C, 2 h); (b) initial rate (bulk PW (0.83 wt %), AN/AA = 10 mol/mol, 70°C).

HPA, corresponding to the reaction halftime, is almost two orders of magnitude greater than that for H-Beta. This is not unexpected because PW is a stronger acid than zeolite [10, 11].

Catalyst reuse. The PW catalyst was found to be reusable, although gradual decline of activity was observed. Better results were obtained when, after the first run, the catalyst was filtered off, washed with CH_2Cl_2, and rerun. Apparently, the treatment with CH_2Cl_2 removed tars more efficiently from the catalyst surface. Such a procedure allowed one to obtain 82% of the initial *p*-MOAP yield in the second run (40% PW/SiO_2 (0.83 wt %), AN/AA = 100/10 mmol, 90°C, 2 h). Coking may cause partial deactivation of the PW catalyst, which was evident from the dark brown color of the catalyst. After the first run, the 40% PW/SiO_2 catalyst was separated, washed with CH_2Cl_2, dried (150°C/0.1 Torr, 1.5 h), and subjected to elemental and thermogravimetric temperature programmed oxidation (TGA/TPO) analysis. From the

Table 1. Surface area and porosity of HPA catalysts

Catalyst	BET surface area, m^2/g	Pore volume, cm^3/g	Pore diameter, Å
PW	7	0.01	59
PMo	3	0.01	68
50% PW/SiO_2	111	0.8	138
40% PW/SiO_2	130	0.4	135
20% PW/SiO_2	184	0.5	126
CsPW	119	0.086	29

Table 2. Acylation of anisole with acetic anhydride (2 h)

Catalyst (amount), wt %[a]	AN/AA, mol/mol	*T*, °C	Yield,[b] %	
			p-MOAP	*o*-MOAP
PW(0.83)	10	70	67	[c]
PW(0.83)	10	90	96	3.8
PW(0.30)	20	70	67	2.0
PW(0.30)	20	90	90	3.5
50% PW/SiO_2(0.83)	10	90	88	4.0
50% PW/SiO_2(0.60)	20	70	77	2.7
50% PW/SiO_2(0.60)	20	90	89	3.3
40% PW/SiO_2(0.83)	10	90	88	4.0
40% PW/SiO_2(0.75)	20	70	80	2.8
40% PW/SiO_2(0.75)	20	90	89	3.3
40% PW/SiO_2(0.88)	20	110	98[d]	2.1
30% PW/SiO_2(0.83)	10	90	82	3.7
30% PW/SiO_2(1.0)	20	70	64	2.3
30% PW/SiO_2(1.0)	20	90	92	3.4
20% PW/SiO_2(0.83)	10	90	79	3.3
20% PW/SiO_2(1.5)	20	70	71	2.5
20% PW/SiO_2(1.5)	20	90	89	3.0
10% PW/SiO_2(0.83)	10	90	78	3.5
10% PW/SiO_2(3.0)	20	70	64	2.3
10% PW/SiO_2(3.0)	20	90	85	3.7
SiW(0.83)	10	70	70	[c]
40% SiW/SiO_2(0.83)	10	70	61	[c]
PMo(0.83)	10	70	0	0
40% PMo/SiO_2(0.83)	10	70	2	0
CsPW(0.83)	10	90	44	1.5

[a] Amount of catalysts per total reaction mixture.
[b] Yield based on acetic anhydride.
[c] Yield of *o*-MOAP ca. 2–3%.
[d] Yield in 10 min.

elemental analysis, the carbon content was found to be 3.2%. The TGA/TPO of the catalyst showed a weight loss of 2.5% at 530°C, which can be attributed to hard coke [20].

Effect of HPA loading. The effect of PW loading on silica upon the initial rate of anisole acylation at 70 and 90°C is shown in Fig. 2. In these experiments, the total amount of PW was kept constant. The activity of PW increases with the loading, passing a maximum at about 50% loading. Such behavior may be explained as a result of increasing the HPA acid strength, on the one hand, and decreasing the HPA surface area, on the other, as the loading increases [10, 11]. It should be noted that the specific catalytic activity (per Keggin unit) of supported HPA is greater than that of bulk HPA. This demonstrates that the reaction occurs via the surface-type catalysis in terms of Misono's classification ("bulk vs. surface type") [8, 9].

Inhibition by product. The inhibition of heterogeneous aromatic acylation by the acylation product has been reported [2, 3]. It is caused by product adsorption on the surface of catalyst (e.g., zeolite) and is, therefore, similar to the reaction inhibition by complex formation when $AlCl_3$ is used as the catalyst. As found here, the product inhibition plays a significant role in the HPA-catalyzed acylation as well. The reaction time course shown in Fig. 3 is typical of a process gradually inhibited by the product formed. A similar course has been found for anisole acylation with zeolite catalysts [3]. It can be seen that the inhibition intensifies at lower temperatures and lower AN/AA ratios as the product adsorption increases. Also it grows stronger when supported PW is used as compared to bulk PW. Apparently, this is because bulk PW has a much smaller surface area (Table 1). The product inhibition is further demonstrated by the addition of *p*-MOAP to the initial reaction mixture, showing that the yield decreases as the product is added (Fig. 4). It should be noted that the addition of byproduct acetic acid (AcOH/AA = 1 : 2 mol/mol) had no effect on the product yield. As the HPA catalyst is reusable, the product inhibition is largely reversible. Choosing higher temperatures and higher AN/AA ratios as well as bulk HPA catalysts could reduce the inhibition.

Acylation of Toluene

Toluene is less reactive than anisole towards electrophilic substitution. The acylation of toluene over zeolite catalysts, although feasible, is more difficult to achieve than that of anisole [3]. Our results on the HPA-catalyzed acylation of toluene with acetic anhydride to yield *para*- and *ortho*-methylacetophenone (*p*-MAP and *o*-MAP) are given in Table 4. Surprisingly, the reaction with HPA catalysts was found to be much less efficient than that with zeolite (e.g., H-Beta) despite the stronger acidity of HPA. Bulk and silica-supported PW yielded only 3–5% *p*-MAP and traces of *o*-MAP at 90–150°C, PhMe/AA = 5–20 mol/mol, and 2–20 h. The acidic salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) performed

even more poorly. Similar results were obtained for the acylation of *p*-xylene with acetic anhydride. In contrast, H-Beta under similar conditions gives 40% *p*-MAP [3] (Table 4). These results could be explained by the well-known strong affinity of bulk HPA towards polar oxygenates [8–11], which would lead to the preferential adsorption of acetic anhydride on HPA, blocking access for toluene to the catalyst surface. To overcome this, the acylation should be carried out at higher PhMe/AA molar ratios. Indeed, at PhMe/AA = 100–200 and with dropwise addition of acetic anhydride, a total acylation yield of 42% was obtained (Table 4). This proves that the preferential adsorption of the more polar acylating agent plays an important role in the acylation of toluene over HPA. It should be noted that this is not the case in the acylation of anisole over HPA because both the aromatic substrate and the acylating agent have comparable polarities. It appears that the hydrophobic zeolites with high Si/Al ratios less strongly differentiate the adsorption than the hydrophilic HPA and, therefore, are more suitable catalysts for the acylation of nonpolar aromatics like toluene.

Fries Rearrangement of Phenyl Acetate

The rearrangement of PhOAc (II) occurs in the liquid phase at 100–150°C to yield 2- and 4-hydroxyacetophenone (2-HAP and 4-HAP), 4-acetoxyacetophenone (4-AAP), and phenol (Table 5). One of the important advantages of HPA, as compared to zeolites or mineral acids (e.g., H_2SO_4), is that the reaction can be carried out both homogeneously and heterogeneously. The homogeneous process occurs in polar media, for example, in neat PhOAc or polar organic solvents like nitrobenzene ($PhNO_2$) or *o*-dichlorobenzene (entries 1–5) that are commonly used for the Fries reaction. All these media will easily dissolve PW at elevated temperatures (ca. 100°C). On the other hand, when using nonpolar solvents such as higher alkanes (e.g., dodecane) that will not dissolve HPA, the reaction proceeds heterogeneously over solid HPA catalysts (entries 7–11). In the latter case, supported HPA, preferably on silica, is the catalyst of choice, as bulk HPA possesses a low surface area (1–10 $m^2\ g^{-1}$). The HPA catalysts are easily separated from the heterogeneous system by filtration and could be reused (entries 8, 9). From the homogeneous systems, HPA can be effectively separated without its neutralization by extraction with water and reused or utilized otherwise. The heterogeneous catalysis in the PhOAc–dodecane media was clearly proved by filtering off the catalyst from the reacting system, which completely terminated the reaction. In contrast, filtration did not affect the reaction course in homogeneous systems, e.g., PhOAc–$PhNO_2$.

Strong inhibition of the HPA-catalyzed process with reaction products was observed both in homogeneous and heterogeneous systems as in anisole acylation. The addition of more HPA catalyst allowed one to reach a higher PhOAc conversion (cf. entries 1 and 2). Some

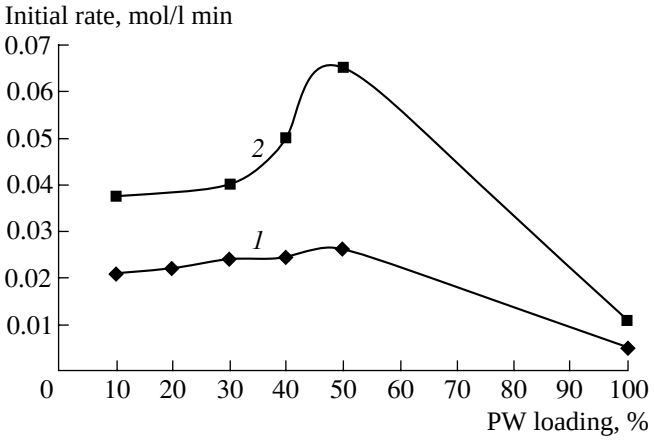

Fig. 2. Effect of PW loading in the PW/SiO_2 catalyst on the initial rate of anisole acylation at AN/AA = 20 mol/mol and a constant total amount of PW (0.010 mmol): (*1*) 70°C; (*2*) 90°C.

catalyst deactivation was also observed. For example, the 40% PW/SiO_2 catalyst separated after the reaction in PhOAc–dodecane 25 : 75 wt % system showed in the second run ca. 80% of its initial activity (entry 9). The catalyst after the first run was significantly coked (C content ca. 13%), which probably caused catalyst deactivation.

The total selectivity towards the sum of PhOH, 2-HAP, 4-HAP, and 4-AAP was found to be over 98%. Some acetic acid and acetic anhydride were also formed. The homogeneous reaction is more efficient than the heterogeneous one because it makes less phenol and more acetophenones, the selectivity to the more valuable *para* acetophenones, 4-AAP and 4-HAP, being also higher. In terms of turnover frequencies, HPA is almost 200 times more active than H_2SO_4 in the homogeneous reaction, as well as more selective to ace-

Table 3. Acylation of anisole with acetic anhydride: HPA versus zeolite (90°C, 2 h)

Reaction conditions	Catalyst		
	10% PW/SiO_2		H-Beta[a] [3]
Catalyst amount, wt %	0.83	0.83	1.33
AN/AA (mol/mol)	10	6	6
Yield of *p*-MOAP,[b] %	78	50	75
TON	780	830	61
TOF, min^{-1}	78	–	1.2

[a] Si/Al = 12.5. [b] Yield based on acetic anhydride.

Table 4. Acylation of toluene with acetic anhydride

Catalyst (amount), wt %[a]	PhMe/AA, mol/mol	*T*, °C	Time, h	Yield,[b] %	
				p-MAP	*o*-MAP
PW(5.5)	20	110	6	3.0	–
CsPW(1.1)	10	90	2	0.3	–
CsPW(1.1)	20	150[c]	2	1.1	–
40% PW/SiO_2 (1.1)	20	110	20	3.5	–
40% PW/SiO_2 (1.1)	20	150[c]	2	5.2	–
40% PW/SiO_2 (1.1)	200	110	22	23	4.0
40% PW/SiO_2 (1.1)	100[d]	110	24	37	4.8
H-Beta (1.9)[e]	20	110	24	40	–

[a] Amount of catalyst per total reaction mixture. [b] Yield based on acetic anhydride. [c] Reaction was carried out in a stainless steel autoclave. [d] Acetic anhydride added dropwise. [e] From [3].

Table 5. Fries rearrangement of phenyl acetate (2 h)[a]

	Catalyst, wt %	Solvent (PhOAc), wt %	*T*, °C	Conversion, %	Selectivity, %			
					PHOH	2-HAP	4-HAP	4-AAP
1	PW(0.60)	PhOAc(100)	150	5.5	49	5.2	5.6	40
2	PW(3.0)	PhOAc(100)	150	19.2	52	5.7	15	28
3	PW(3.0)	$PhNO_2$(25)	150	45.8	52	12	24	12
4	PW(0.60)	$PhNO_2$(25)	130	21.0	46	7.8	18	27
5	PW(0.60)	$PhNO_2$(50)	100	10.5	55	5.1	10	29
6	H_2SO_4(1.4)	$PhNO_2$(25)	130	12.8	67	9.4	7.6	16
7	PW(0.60)	Dodecane(25)	130	3.1	69	8.0	0	23
8	40% PW/SiO_2(1.5)	Dodecane(25)	130	8.3	62	10	6.0	22
9	40% PW/SiO_2(1.5)[b]	Dodecane(25)	130	6.7	51	11	5.0	32
10	10% PW/SiO_2(6.0)	Dodecane(25)	130	11.8	66	8.0	9.6	16
11	40% PW/SiO_2(3.3)[c]	Dodecane(36)	160	18.0	66	11	8.2	14
12	*H*-Beta (1.3)[c,d]	Dodecane(36)	160	9.3	38	32	6.4	24
13	CsPW(0.67)	$PhNO_2$(25)	130	8.7	49	6.1	4.4	41

[a] The reaction with PW is homogeneous in PhOAc and $PhNO_2$ and heterogeneous in dodecane. [b] Reuse of the run given in entry 8. [c] 5 h. [d] Si/Al = 11 [4].

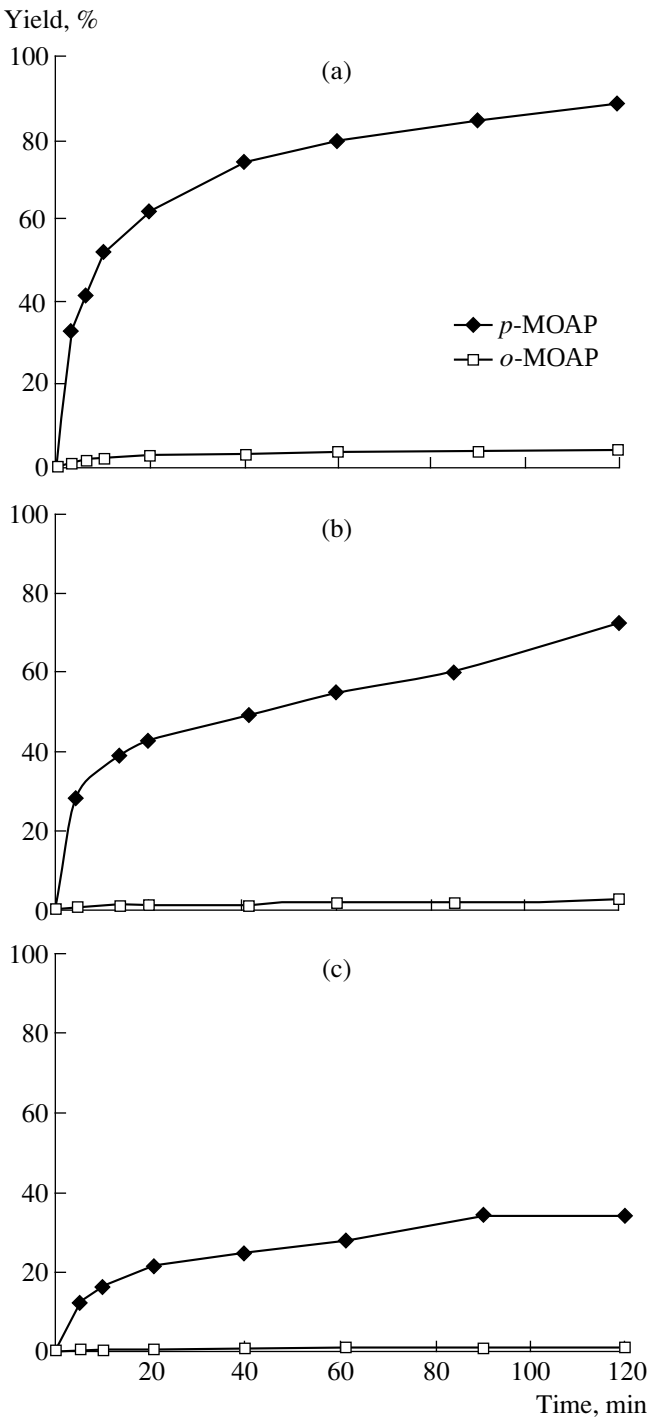

Fig. 3. Yield–time plots for the acylation of anisole with 40% PW/SiO_2 (0.83 wt %): (a) 90°C, AN/AA = 10 mol/mol; (b) 70°C, AN/AA = 10 mol/mol; (c) 70°C, AN/AA = 5 mol/mol. Yields are based on acetic anhydride.

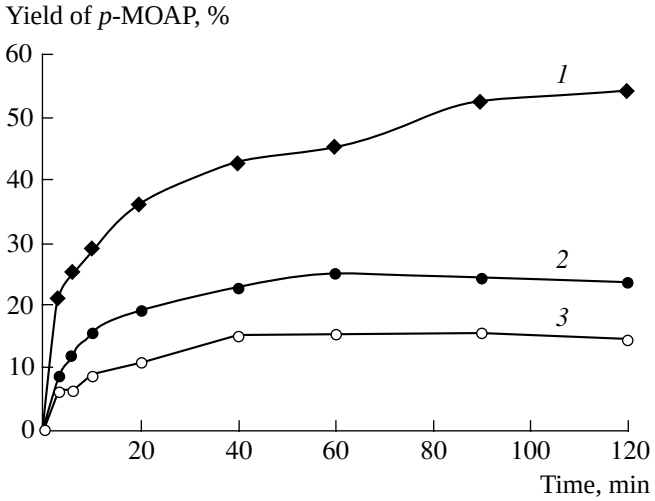

Fig. 4. Inhibition by product in the acylation of anisole (40% PW/SiO_2 (0.83 wt %), AN/AA = 10 mol/mol, 70°C, 2 h): (*1*) no *p*-MOAP added; (*2*) *p*-MOAP added initially, AA/*p*-MOAP = 2 mol/mol; (*3*) *p*-MOAP added initially, AA/*p*-MOAP = 1 mol/mol. Yields are based on acetic anhydride.

tophenones (cf. entries 4 and 6). In heterogeneous systems, HPA is also two orders of magnitude more active than H-Beta zeolite, which is one of the best zeolite catalysts for this reaction (cf. entries 11 and 12). However, H-Beta shows a higher total selectivity to acetophenones than HPA. It should be pointed out that HPA in homogeneous systems gives a higher selectivity to *para* acetophenones 4-AAP and 4-HAP than H-Beta. The efficiency of solid HPA (at constant loading) increases in the order PW < 40% PW/SiO_2 < 10% PW/SiO_2 in which the number of accessible proton sites increases (cf. entries 7, 8, and 10). Insoluble salt CsPW [8, 9] is an efficient solid catalyst for the reaction in polar media such as $PhNO_2$ (entry 13). Although less active per unit weight than the homogeneous PW or PW/SiO_2, it is more selective to acetophenones than HPA. The explanation for this may be that the less hydrophilic Cs salt [8, 9] possesses stronger proton sites than the solid PW or PW/SiO_2; the latter two catalysts, from TGA, retain 4–6 H_2O molecules per Keggin unit after pretreatment at 150°C.

CONCLUSION

The Keggin-type heteropoly acid PW, bulk or silica-supported, is a highly efficient solid-acid catalyst for the liquid-phase acylation of anisole with acetic anhydride and the Fries rearrangement of phenyl acetate. The catalyst can be reused after a simple workup. HPA is two orders of magnitude more active than zeolite H-Beta for these reactions—that is in line with the stronger acidity of HPA. Similarly to the reaction with zeolite catalysts, the HPA-catalyzed acylation is inhibited by the product because of the strong adsorption of the product on the catalyst surface. In contrast to anisole, the HPA-catalyzed acylation of toluene with acetic anhydride is far less efficient than that with H-Beta. Evidence is provided that the activity of HPA in toluene acylation is inhibited by preferential adsorption of ace-

tic anhydride on the catalyst. Apparently, the hydrophobic zeolites (e.g., H-Beta) less strongly differentiate the adsorption of the aromatic substrate and acylating agent than the hydrophilic HPA and, therefore, are more suitable catalysts for the acylation of nonpolar aromatics like toluene.

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