

# Esterification of *n*-Butanol with Acetic Acid in the Presence of Heteropoly Acids with Different Structures and Compositions

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**Abstract**—The esterification reaction of *n*-butanol with acetic acid ([BuOH] : [HOAc] = 1 : 15 mol/mol; 55°C, 5% H<sub>2</sub>O) was studied in the presence of tungsten heteropoly acids of the Keggin (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, H<sub>5</sub>PW<sub>11</sub>TiO<sub>40</sub>, H<sub>5</sub>PW<sub>11</sub>ZrO<sub>40</sub>, and H<sub>3</sub>PW<sub>11</sub>ThO<sub>39</sub>) and Dawson structure (α-H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, H<sub>6</sub>P<sub>2</sub>W<sub>21</sub>O<sub>71</sub>(H<sub>2</sub>O)<sub>3</sub>, H<sub>6</sub>As<sub>2</sub>W<sub>21</sub>O<sub>69</sub>(H<sub>2</sub>O), and H<sub>21</sub>B<sub>3</sub>W<sub>39</sub>O<sub>132</sub>). The reaction orders with respect to H<sub>6</sub>P<sub>2</sub>W<sub>21</sub>O<sub>71</sub>(H<sub>2</sub>O)<sub>3</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>69</sub> are equal to 0.78, 1.00, and 0.97, respectively. It was found that the reaction rate depends on the acidity, as well as on the structure and composition of heteropoly acids. The H<sub>21</sub>B<sub>3</sub>W<sub>39</sub>O<sub>132</sub> heteropoly acid is most active, whereas the Keggin-structure heteropoly acids exhibit the lowest activities. Of the Keggin structure heteropoly acids, H<sub>5</sub>PW<sub>11</sub>ZrO<sub>40</sub> exhibits the highest activity because of the presence of a Lewis acid site in its structure.

## INTRODUCTION

The esterification reaction of *n*-butanol with acetic acid



is of considerable interest as a method for preparing butyl acetate (BA), which is widely used as an intermediate in organic synthesis [1].

Reaction (I) occurs in the presence of homogeneous or heterogeneous acid catalysts such as H<sub>2</sub>SO<sub>4</sub> [1], sulfo cation exchangers [2], and zeolites (HZSM-5, HY, and H-mordenite) [3] etc. According to published data [4–6], the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> heteropoly acids (either bulk or supported on clay or silica gel) also successfully catalyze this reaction.

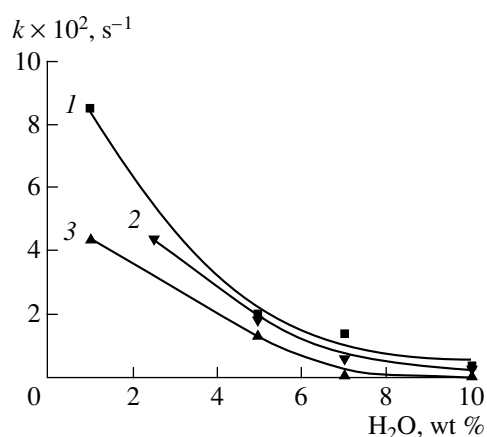
A wide range of heteropoly acids is known, which are increasingly in use as catalysts in acid-type reactions [7, 8]. It was found that, apart from the acidity, the structure and composition of heteropoly anions play an important role in heteropoly acid catalysis [8]. In this work, reaction (I) was studied in the presence of tungsten heteropoly acids of Keggin (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>; H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>; H<sub>3</sub>PW<sub>11</sub>ThO<sub>39</sub>; and H<sub>5</sub>PW<sub>11</sub>XO<sub>40</sub>, where X(IV) = Ti or Zr) and Dawson structure types (α-H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>, H<sub>6</sub>P<sub>2</sub>W<sub>21</sub>O<sub>71</sub>(H<sub>2</sub>O)<sub>3</sub>, H<sub>6</sub>As<sub>2</sub>W<sub>21</sub>O<sub>69</sub>(H<sub>2</sub>O), and H<sub>21</sub>B<sub>3</sub>W<sub>39</sub>O<sub>132</sub>).

## EXPERIMENTAL

**Reagents.** H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> · 15.4H<sub>2</sub>O and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> · 17.5H<sub>2</sub>O were prepared by recrystallization of chemi-

cally pure compounds from water. H<sub>6</sub>P<sub>2</sub>W<sub>21</sub>O<sub>71</sub>(H<sub>2</sub>O)<sub>3</sub> · 28.7H<sub>2</sub>O, α-H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> · 17.0H<sub>2</sub>O, H<sub>5</sub>PW<sub>11</sub>TiO<sub>40</sub> · 14.2H<sub>2</sub>O, and H<sub>5</sub>PW<sub>11</sub>ZrO<sub>40</sub> · 16.5H<sub>2</sub>O were synthesized by electrodialysis according to published procedures [9–11]. H<sub>3</sub>PW<sub>11</sub>ThO<sub>39</sub> · 12.7H<sub>2</sub>O was also prepared by electrodialysis analogously to H<sub>5</sub>PW<sub>11</sub>XO<sub>40</sub> [10] (relevant data will be published elsewhere). H<sub>21</sub>B<sub>3</sub>W<sub>39</sub>O<sub>132</sub> · 73.7H<sub>2</sub>O and H<sub>6</sub>As<sub>2</sub>W<sub>21</sub>O<sub>69</sub>(H<sub>2</sub>O) · 17H<sub>2</sub>O were synthesized according to procedures published in [12] and [13], respectively. The purity of the heteropoly acids was monitored by <sup>31</sup>P and <sup>11</sup>B NMR spectroscopy. The amounts of hydrate water in heteropoly acids were determined by weight loss upon heating at 500°C. Acetic acid of analytical grade was purified by distillation; *n*-butanol of chemically pure grade, decane of reagent grade, and hexane of reagent grade were used without additional purification.

**Kinetic measurements.** The reaction was performed in a thermostatted glass reactor equipped with a magnetic stirrer and a backflow condenser at 55°C and [heteropoly acid] = 10<sup>−3</sup> mol/l in an aqueous acetic acid medium ([BuOH] : [HOAc] = 1 : 15 mol/mol; 5 wt % H<sub>2</sub>O). The reaction mixture was sampled at regular intervals; the catalyst was removed by shaking with a decane–water mixture (1 : 5 by volume); and the organic layer was analyzed by GLC. A Tsvet 500 chromatograph with a metal column (2 m × 3 mm) packed with Carbowax 20M on Chromaton N-AW-DMCS (0.16–0.25 mm) was used; nitrogen was the carrier gas (30 ml/min). The column temperature was programmed as follows: 80°C (15 min); 60 K/min; and 180°C (15 min). Hexane was an internal standard and a flame-



**Fig. 1.** Rate constant of reaction (I) as a function of water concentration in the presence of  $10^{-3}$  mol/l heteropoly acids: (1)  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  (2)  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ , and (3)  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

ionization detector (FID) was used. Under conditions of a considerable excess of acetic acid, the accumulation of the reaction product (butyl acetate) obeys a rate law for a reversible first-order reaction. On this basis,

the reaction rate constants were calculated from an  $\ln C_{\text{BuOAc}} - \tau$  linear anamorphosis.

**Physicochemical measurements.**  $^{31}\text{P}$  NMR spectra were measured on a Bruker MSL-400 instrument at a frequency of 161.98 MHz in a range of 5 kHz with reference to 85%  $\text{H}_3\text{PO}_4$ .

The IR spectra of adsorbed pyridine were measured on a Shimadzu FTIR-8300 spectrometer over a range of  $1400\text{--}1700\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$ . Heteropoly acid samples were pelletized and preheated in oxygen at  $300^\circ\text{C}$  for 2 h. Pyridine was adsorbed at  $150^\circ\text{C}$  for 15 min; thereafter, the sample was evacuated at  $150^\circ\text{C}$  for 30 min, and the IR spectrum was recorded.

## RESULTS AND DISCUSSION

Heteropoly acids efficiently catalyze reaction (I) at  $50\text{--}70^\circ\text{C}$  and a catalyst concentration of  $(1\text{--}5) \times 10^{-3}$  mol/l. In this case, 1–10% dibutyl ether was formed in the system in addition to butyl acetate, which is the main product (see the table).

Under conditions when all of the reactants are simultaneously introduced into the system, the reaction is of first order with respect to butanol. Figure 1 dem-

Reaction characteristics for butanol esterification with acetic acid in the presence of various heteropoly acids ( $10^{-3}$  mol/l).  $[\text{BuOH}] : [\text{HOAc}] = 1 : 15$  mol/mol;  $55^\circ\text{C}$ ; 5 wt %  $\text{H}_2\text{O}$

Heteropoly acid	Time, min	Butyl acetate yield, mol %	Dibutyl ether yield*, mol %	$k \times 10^2, \text{s}^{-1}$
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	60	30.5	0.9	1.13
	180	88.8	5.2	
$\text{H}_5\text{PW}_{11}\text{TiO}_{40}$	60	28.2	1.3	1.06
	180	80.2	5.5	
$\text{H}_3\text{PW}_{11}\text{ThO}_{39}$	60	6.8	Traces	0.60
	180	20.8	0.6	
$\text{H}_5\text{HW}_{11}\text{ZrO}_{40}$	60	45.1	2.4	1.78
	120	89.3	4.9	
$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	60	30.8	2.6	1.18
	180	90.1	5.9	
$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	60	70.2	5.9	2.29
	90	90.6	7.8	
$\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$	60	44.7	4.7	2.23
	90	89.7	7.7	
$\text{H}_{21}\text{B}_3\text{W}_{39}\text{O}_{132}$	60	75.2	7.8	2.88
	90	90.3	9.7	
$\text{H}_6\text{As}_2\text{W}_{21}\text{O}_{69}(\text{H}_2\text{O})$	60	49.1	2.4	1.80
	120	90.3	4.9	

\* Based on reacted butanol.

onstrates the reaction rate constants as functions of the water content of the system for heteropoly acids of three structural types. It can be seen that the reaction rate dramatically decreases for all of the heteropoly acids as the water content of the reaction mixture increases. It is likely that this is primarily due to a decrease in the acidity of acetic acid solutions of heteropoly acids with increasing water content [14]. The order of reaction with respect to a heteropoly acid is close to or lower than unity: 0.78 for  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$ , 1.0 for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , and 0.97 for  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ . A lower order of the reaction in the case of  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  can result from the structure peculiarities of the heteropoly anion (Fig. 2).

The reaction rate in the presence of  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  significantly depends on the order in which the reactants are added. As can be seen in Fig. 3, the heteropoly acid added immediately after mixing all of the reactants (HOAc,  $\text{H}_2\text{O}$ , and *n*-BuOH) exhibited a higher catalytic activity than that of the heteropoly acid preexposed to aqueous acetic acid for 1–4 h. Such behavior was not observed in the other heteropoly acids studied.

According to  $^{183}\text{W}$  NMR-spectroscopic and crystallographic data [15], the anion of  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  contains water molecules, which are coordinated to three W atoms in an equatorial zone and can enter exchange reactions with solvent molecules. Data obtained by  $^{31}\text{P}$  NMR spectroscopy and kinetic measurements indicate that, in our case, water molecules are replaced by acetic acid molecules.

The  $^{31}\text{P}$  NMR spectrum of an  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  solution in 100% acetic acid (Fig. 4) exhibits three signals with  $\delta$  –12.7 (initial heteropoly acid), –12.5, and –11.6 ppm. Upon the addition of water to the solution, all lines are shifted upfield because of a change in the magnetic susceptibility of the solution. At a water content of 10%, two lines of the lowest intensities at  $\delta$  –12.5 and –11.6 ppm disappeared. Different values of  $^{31}\text{P}$   $\delta$  for  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  in acetic acid and aqueous solutions primarily result from differences in the magnetic susceptibility of solutions; this results in a difference between  $\delta$  approximately equal to 0.8 ppm. The  $^{31}\text{P}$  NMR spectra of Keggin and Dawson structure heteropoly acids in neat and aqueous acetic acid always exhibit one signal; this fact can be explained by the absence of detectable exchange reactions in the anion structure of heteropoly acids.

Based on the experimental data, we believe that, in solutions in practically anhydrous acetic acid, two of three water molecules that enter the composition of the heteropoly anion and are located at the periphery (Fig. 2) are replaced with HOAc molecules to form the heteropoly acids  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_2(\text{HOAc})$  ( $^{31}\text{P}$   $\delta$  –12.5 ppm) and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})(\text{AcOH})_2$  ( $^{31}\text{P}$   $\delta$  –11.6 ppm). The third water molecule is located within the heteropoly anion, and it is inaccessible to such an exchange. These substitution reactions are

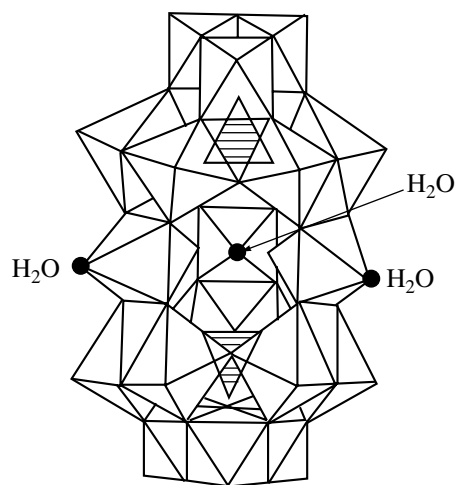


Fig. 2. Structure of the heteropoly anion  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$ .

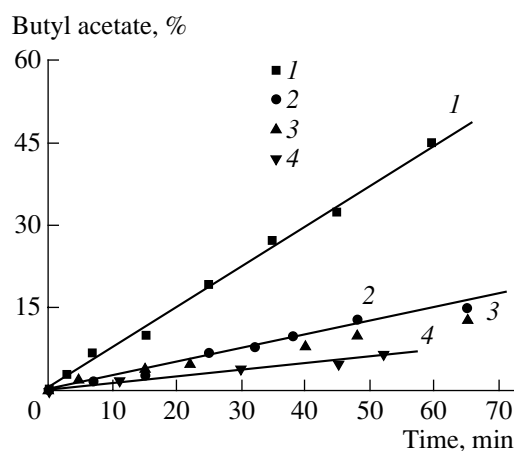
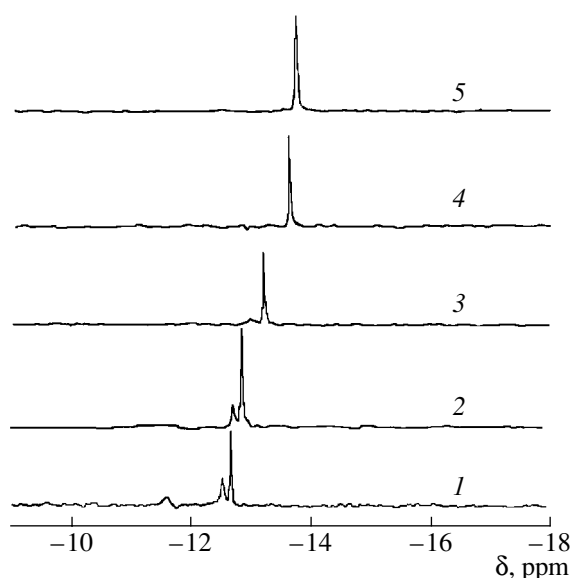
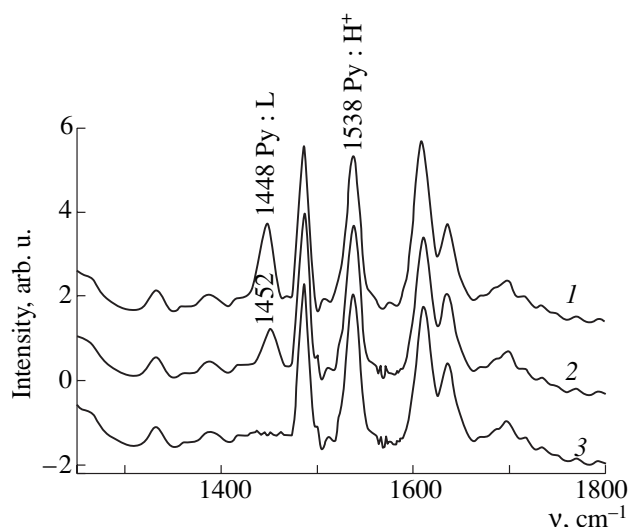


Fig. 3. Kinetics of the accumulation of butyl acetate in the presence of  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  at different modes of adding the reactants: (1) the heteropoly acid added immediately after mixing the ingredients, (2) butanol added 45 s after holding the heteropoly acid in 93% acetic acid at 55°C, (3) butanol added after 1 h, and (4) butanol added after 5 h.

reversible because the line intensities at –12.5 and –11.6 ppm decrease with the amount of water in acetic acid. The mono- and diacylated derivatives of the  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  heteropoly acid can be considered as hepta- and octabasic heteropoly acids, respectively. An increase in the basicity of heteropoly acids leads to a decrease in their acidity [16]. Because of this, the catalytic activity of  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  in the reaction, which is added simultaneously with the other reactants, is higher than that of  $\text{H}_7\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_2(\text{AcO})$  or  $\text{H}_8\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})(\text{AcO})_2$ , which appear upon a pre-exposure of the heteropoly acid to aqueous acetic acid; this behavior was observed experimentally (Fig. 3).

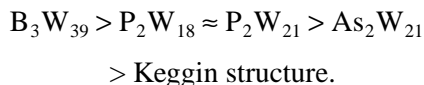


**Fig. 4.**  $^{31}\text{P}$  NMR spectra of  $5 \times 10^{-3}$  mol/l  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3$  solutions in acetic acid with different water concentrations: (1) no water added, (2) 2.5 vol %, (3) 10 vol %, (4) 50 vol %, and (5) aqueous heteropoly acid solution.

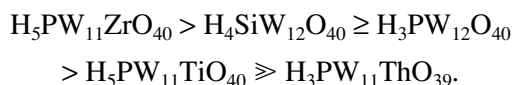


**Fig. 5.** IR spectra of pyridine adsorbed on the surfaces of (1)  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$ , (2)  $\text{H}_5\text{PW}_{11}\text{TiO}_{40}$ , and (3)  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

For structurally different heteropoly acids, the activity on a [heteropoly acid] basis depends on the structure (see the table) and decreases in the order



For heteropoly acids of the same type (Keggin structure), the activity decreases in the order



The above orders of activity are consistent with changes in the dissociation constants in acetic acid solutions, as calculated by a conductometric technique [17]. We attempted to find the reason for the high activity of  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$  by studying the acid properties of heteropoly acids using IR spectroscopy. Figure 5 demonstrates the IR spectra of pyridine adsorbed on Keggin structure heteropoly acids. The spectra of  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$  and  $\text{H}_5\text{PW}_{11}\text{TiO}_{40}$  exhibit absorption bands attributed to Brønsted ( $1540\text{ cm}^{-1}$ ) and Lewis (about  $1450\text{ cm}^{-1}$ ) acid sites [18], whereas a band at about  $1450\text{ cm}^{-1}$  is absent from the spectrum of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . The band intensity at about  $1450\text{ cm}^{-1}$  for a sample of  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$  is higher than that for  $\text{H}_5\text{PW}_{11}\text{TiO}_{40}$  by a factor of  $\sim 2.5$ . It is likely that in reaction (I), as well as in the reaction of acetone dimerization [7], in addition to Brønsted acid sites, Lewis sites significantly contribute to the catalytic activity of  $\text{H}_5\text{PW}_{11}\text{ZrO}_{40}$ . In this case, the effect of acid sites due to the presence of the Zr(IV) ion in the heteropoly acid composition is much higher than the effect of analogous sites due to the presence of the Ti(IV) ion.

Published data [8] indicate that not only the acidity of heteropoly acids but also the structure and composition of the anions affect the acid-catalytic properties of heteropoly acids. Nevertheless, the results of this work and previously published data [7, 19] demonstrate that the catalytic activity of heteropoly acids in some reactions (butyl acetate synthesis and acetone condensation) can be predicted from only their acid properties.

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